Vibrational, Electrical and Optical Studies on Pectin- based Polymer Electrolyte

S.Kavitha[1], N.Vijaya[1], R.Pandeeswari[1], M.Premalatha[2]

[1]*Department of Physics, S.F.R. College for Women, Sivakasi--626123, Tamil Nadu, India*

[2]*Materials Research Center, Coimbatore-641045, Tamil Nadu, India*

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Abstract - *This work presents the synthesis and characterization of biopolymer pectin - based polymer electrolyte. Proton conducting polymer electrolytes consisting of pectin as host polymer and ammonium nitrate (NH_4NO_3) as complexing salt in different compositions have been prepared by solution casting technique using distilled water as solvent and characterized by FTIR, AC impedance spectroscopy and UV-Visible spectral analyses. The FTIR analysis reveals complexation behaviour of the electrolytes. The ionic conductivity of pure pectin is found to be 5.15×10^{-9} S cm^{-1} at ambient temperature. The highest conductivity of 6.64×10^{-5} S cm^{-1} has been obtained for the polymer electrolyte with 70 mol% pectin and 30 mol% NH_4NO_3 at ambient temperature. The conductivity of the electrolyte increases with increasing temperature for all compositions. UV- Visible analysis indicates that the bandgap energy decreases with the addition of NH_4NO_3.*

Key Words: biopolymer, FTIR, ionic conductivity, activation energy, modulus spectra, band gap energy.

1. INTRODUCTION

Solid polymer electrolytes (SPEs) are an important class of materials due to its application for the development of fuel cells, solid state batteries, sensors and electrochemical devices [1]. SPEs have the dimensional stability, processability, flexibility, electrochemical stability, safety and long life. So it is anticipated to replace the established organic sol–gel electrolyte [2]. Most of the SPEs have been developed using synthetic polymers, such as PVA [2], PVP [3], PAN [4], etc. The proton-conducting polymer electrolytes have received a great deal of interest because of their unique application as solid electrolytes in the electrochemical devices.

Recently, research on new materials from renewable sources as the possible electrolyte host has grown vigorously, since synthetic polymers are obtained from finite sources and are harmful to the environment. Natural polymers are well known for their biodegradation properties, richness in nature and low cost. The use of natural polymers in electrolytes could overcome the main shortcoming of synthetic ones, which are mostly insoluble in the solvents [5]. Generally, the addition of inorganic salts into a polymer matrix can improve its conductivity. The biopolymer pectin is a polymer of natural origin. Because of its excellent biodegradable and biocompatible nature, it is used for eco-friendly biodegradable applications in the pharmaceutical and biotechnology industry. It has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Pectin is commercially extracted from different citrus products like apple, pomace, and oranges under mildly acidic conditions [6]. It consists chiefly of partially methoxylated polysaccharide. It is water soluble with fairly good bio-degradable nature which can be exploited for designing polymer films. Ammonium salts are very good proton donors as per the literature survey [7]. Ammonium nitrate (NH_4NO_3) is a white crystalline solid at room temperature and pressure. Commonly, it is used in agriculture as fertilizer [8]. The present study is focused on the preparation and characterization of pectin doped with NH_4NO_3 polymer electrolyte films.

2. EXPERIMENTAL

Polymer electrolytes have been prepared with pectin (Tokyo Chemical Industry Co Limited, Japan) and NH_4NO_3 (Spectrum, India) of various compositions such as (100:0), (90:10), (80:20), (70:30), and (60:40) in molar ratios using distilled water as solvent by solution casting technique. Appropriate quantities of pectin and NH_4NO_3 are dissolved in distilled water and the mixtures are stirred continuously in a magnetic stirrer for two days to get homogeneous solution. Finally, these solutions are casted in polypropylene petri dishes and evaporated at 50 ^{0}C in hot air oven. Free standing films of thickness of 0.003833-0.0098 cm have been obtained after 24 hours.

