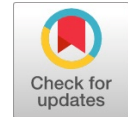# Dielectric Behaviour of PVA and Cornstarch Polymer Blend Electrolytes

M. Anandha Jothi, D. Vanitha, S. Asath Bahadur

***Abstract**: Simple film preparation method of solution casting has been used for making of biodegradable PVP and Cornstarch blend polymer electrolytes. Ion dynamics in polymer film membranes has been understood by conductivity and dielectric studies. The combination of 60wt% PVA and 40wt% Corn Starch is having the high conductivity value of 1.56×10^{-9} S cm^{-1} at ambient temperature and when the temperature increases, the conductivity also linearly increases to obtain 4.93×10^{-9} S cm^{-1} at 363 K which due to ion hopping mechanism in the polymer matrix. The frequency dependence of dielectric permittivity, dissipation factor (tangent loss) and electrical modulus have been used to know about dielectric behaviours of the polymer blend electrolytes. In dielectric studies, Non-Debye behaviour was observed in all samples.*

Keywords: PVA, Cornstarch, Polymer blend, Conductivity and Dielectric studies.

I. INTRODUCTION

In recent times, polymer materials are plays significance role in sophisticated high energy electrochemical devices [1-4]. Poly (vinyl alcohol) (PVA) is soluble in water. It is the cheapest biodegradable polymer with excellent film forming capacity and it's containing semi crystalline nature [5, 6]. Since decades ago, numerous endeavours have been centred on blending of natural polymers to prepare new materials with wanted properties. In this, corn starch is a natural, cheap copious and soluble in water [7-9]. Polymer blending is one of the techniques for developing the conductivity of electrolytes in electrochemical devices. Cornstarch is favored in light of the fact that it has the smallest particle size and furnishes better scatterings in blends with thermoplastic polymer. In this Cornstarch polymer composed of a mixture of linear amylase and branched amylopectin polysaccharide chain [10]. However, most of natural polymer such as Cornstarch formed very low thin film conductivity [11]. In efforts to overcome the disadvantages such as brittleness, many efforts are carried out to combine starch with synthetic polymers. In this work, conductivity, thermal and dielectric behavior of PVA: Cornstarch blend has been investigated.

II. EXPERIMENTAL

A. Materials and Preparation method

Polyvinyl alcohol and Corn starch with linear monomer formula of C_2H_4O and $C_6H_{10}O_5$ were purchased from Sd fine-chem (SDFCL) and SRL chemicals (SISCO RESEARCH LABORATORIES PVT. LTD) respectively.

Different wt. % of Cornstarch was dissolved in 50 ml of double distilled (DD) water. The solution was heated at 75°C for 30 minutes in magnetic stirrer. Then the solution is cooled to room temperature. Later than various wt % of PVA were added to that solution under constant stirring. After 24 hours, the solution becomes homogeneous. The formed homogenous polymer blend solutions were transferred into Petri dishes and left to dry at ambient temperature for removal of solvent in the polymer membrane. Three days later, approximately 0.15 mm thickness of transparent polymer film was expelled from Petri dish for further analysis. All the polymer films were air tightly preserved under room temperature. The coding of the different composition of PVP and Cornstarch blend polymer electrolytes were as shown in Table I. The schematic image of preparation method was as shown in Fig 1.
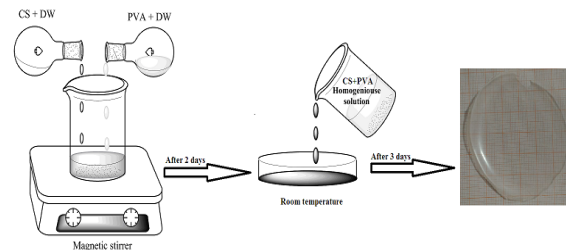

Fig. 1.Preparation method of polymer film

Table -I: Polymer film coding

PVA: Cornstarch (wt. %)	Film code
0:100	VA-00
20:80	VA-20
40:60	VA-40
60:40	VA-60
80:20	VA-80

Retrieval Number: A11721291S419/2019©BEIESP
DOI:10.35940/ijeat.A1172.1291S419
Journal Website: www.ijeat.org

