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# Effect of Sodium Iodide on Structural, Electrical and Optical Properties of Polyethylene Oxide/ Carboxymethyl Cellulose Blends

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## Abstract

*The production of highly potential Solid Polymer Electrolyte (SPE) materials has been the subject of extensive research. Due to their high flexibility, superior processability and enhanced resistance to electrodes during the charging/discharging process, they found to exhibit wide applications when compared to liquid or gel. In the present study, SPE films with 30/70 composition of Polyethylene oxide/Carboxymethyl cellulose blend, doped with Sodium Iodide (NaI) were prepared using a simple solution cast technique. The optical properties of the prepared samples were studied by UV–Vis spectroscopy technique and the results show that, the energy band gap decreases with the increase of salt concentration which is due to the enhancement of amorphous nature with the concentration of salt and is as evidenced from X-Ray diffraction studies. The electrical properties of the samples were studied using impedance analyser. The dielectric constant of the prepared samples decreases exponentially with frequency of applied electric field. In addition, the AC conductivity of the blend was found to increase with increase in salt concentration and the maximum conductivity was observed for 0.03% NaI salt doped Polyethylene oxide/Carboxymethyl cellulose blend. Thus, the said samples can be used in the preparation of SPE's.*

**Keywords:** *Electrical Conductivity, Polymer Blend, Solid Polymer Electrolyte*

## 1.0 Introduction

Nowadays the preparation and investigation of solid polymer electrolyte membranes are being carried out by many researchers, which plays an important role in fuel cell towards the conversion of chemical energy into electrical energy[1,2]. Investigations are in progress to improve the electrical & photosensitive characteristics of the blend for their marketing applications in the area of solid state electrochemical devices. The enhancement of electrical conductivity is not only key factor for crystallization by blending in suitable composition, but also can be done through the addition of alkali salt as dopant. Specifically, Polyethylene oxide based solid polymer blend electrolyte complexing with alkali metal is an exciting candidate in this field[3-8].

Phenomena involved in polymer electrolyte membrane fuel cell operation are complex; specifically, they involve charge transport, heat transfer, multi-phase flows and electrochemical reactions. So that one of the

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main essential properties to achieve in solid polymer electrolyte membrane in the fabrication of fuel cell is the ionic conductivity in charge transport mechanism. This can be achieved mainly by two methods. One is by increasing the amorphous phase in material structure and another is by enhancing the mobile ions. In view of its thermal & chemical stability, Poly Ethylene Oxide (PEO) is considered as one of the interesting host materials. In concerning with the structure, it partially possesses crystalline and amorphous regions at room temperature. Ionic conductivity, being a highly essential characteristic property in the solid polymer electrolyte is found favourable in amorphous phase rich materials. It is therefore, achieved by blending the PEO with amorphous rich polymer Na-CMC in proper composition. Hence in the present study, it is intended to prepare PEO/Na-CMC polymer blend.

Owing to its unique characteristics, Na-CMC is chosen as another polymer component for the preparation of polymer blend with PEO. It is the derivative of cellulose and prepared by the process of etherification of the hydroxyl groups with sodium monochloroacetate in the presence of aqueous alkali[9]. More importantly, Na-CMC exists in amorphous rich phase which is the favourable condition for faster movement of ions compared to other semi-crystalline polymers. Being hydrophilic in nature, it can be easily dissolved in cold/hot water. In addition, it is an organic polymer with typical characteristics such as natural, renewable, non-toxic, rich abundance, biodegradable & biocompatible[10-11].

The ionic conductivity of solid polymer electrolyte can further be improved by complexing the prepared polymer blend with alkali metal ions and in this direction attempts have been done by several researchers[3,5,12,13]. In most of the cases the alkali metal ions used are Li+ and Na+. Solid-state polymer batteries based on Lithium are extensively studied and generally preferred than others because of their typical characteristics such as good recyclability, high energy densities, safety and reliability[5,14,15]. They also have several drawbacks such as highly volatile nature, relatively more expensive and less abundant compared to sodium ion based batteries. Hence, in the present study, the effect of NaI on optical, structural and electrical properties of PEO/Na-CMC polymer blend electrolyte has been investigated.