The FTIR spectra for polymer electrolytes have been recorded in transmission mode using a SHIMADZU-IR AFFINITY-1 spectrophotometer in the frequency range (400 – 4000 cm^{-1}). The electrical measurements have been performed on the electrolyte films in the frequency range of 42 Hz -1 MHz by applying 1 V sinusoidal signal over the temperature range from 303 K to 333 K by sandwiching them between aluminum blocking electrodes using HIOKI 3532 – 50 LCR Hi-Tester interfaced with a computer. The UV-Vis spectra are obtained from the UV-2400 PC series spectrometer for the samples within 200-900 nm range of UV- spectrum.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Analysis

The purpose of measurement of FTIR of pure pectin and 70 mol% pectin doped with 30 mol% NH_4NO_3 polymer electrolytes is to confirm the complex formation of the salt with the polymer. **Fig - 1** illustrates the FTIR spectra of pure pectin and 70 mol% pectin – 30 mol% NH_4NO_3 polymer electrolytes. The different characteristic absorption peak positions and their assignments for the electrolytes are listed in **Table -1**.

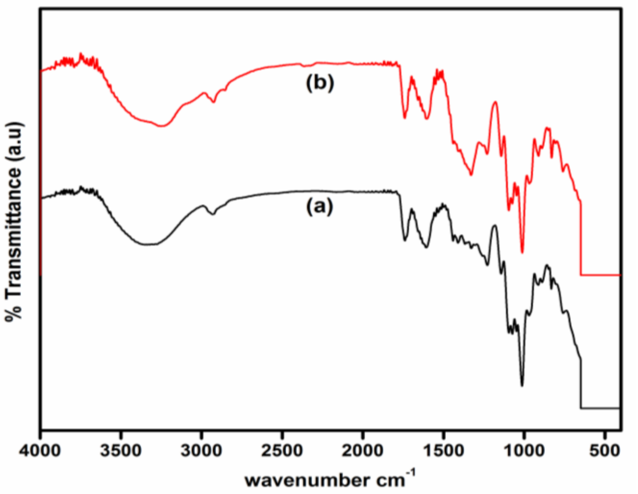

Fig -1: FTIR spectra of (a) pure pectin and (b) 70 mol% pectin - 30 mol% NH_4NO_3 films.

Chinkap Chung et al. (2004) [9] have mentioned that the O-H and C-H stretching modes for pure pectin occur in the range (3650 - 3100) cm^{-1} and (2980 - 2800) cm^{-1} respectively. The broad absorption peak of pure pectin centered at 3351 cm^{-1} can be attributed to O-H stretching and it is found to be shifted to 3250 cm^{-1} in 70:30 composition of pectin - NH_4NO_3 film. The peak of pure pectin at 2931 cm^{-1} assigned to C-H stretching is shifted to 2926 cm^{-1} in 70:30 composition of pectin - NH_4NO_3 film. The absorption peak of pure pectin at 1739 cm^{-1} attributed to C=O stretching of ester and acid is found to be shifted to 1740 cm^{-1} in 30 mol% NH_4NO_3- doped system [10]. A new peak appears at 1328 cm^{-1} in 70 mol% pectin - 30 mol% NH_4NO_3 film.

A peak at 1608 cm^{-1} corresponding to COO- asymmetric stretching observed in the range (1630-1600 cm^{-1}) [11] for pure pectin is shifted to 1603 cm^{-1} in the NH_4NO_3 - doped film. A peak at 1224 cm^{-1} assigned to C=O stretching occurs in the range (1300-1000) cm^{-1} in pure pectin as reported by ***Jitter singthong et al. (2004)*** [11]which is found to be shifted to 1230 cm^{-1} in the salt doped film. The shift in frequencies of the characteristic absorption peaks and the appearance of a new peak can be due to the interaction of the salt with the polymer matrix which confirms the complex formation between the biopolymer pectin and the salt, NH_4NO_3.

Table -1: Vibrational peaks and assignments for all compositions of pectin - NH_4NO_3 polymer electrolytes

S. No.	Pure pectin	70:30	Frequency Range	Assignment
1.	3351	3250	3100-3650	O-H stretching
2.	2931	2926	2800-3000	C-H stretching
3.	1739	1740	1690-1760	C=O stretching of ester and acid
4.	1608	1603	1600-1630	COO-asymmetric stretching
5.	1224	1230	1000-1300	C=O stretching

3.2 Complex Impedance Analysis

The behaviour of the electrochemical system can be studied by means of impedance plots over a wide range of frequencies at different temperatures by applying an AC voltage or current [12]. **Fig - 2(a) and (b)** shows the impedance (Nyquist) plots of pure pectin and various compositions of pectin - NH_4NO_3 electrolytes at 303 K.

