Research Paper

Investigation of A Novel Biodegradable Blend Polymer Electrolyte Based on PVA and Agar

PHYSICS

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ABSTRACT   *Recently, biodegradable polymer electrolytes have gained interest for their application in solid state devices. A novel blend polymer electrolyte with a combination of biodegradable polymer- Poly vinyl alcohol (PVA) and natural polymer- Agar has been prepared by solution casting technique. XRD analysis reveals the amorphous nature of the polymer samples. The ionic conductivity of the prepared polymer electrolyte is found by ac impedance spectroscopy analysis. The maximum ionic conductivity is 3.6738×10^{-7} S cm^{-1} at ambient temperature for the film of composition 70mol% PVA:30mol% Agar. The lowest relaxation time at ambient temperature has been found to be 1.479×10^{-5} sec for 70% mol PVA and 30% mol Agar.*

Introduction:

Energy conversion or storage devices play a vital role in day-today life as power demand is increasing very rapidly which cannot be attained by the depleting fossil fuels. The other major challenges are "global warming" and pollution. In order to meet these challenges, we need a renewable, biodegradable and green energy source. Batteries and fuel cells which serve as power sources in means of transportation and electronic gadgets have 'polymer electrolyte' as the key component. Polymer electrolytes are solid membranes which effectively act as the separators between the two electrodes in an electrochemical cell, preventing electrical short circuits whilst still allowing ionic current to flow through it. These polymer electrolytes have gained much interest due their wide applications such as electrochromic windows, electrochemical sensors, supercapacitors and proton exchange membrane fuel cells (PEMFC).

Over the last few years, commercial agar has been extensively tested in order to apply it as an electrolyte in solid state devices [1].Agar is a gelatinous, non-toxic and biodegradable substance derived from marine algae [2]. It is the resulting mixture of linear polysaccharides Agarose and Agropectin.Ionic conductivity of Agar doped with NiO particles has been done by Dalal Jaber Suliman Abdullah Audeh[3]. Samples of agar- based electrolytes with different ionic liquids were prepared and characterized by physical and chemical analyses[4].Agar-agar is insoluble in cold water, but it dissolves readily in boiling water. Agar being amorphous in nature can exhibit high conductivity.

PVA is an atactic material that exhibits crystallinity with partial amorphous nature. In terms of microstructure, it is composed mainly of 1,3-diol linkages [-CH$_2$-CH(OH)-CH$_2$-CH(OH)-] but a few percent of 1,2-diols [-CH$_2$-CH(OH)-CH(OH)-CH$_2$-] occur, depending on the conditions for the polymerization of the vinyl ester precursor. Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It has high tensile strength and flexibility. PVA is nontoxic and biodegrades slowly. Characterization of PVA based gel polymer electrolytes with NH$_4$SCN has been reported [5]. Many works with PVA blended with PAN, PHU, PMMA have been reported. But no work has been done with the combination of PVA and Agar.

This paper describes the preparation and characterization of PVA, a biodegradable polymer blended with a biopolymer, Agar. XRD and ac impedance spectroscopic techniques are employed for the analysis of the prepared samples.

2. Experimental Technique:

Polymer film of PVA (Merck): Agar (Colloids Impex Pvt Ltd) of different compositions (100:0, 90:10, 80:20, 70:30, 60:40) are prepared using solution casting technique. Suitable amount of PVA is dissolved in water at 100°C in the magnetic stirrer. After PVA is completely dissolved, suitable amount of Agar is added in the same solution and stirred well at the same temperature. Then the homogenous solution is poured in the polypropylene petri dish and allowed to evaporate in vacuum oven at 60ºC. Smooth uniform thin film which is transparent has been obtained in 24 hours. Then the film is carefully removed from the petri dish and kept in an air tight cover.

In the present work, the synthesized films are characterized by XRD - to study the amorphous nature of PVA & Agar blend polymer film and AC impedance spectroscopic technique - to determine ionic conductivity. XRD patterns are recorded with XPERT-PRO Diffractometer system using Cu Kα radiation in the range of 2θ = 10° to 80°.The impedance studies are made using a computer controlled HIOKI 3532 LCR meter over a frequency range of 42 Hz to 5 MHz with a cell having aluminium blocking electrodes.