# 2.0 Materials and Methods

## 2.1 Preparation of Films

PEO/Na-CMC-NaI films were prepared using well known solution cast technique in 30/70 composition with 0.01%, 0.02% and 0.03% of NaI. Films were obtained by pouring the solution consisting of specific wt.% of PEO (average molecular weight 200,000 g/mol) and Na-CMC (average molecular weight 294,828 g/mol) with NaI salt dissolved in double distilled water for varied concentrations onto a polypropylene plate and then dried at room temperature. Finally, the films were removed slowly from the petridish and were ready for the characterization.

## 2.2 Experimental Method

XRD analysis was carried out by irradiating the samples with Copper-Kα radiation having the wavelength of 1.540Å in X Ray diffractometer. Optical properties of the samples were studied using digitalized double beam UV-Vis spectrophotometer wherein, the absorbance was recorded in the wavelength range of 200-1100nm. The impedance analyzer was used to study dielectric properties of the samples in terms of dielectric constant, energy dissipation factor, dielectric loss & AC conductivity in the frequency range 50Hz–1MHz.

# 3.0 Results & Discussion

## 3.1 X-Ray Diffraction Studies

In polymer like materials the phase, structure and particle size can be analyzed by X-Ray diffraction technique. Even though, usually polymers exhibit mixed phase of crystalline and amorphous, Na-CMC is found to possess high degree of amorphous nature when compared to PEO. The X ray diffractograms of pure PEO, CMC and polymer blends doped with different concentrations of NaI (0.01, 0.02,0.03%) are shown in Figure 1a & 1b respectively. From Figure 1a, it is observed that, PEO exhibits sharp (intensified) peaks at 19.22 and 23.43 degree whereas, Na-CMC has broad hump. Therefore, the blend of PEO and Na-CMC is expected to exhibit higher amorphous phase than pure PEO. This has been witnessed with the x ray diffractogram of PEO/CMC polymer blends with 30/70 composition (Figure 1b). Figure 1b reveals that,

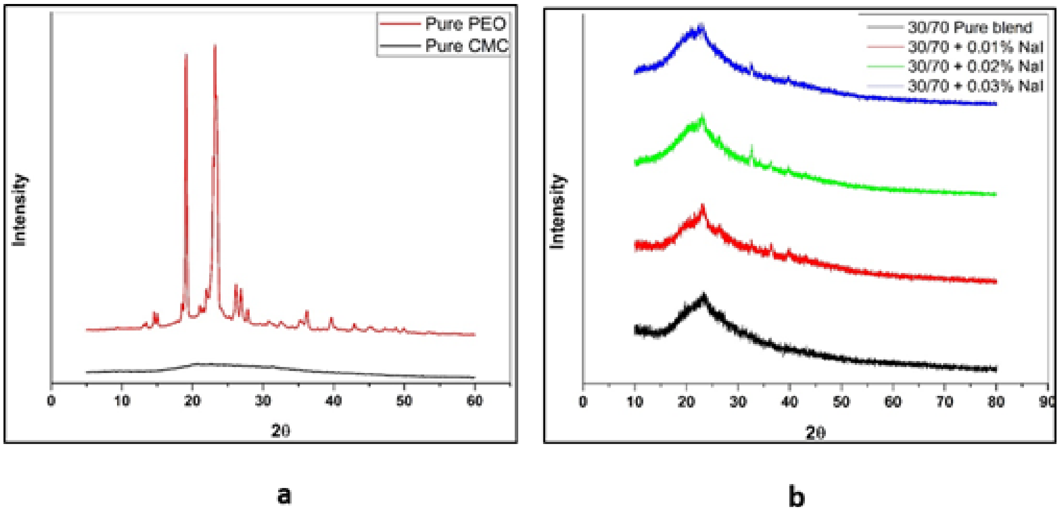


**Figure 1.** XRD spectra of a) Pure PEO, Na-CMC b) NaI doped 30-PEO/70-Na-CMC polymer blends

except less intensified peaks at 19.22 and 23.43 degree which are due to PEO, no other peaks were observed. But upon doping the blend with NaI salt, several additional peaks arise due to the presence of inorganic metal ion. This confirms the complexation of NaI salt in the blend.