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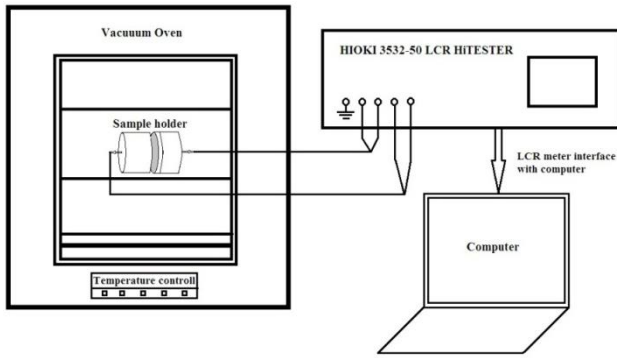
B. Experimental technique

Fig. 2.Experimental setup of Conductivity and Dielectric studies

The conductivity and dielectric behaviour of the prepared polymer films were determined with help of HIOKI 3532-50 LCR over the frequency range of 42 Hz to 1000000 Hz at different temperature. Samples were mounted on the holder with silver electrodes (SE) under spring pressure with the configuration SE∥SPE∥SE. The ends of these two electrodes were connected to LCR meter and it was interfaced with computer for further analysis. Temperature dependent conductivity of the samples were carried out for x wt. % of PVA: y wt. % of Cornstarch (x = 0, 20, 40, 60 and 80 wt. % & y = 100, 80, 60, 40 and 20 wt. %) polymer blend membrane, under the same frequency and temperature various from ambient temperature to 363 K.

III. RESULTS AND DISCUSSION

A. Temperature dependent Conductivity / Composition dependence Conductivity at different Temperature
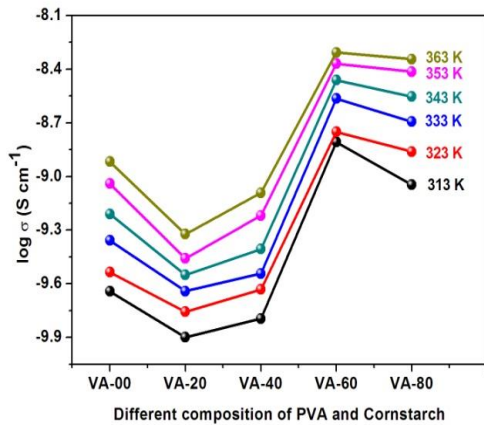

Fig. 3.Composition dependence conductivity of PVA: Cornstarch blend electrolytes at various temperatures

Fig 3 exemplifies the variation of conductivity as a function of different wt. % composition of PVP and Cornstarch at different temperatures. The composition of VA-60 has reached the higher conductivity of 1.5×10^{-9} S cm^{-1} at ambient temperature. The complete complexion of polymer blend is obtained for 60 wt. % of PVP and 40 wt. % of Cornstarch. The conductivity is increased due to the the easy movement of the mobile charge carriers. When rising the temperature, the conductivity of all the composition of

polymer blends are linearly increases (Arrhenius behaviour) as clearly shown in Fig 3. Because of the polymer matrices have been expended to form the free volume and unoccupied spaces for migration of ions according to ion hopping mechanism [12]. Then the conductivity is increased to reach the value 4.93×10^{-9} S cm^{-1} at 363K for the same sample VA-60. This rise in conductivity values arises due to the increase in flexibility of the polymer electrolyte [13] and the inter- and intra chain hopping from chain bonding rotations and thereby increasing the number of density and mobility of ions [14].

Tabe- II: Conductivity and activation energy for all composition of PVA and Cornstarch

Samples	σ (S/cm)		E_a (eV)
	303 K	**363 K**	
VA-00	2.3×10^{-10}	1.2×10^{-9}	0.32365
VA-20	1.4×10^{-10}	4.8×10^{-10}	0.29897
VA-40	1.8×10^{-10}	8.1×10^{-10}	0.24377
VA-60	1.5×10^{-9}	4.9×10^{-9}	0.23175
VA-80	6.7×10^{-10}	4.5×10^{-9}	0.3095