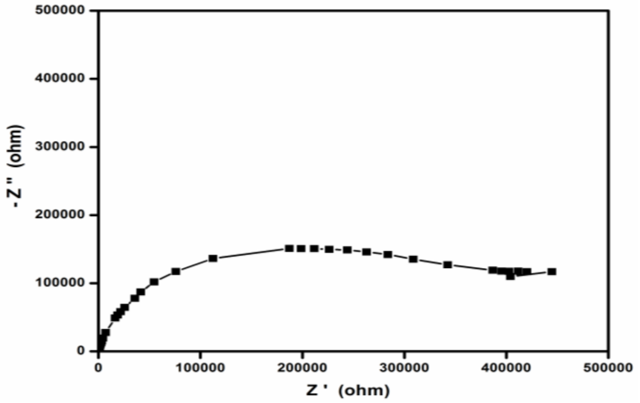

Fig -2(a): Nyquist plot of pure pectin at 303 K

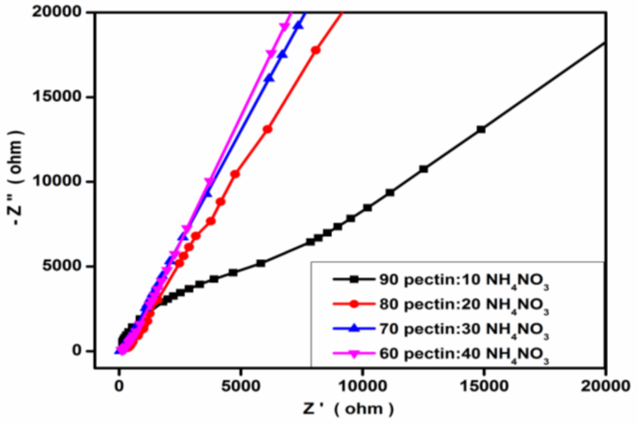

Fig -2(b): Nyquist plots of various compositions of pectin - NH_4NO_3 polymer electrolytes at 303 K

The plots show a high frequency semicircle and a low frequency spike. The disappearance of the semicircle for higher salt concentration suggests the prevailing of the resistive component of the polymer electrolytes [13]. The semicircle may be due to the bulk effect of the electrolyte and the spike may be due to the effect of the blocking electrodes [3]. The ionic conductivity is calculated using the relation:

$$\sigma = l / (R_b A) \quad \text{-------------} \quad (1)$$

where l is the thickness of the polymer electrolyte, R_b is the bulk resistance and A is the surface area of the electrolyte in contact with the electrodes. It has been deduced from **Table - 2** that the highest ambient temperature ionic conductivity is 6.64×10^{-5} S cm^{-1} for the 70 mol% pectin - 30 mol% NH_4NO_3 polymer electrolyte.

Table -2: Conductivity values of Pectin - NH_4NO_3 polymer electrolytes from the Nyquist plots

Pectin-NH_4NO_3 (mol%)	**Ionic conductivity (σ, S cm^{-1}) at different temperatures**			
	303 K	**313 K**	**323 K**	**333 K**
Pure pectin	5.15×10^{-9}	1.03×10^{-8}	2.86×10^{-8}	6.45×10^{-8}
90:10	3.28×10^{-7}	6.84×10^{-7}	1.06×10^{-6}	1.67×10^{-6}
80.20	4.25×10^{-6}	6.71×10^{-6}	1.06×10^{-5}	1.35×10^{-5}
70:30	6.64×10^{-5}	8.31×10^{-5}	9.07×10^{-5}	9.15×10^{-5}
60:40	8.34×10^{-6}	1.47×10^{-5}	1.77×10^{-5}	6.31×10^{-5}

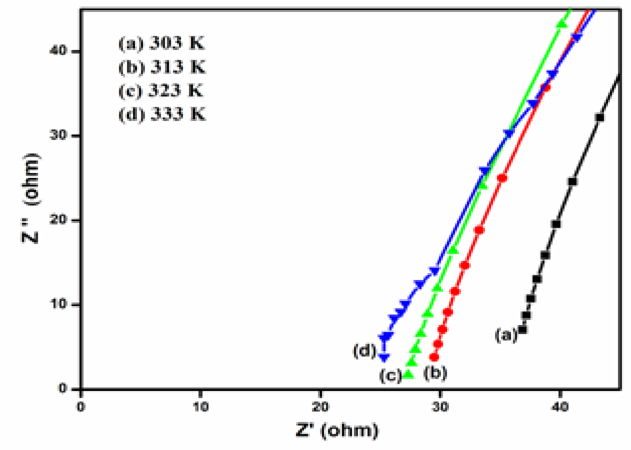

Fig -3: Nyquist plot for 70 mol% pectin – 30 mol% NH_4NO_3 polymer electrolyte at different temperatures.