## 3.2 Optical Energy Band Gap

The study of optical property is an essential one to measure the low energy band gap and wide energy band gap in view of their applications. Hence, by measuring the absorbance using UV-Vis spectrometer, the energy band gap of the prepared polymer blends was estimated. The optical band gap energy of the blend of 30-PEO/70-Na-CMC composition was estimated graphically and is found to be 4.85eV. It is observed that upon doping with 0.01%, 0.02% and 0.03% NaI, the optical band gap energy decreases and is 4.59eV, 4.54eV and 4.02eV respectively and can be noticed in Figure 2. Hence it can be seen that, the optical band gap energy reduces with NaI concentration and hence it influences the optical conductivity. Since, the prepared samples exhibit the optical band gap energy of more than 4 eV, these samples can be considered as having wide optical energy band gap which have applications in the fabrication of several optoelectronic devices like laser, green and blue LEDs.

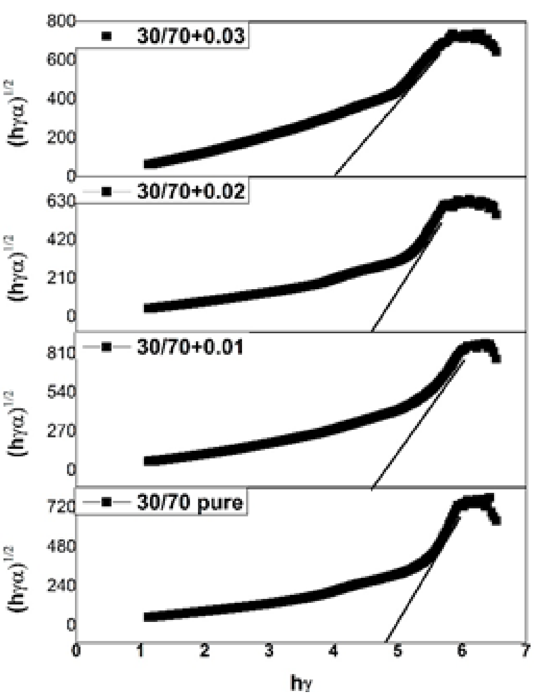


**Figure 2.** Indirect band gap energy plot of NaI doped 30-PEO/70-Na-CMC blends.

## 3.3 Dielectric Parameters

The dielectric properties of pure 30-PEO/70-Na-CMC and NaI doped polymer blends were studied in terms of dielectric loss and dielectric constant which were estimated using dielectric complex equation (1)

$$\varepsilon_r = \varepsilon' + i\varepsilon'' \quad (1)$$

where $\varepsilon_r$ is complex dielectric permittivity, $\varepsilon'$ is the real term called as dielectric constant measures the ability of the sample to hold electrical charges and $\varepsilon''$ is imaginary term called dielectric loss that measures the loss of energy during the migration of ions in the applied electric field. The dielectric constant of the prepared sample can be calculated using equation (2)

$$\varepsilon' = \frac{tC_p}{A\varepsilon_0} \quad (2)$$

where, t & A refers to thickness and area of the sample, $C_p$ is parallel capacitance and tanδ is energy dissipation factor measured by the instrument. The polarization effect in the electrode – electrolyte interface with the function of applied field frequency can be realized by the study of dielectric constant. In the present study, the dielectric study of pure 30-PEO/70-Na-CMC blend composition and that of doped with NaI is carried out so that the space – charge polarization can be understood. Figure 3a illustrates the dependence of dielectric constant with the applied field frequency. As evident from the figure, the dielectric constant is found to decrease with the increase of frequency. This may be attributed to the inability of several dipoles to rotate in the direction of the applied field with the increase of frequency. This is in view of insufficient time for the dipoles to align in the direction of applied electric field. Hence, the sample possesses high value of dielectric constant in low frequency region and low & maintains constant in high frequency region. This results in decrease of polarization of charges with the increase of frequency and maintains constant.