B. Arrhenius behaviour

The temperature dependent conductivities of PVA-Cornstarch polymer electrolyte system investigated at temperature range of 313 to 363K as shown in figure 4. When the temperature increases from ambient temperature to higher temperature, the polymer matrices have been expended to form the free volume and unoccupied spaces for migration of ions. In this way conductivity of ions in PEs have been improved with increasing temperatures according to ion hopping mechanism. The conductivities are linearly increased by rising temperature in all the PE samples to obey the Arrhenius behaviour as shows in figure 4. Using linear fitting to the curves from logσ versus 1000/T graph, then found the slope value from this plot. This slope value used for the calculation of activation energy E_a for the PEs.
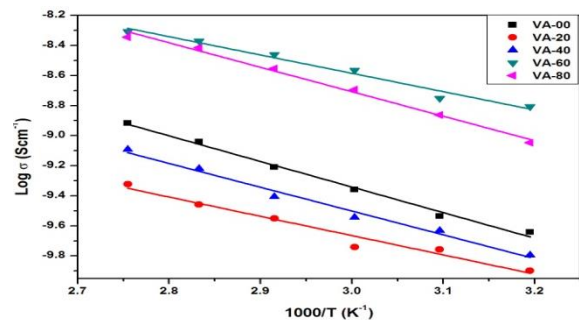

Fig. 4.Arrhenius plot for samples VA-00, VA-20, VA-40, VA-60 and VA-80

Activation energy E_a was calculated using the Arrhenius rule, as given below

$$\sigma\,(T) = \sigma_o \exp\,(-E_a / KT) \qquad (1)$$

where $\sigma(T)$ denote the temperature dependent conductivity (S cm^{-1}), σ_o is the pre-exponential factor, E_a is the activation energy (eV), K is the Boltzmann constant (J K^{-1}) and T is absolute temperature (K).High conducting sample VA-60 has low activation energy of 0.23eV.

C. Dielectric Studies

An examination on the dielectric behavior of the polymer electrolyte encourages us to comprehend the polarization impact at the electrode-electrolyte interface. The complex dielectric $\varepsilon*$ of a system is expressed as,

$$\varepsilon* = \varepsilon_r - i\varepsilon_i \qquad (2)$$

Where ε_r is a measure of the charge stored in the material, while ε_i corresponds to the amount of energy loss to move ions.
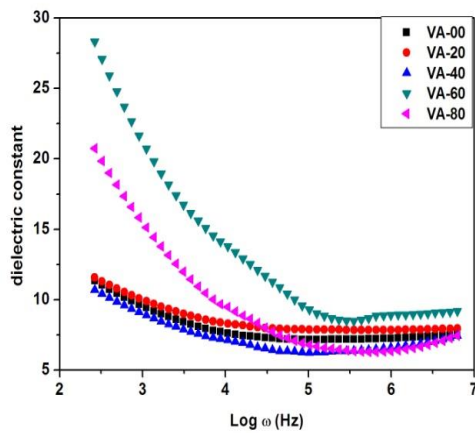

Fig.5a. Frequency dependence of dielectric constant (ε_r) for all composition of PVA: Cornstarch blend electrolytes at ambient temperature
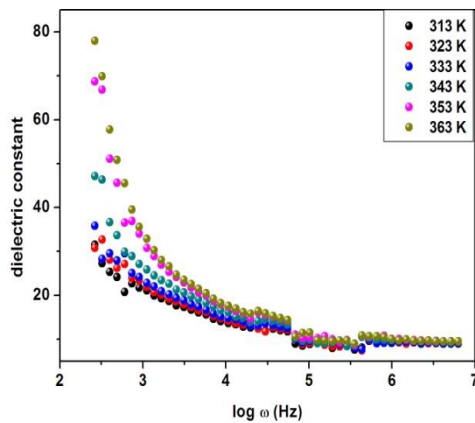

Fig.5b. Dielectric constant (ε_r) for VA-60 sample at different temperature all composition at ambient temperature

The equations for the dielectric constant ε_r and dielectric loss ε_i are shown as follows

$$\varepsilon_r = Z_i / \omega C_0(Z_r^2 + Z_i^2) \qquad (3)$$

and $\quad \varepsilon_i = Z_r / \omega C_0(Z_r^2 + Z_i^2) \qquad (4)$

Where Z_i is an imaginary part of impedance (Ω), Z_r is a real part of impedance (Ω), C_0 is vacuum capacitance (F) and ω is angular frequency (Hz).