3.Results and discussions

XRD Analysis:

X-ray diffraction (XRD) studies have been carried out to investigate the occurrence of complex formation between the two polymers and amorphous nature of the polymer complex. The XRD patterns of the blend polymer electrolyte with different composition of PVA: Agar are shown in **FIGURE 1**.
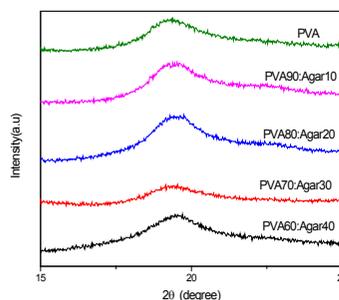

FIGURE 1 Diffractograms of pure PVA and different compositions of PVA : Agar

From **FIGURE 1,** it is observed that a broad peak around 19.6o [6] ascribed to the pure PVA is found to decrease in intensity and increase in full width half maximum for 70 PVA: 30Agar blend polymer electrolyte. It is also observed that this peak has been slightly shifted in the PVA: Agar complexes. These changes reveal the amorphous nature of the blended 70 PVA: 30Agar system.

Impedance analysis:
The electrical characterization of PVA: Agar blend polymer films have been performed using AC impedance spectroscopy technique. **FIGURE 2** shows the Cole-Cole (Nyquist plot) of different concentrations of PVA:Agar polymer electrolytes.
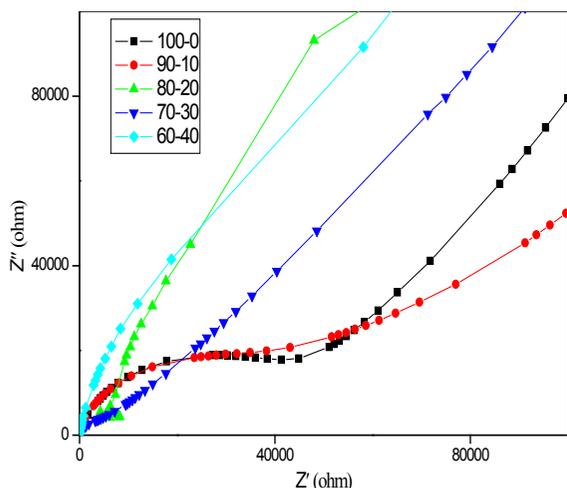

FIGURE 2 Cole-cole plot of PVA: Agar of various compositions

Each plot consists of a high frequency semi-circle and a low frequency spike due to the effect of blocking electrodes. The semicircle corresponds to bulk resistance of the blend polymer film [7]. The value of bulk resistance R_b was found by extrapolating the intercept of either the semicircle or the spike to the real impedance axis (Z') of the cole-cole plot.

The ionic conductivity values of the polymer electrolytes are calculated by using the equation,

$\sigma = l/R_b A$

where l and A are the thickness and area of the electrolyte film respectively and R_b is the bulk resistance of the electrolyte film.

It is found that as the concentration of agar increases, the ionic conductivity values also increases, which is due to the increase in the mobility of charge carriers in the polymer blend and also due to the increase in amorphous nature of the polymer electrolyte which reduces the energy barrier thereby facilitating the fast ion transport [8]. The maximum ionic conductivity is obtained for the membrane of 70 mol% of PVA: 30 mol% of Agar. The ionic conductivity decreases for higher concentration of Agar (40 mol%) which may be ascertained due to formation of ion pairs or ion clusters which restricts the mobility of the charge carriers in the matrix [9].