## 3.4 AC Conductivity

The AC conductivity of pure 30-PEO/70-Na-CMC blend and the one doped with NaI were calculated using the dielectric constant which was measured using impedance analyzer in the frequency range of 50-$10^6$ Hz. The equation 3 is used to calculate AC conductivity

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan\delta \quad (3)$$

where ε' & $\varepsilon_0$ represent the dielectric constant and permittivity of free space respectively, ω is angular frequency and tanδ is dissipation factor measured from the instrument. It is evident from Figure 3b that the AC conductivity is less in lower frequency region due to the effect of interfacial impedance or the space charge polarization influencing non-Debye characteristics for the said samples[16].

From the Figure 3b, it can also be seen that, the conductivity is found to increase with increase in the concentration of NaI. This is due to the rise of mobility of ions due to the increase in the concentration of dopant. In the present work, the maximum conductivity at room temperature is obtained for 0.03% NaI dopant and it is 1.95 x $10^{-3}$ $Scm^{-1}$ in the measured frequency range. This may be attributed to the hopping mechanism in which mobility of ion from one coordination site to another following with the creation of the vacancy in preoccupied site for new incoming ion[17-20].

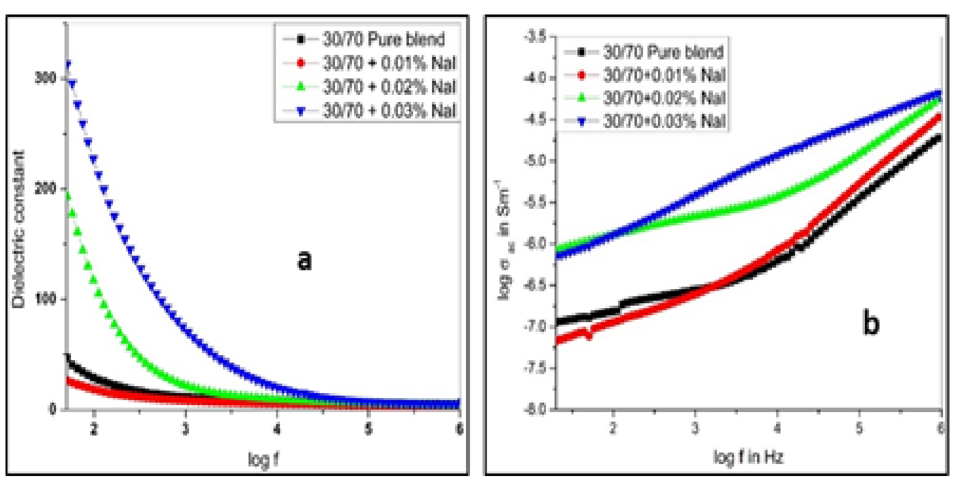


**Figure 3.** Plot of a) Dielectric constant and b) AC conductivity of 30-PEO/70-Na-CMC blend doped with different concentration of NaI.

## 4.0 Conclusion

The polymer blend films of 30-PEO/70-Na-CMC composition doped with varied concentration of NaI were prepared using simple solution cast method. The effect of the dopant on optical, structural and electrical properties were studied. The variation in the intensity peaks of pure PEO and Na-CMC in X-Ray diffraction upon doping evidences the mixing of dopant in the blend. The decrease of optical band gap energy with increasing concentration of dopant and the values greater than 4eV suggests the material exhibiting wide optical band gap energy so that these can be used in the preparation of several optoelectronic devices. The dielectric property of the studied samples obeys usual behavior of polymers. In addition, the conductivity of the studied samples exhibit increasing behavior with the concentration of dopant and the high conductivity is observed for 0.03% of dopant. Hence the said sample can find applications as solid polymer electrolytes membrane in the fabrication of fuel cell.

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