Fig -3 shows the impedance plot for highest conductivity sample (70 mol% pectin- 30 mol% NH_4NO_3) at different temperatures. The disappearance of the high frequency semicircle for the highest conductivity sample indicates that the total conductivity is mainly the result of ion conduction [12]. It has been observed from this fig - that the bulk resistance value decreases with increase of temperature resulting in an increase in ionic conductivity.

3.3 Temperature Dependent Conductivity

The temperature dependence of conductivity of the electrolytes for all compositions of pectin - NH_4NO_3 over the temperature range 303-333 K is shown in **Fig - 4.**

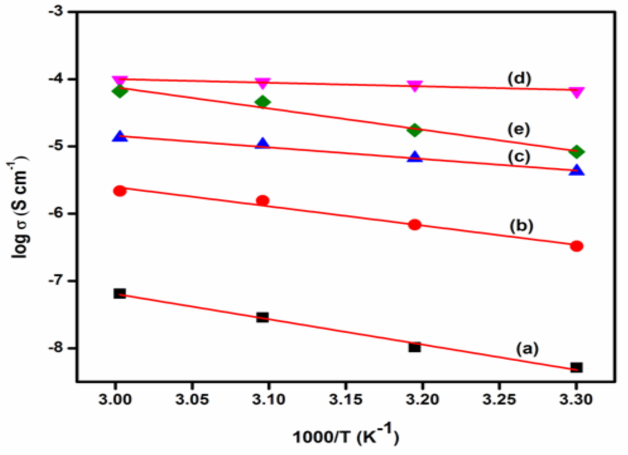

Fig -4: Temperature dependence of ionic conductivity of (a) pure pectin (b) 90 mol% pectin - 10 mol% NH_4NO_3 (c) 80 mol% pectin - 20 mol% NH_4NO_3 (d) 70 mol% pectin - 30 mol% NH_4NO_3 and (e) 60 mol% pectin - 40 mol% NH_4NO_3 polymer electrolytes

It has been observed that the ionic conductivity of the electrolyte increases linearly with increase of temperature for all compositions of pectin and NH_4NO_3. The linear variation of logσ vs. 1000/T plots for all polymer electrolytes suggests an Arrhenius type thermally activated process given by the equation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad \text{-------------} \quad (2)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy for conduction, k is the Boltzmann constant and T is the absolute temperature. The activation energy, E_a calculated from the slope of the plots and the regression value for all the compositions of pectin - NH_4NO_3 electrolytes have been presented in **Table -3**. It is noticed that the regression values for the plots are close to unity indicating that the temperature dependent conductivity for all the complexes obeys Arrhenius equation.

Table -3: Activation energy of Pectin - NH_4NO_3 polymer electrolytes from the Arrhenius plots

Composition of Pectin - NH_4NO_3	**E_a (eV)**	**Regression value**
Pure pectin	0.75	0.99
90:10	0.57	0.97
80.20	0.34	0.98
70:30	**0.11**	**0.90**
60:40	0.63	0.97

The activation energy is found to decrease with increasing salt concentration; this is due to the increase in amorphous nature of the polymer electrolyte that facilitates the ionic motion in the polymer network [4]. The activation energy varies from 0.75 to 0.11 eV with the minimum activation energy (0.11eV) for the composition (70 mol% pectin - 30 mol% NH_4NO_3) that gives the highest conductivity.

3.4 Compositional Dependence Conductivity

Fig -5 represents the ionic conductivity of polymer electrolytes at room temperature and activation energy as a function of salt concentration.