The complex impedance plot of the highest conductivity sample 70 mol% of PVA: 30 mol% of Agar at different temperatures is shown in FIGURE 3.
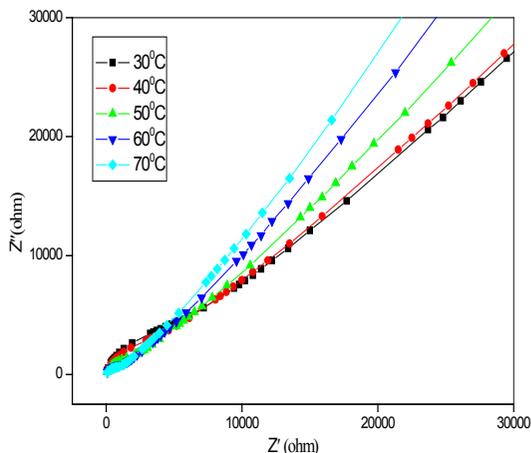

FIGURE 3 Cole-Cole plot of 70 PVA : 30 Agar polymer electrolyte at various temperatures

It is observed from the plot that the semicircle decreases with increase in temperature. At higher temperatures, the semicircle disappears indicating the prevailing of the resistive component of the electrolyte system [10]. The decrease in resistance of the polymer electrolyte is due to the enhancement of the ionic mobility and the number of carrier ions with temperature [11].

Loss tangent spectra:
The dielectric relaxation parameter of the polymer electrolytes can be obtained from the study of tan δ as a function of frequency. The dielectric loss tangent (tan δ) can be defined as,

tan δ= ε''/ ε'

where **ε'**- dielectric constant

ε''- dielectric loss

The variation of tan δ with frequency for all the prepared PVA : Agar blend polymers at 303K is presented in **FIGURE 4**.
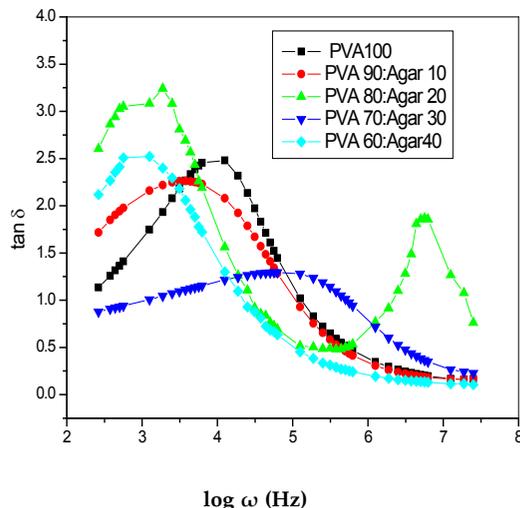

FIGURE 4 Variation of tan δ with frequency for different mol% of PVA : Agar blend polymer electrolytes.

It is inferred from the figure that the value of tan δ increases with increase in frequency and attains a maximum which then declines with frequency value. With increase in the agar concentration, the magnitude of the loss decreases and the loss peak shifts towards higher frequency. The angular frequency of the applied field ω_p, at which the (tan δ)$_{max}$ occurs, defines the relaxation time, $\tau = 1/\omega_p$ [12].

Table 2: Relaxation time for various compositions of PVA: Agar polymer electrolytes.

Composition PVA:Agar	ω_p	τ (s)
90 : 10	3698.28	2.7039×10^{-4}
80 : 20	1952.54	5.1215×10^{-4}
70 : 30	67608.29	1.4791×10^{-5}
60 : 40	879.022	1.1376×10^{-3}

Table 2 shows the calculated relaxation time values for prepared PVA: Agar blend polymer electrolytes at room temperature. The lowest relaxation time at ambient temperature has been found to be 1.4791×10^{-5} s for 70 mol% PVA : 30 mol% Agar blend polymer electrolyte. The relaxation time decreases with increase in Agar content. This means increase in Agar content shortens the relaxation time which speeds up mobile ion transition and make higher conductivity [13].

Conclusion:

The proton conducting polymer electrolytes based on PVA: Agar in different concentration ratios are prepared by solution casting technique. The X-ray diffraction patterns of the polymer electrolytes reveal the increase in amorphous nature of the polymer with the increase of agar concentration. The ac conductivity values for all the prepared polymer electrolytes have been evaluated using impedance spectroscopic analysis at different temperatures. The maximum ionic conductivity of 3.6738×10^{-7} Scm^{-1} has been obtained for 70mol%PVA: 30mol% Agar blend polymer electrolyte. A low relaxation time 1.4791×10^{-5} s has been observed for the electrolyte having highest ionic conductivity.

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