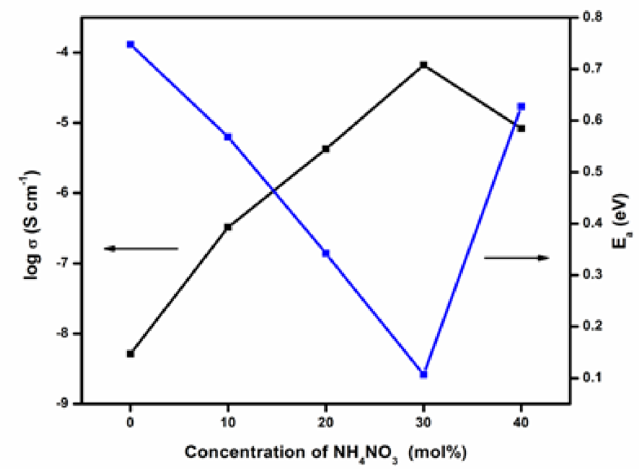

Fig -5: Variation of conductivity and activation energy as a function of NH_4NO_3 concentration

The dependence of ionic conductivity on the salt concentration gives the information about the specific interaction between the salt and the polymer matrix. In the microscopic view, the magnitude of the ionic conductivity is given as,

$$\sigma(T) = \sum q_i \mu_i n_i \quad \text{-----------} \quad (3)$$

where,

n_i– the number of charge carriers of type *i*

q_i – charge on each carrier

μ_i– mobility of charge carriers.

It has been observed from the Fig -5 that the ionic conductivity increases with increasing salt concentration up to 30 mol% and decreases at higher salt concentration (40 mol%). The increase in conductivity with increasing salt concentration may be due to the increase in the number of mobile charge carriers and increase in amorphous nature of the polymer electrolyte [4]. The decrease in conductivity at higher salt concentration can be assigned to either incomplete dissociation of salt or the formation of ion multiples. The highest conductivity polymer electrolyte (70 mol% pectin-30 mol% NH_4NO_3) has lowest activation energy (0.11 eV). It is noteworthy that the polymer electrolytes with low values of activation energies are suitable for device applications.

3.5 Modulus Spectra Analysis

The modulus formalism is a very important and suitable tool to determine, analyze and interpret the dynamical aspects of electrical transport process in the material. The phenomena of modulus studies can be analyzed using the equation given below:

$$M^* = \frac{1}{\varepsilon^*} = M' + iM'' = \frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2} + \frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2} \quad \text{----} \ (4)$$

where M' and M'' are the real and imaginary parts of electrical modulus.

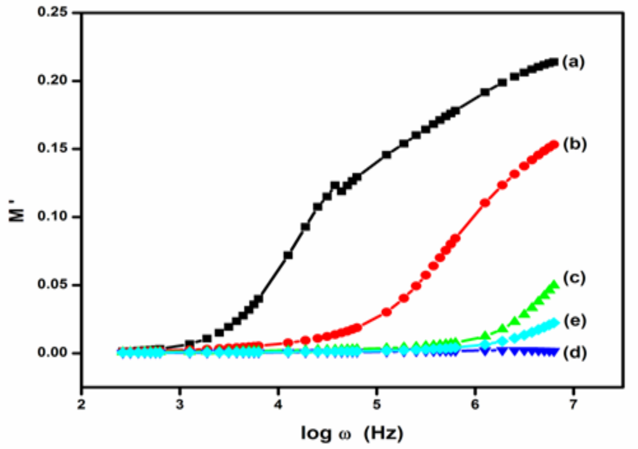

Fig -6(a): Frequency dependence of M' (ω) for (a) pure pectin (b) 90 mol% pectin - 10 mol% NH_4NO_3 (c) 80 mol% pectin - 20 mol% NH_4NO_3 (d) 70 mol% pectin - 30 mol% NH_4NO_3 and (e) 60 mol% pectin - 40 mol% NH_4NO_3 polymer electrolytes at 303 K

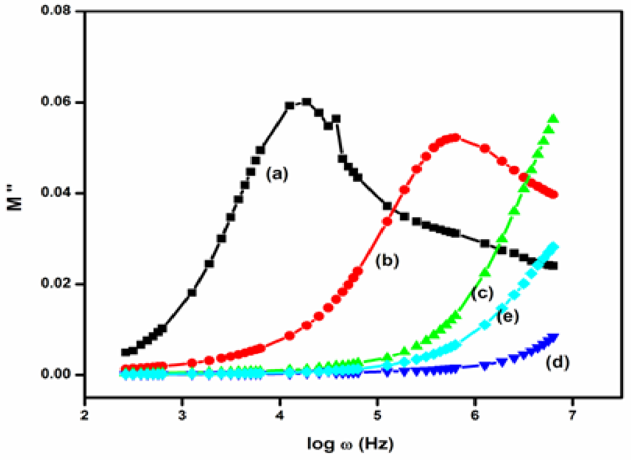

Fig -6(b): Frequency dependence of M''(ω) for (a) pure pectin (b)90 mol% pectin - 10 mol% NH_4NO_3 (c) 80 mol% pectin - 20 mol% NH_4NO_3 (d)70 mol% pectin - 30 mol% NH_4NO_3 (e) 60 mol% pectin - 40 mol% NH_4NO_3 polymer electrolytes at 303 K

Fig -6 (a) and (b) shows the variation of M′ and M″ against logω for different concentrations of pectin with NH_4NO_3 at 303 K. Both plots show an increase at the high frequency end. The dispersion peaks observed in the frequency dependence of M″ plot for the polymer electrolytes show features of an ionic conduction [14]. The plots show that both M′ and M″ decrease towards low frequencies due to negligible contribution of electrode polarization.

3.6 UV-Vis Spectral Analysis

Measurement of the absorption spectrum is the most direct method for investigating the band structure of materials. The plots of $(\alpha h\nu)^2$ versus photon energy (hν) for pure pectin and 70 mol% pectin doped with 30 mol% NH_4NO_3 films are shown in **Fig -7.**

The energy band gap was calculated from the relation

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \text{ --------- } (4)$$

where, hν is the photon energy, α is the absorption coefficient, E_g is the band gap energy and A is the characteristic parameter.

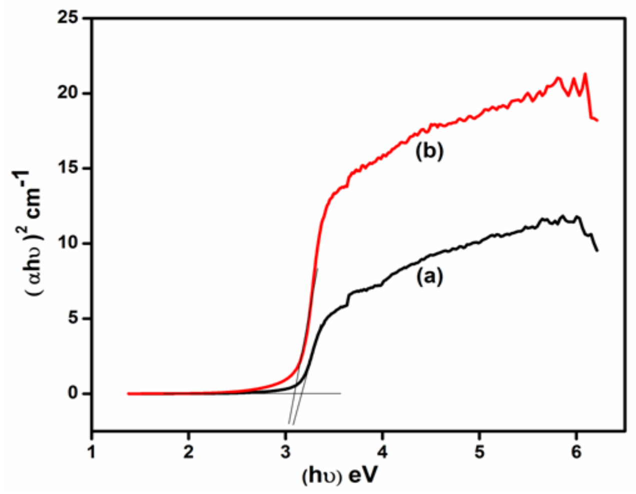

Fig -7: (a) UV-Vis spectra for pure pectin and (b) 70 mol% pectin – 30 mol% NH_4NO_3 polymer electrolytes

From the graph, the values of the direct band gap energies are evaluated. This energy has been calculated from the plots by extrapolating the straight line portion of the curve to zero absorption coefficient value [15]. The linear nature of the plots at the absorption edge confirms that pure pectin and 70 mol% pectin doped with 30 mol% NH_4NO_3 polymer electrolytes have direct band gaps. The energy gap is equal to 3.15 eV for pure pectin and 3.09 eV for 70 mol% pectin – 30 mol% NH_4NO_3. It is noticed that the bandgap energy decreases with the addition of NH_4NO_3.

4. CONCLUSION

The vibrational, electrical and optical properties of the solid polymer electrolyte based on the biopolymer pectin doped with NH_4NO_3 prepared by the solution casting technique have been studied. FTIR analysis reveals the possible bonding present in the polymer - salt complex and confirms the complex formation between the polymer and the salt. The 70 mol% pectin doped with 30 mol% NH_4NO_3 film has high conductivity of 6.64×10^{-5} S cm^{-1} at 303 K with low activation energy equal to 0.11 eV. The temperature dependent conductivity obeys Arrhenius relation. The modulus behavior of the polymer-salt complex is also studied. The optical bandgap for pure pectin and 70 mol% pectin doped with 30 mol% NH_4NO_3 has been calculated and it is found that the bandgap energy decreases with the addition of NH_4NO_3. Since pectin is eco-friendly, electrically effective, cheap and found in abundance, the polymer membrane made out of it can form a best substitute for synthetic polymer membrane in various electrochemical devices.

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