Fig. 5a and 5b gives the variation of dielectric permittivity ε_r with respect to frequency at ambient temperature and different temperature respectively. Form the figure, it is confirmed that the dielectric constant decrease by increasing the frequency. The concentration ratio of PVA in the polymer blend matrices (VA-60) shows the high dielectric constant. Since, Composition dependence Conductivity result also replicate the same sample VA-60 has higher conductivity than other samples. At the low-frequency window, the dielectric constant is maximum which is due to the space charge polarization at electrode ‖ electrolyte interface.
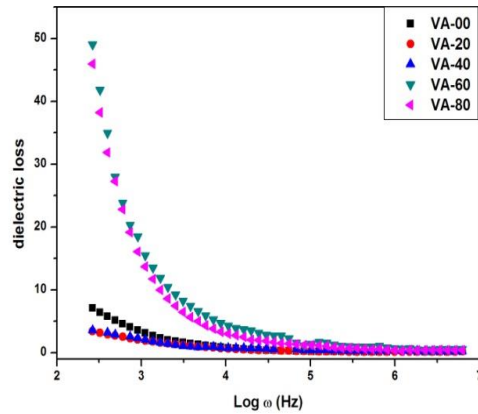

Fig. 6a. Frequency dependence of dielectric loss (ε_i) for all composition of PVA: Cornstarch blend electrolytes at ambient temperature
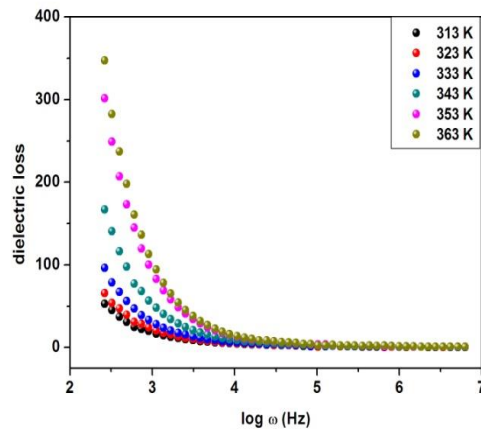

Fig. 6b. Dielectric loss (ε_i) for VA-60 sample at different temperature all composition at ambient temperature

For all the SPEs, the conduction path way is influenced by the number of charge carriers, the concentration of mobile ions and the availability of connecting polar domain [15].This nature also confirms the non-Debye dependence [16].The dielectric constant decreases for rest of the other concentration (VA-00, VA-20, VA-40) .

This is because of the aggregation of ions, leading to decrease in the number of mobile charge carriers and hence the mobility. The same behaviour is observed in Fig. 5b. When apply heat to the polymer membrane, it's become elongated to obey the free volume theory, increase the flexibility and also improve the amorphous nature. In this way the dielectric constant improved by applying of heat in the polymer membrane. So the dielectric constant of the higher conducting sample increases by rising of temperature. The same behaviour is observed for dielectric loss and it is shown in the fig. 6a and 6b.The dielectric loss reaches the saturation value at high frequencies because of the reduction of charge carriers at the boundary among electrode and electrolyte. The interrupted reversals of the electric field takes place quickly at high frequencies where there is a shortage of ion diffusion in the direction of the field [17]. The polarization is then decreased, leading to the decrease in the values of ε_r and ε_i.

D. Modulus studies

The Modulus analysis is used to The display conductivity relaxation process and ion hopping mechanism in polymer electrolytes. The variation in the values of M' and M″ with frequency are portrayed in Figure 4a and 4b, separately.
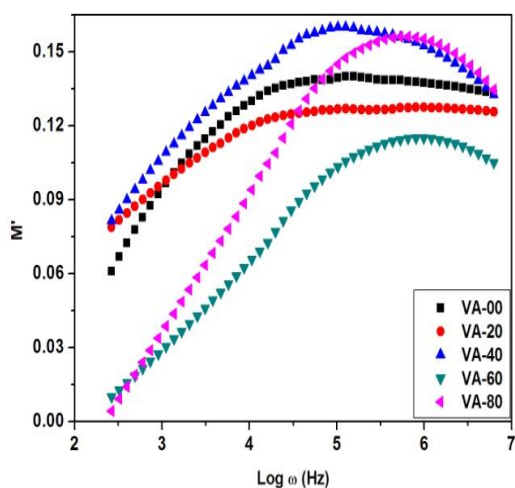

Fig. 7. Variation of the real part of the modulus (M′) for all composition of PVA: Cornstarch blend electrolytes at ambient temperature

Fig 7 reveals the real part of the modulus (M') for all composition of PVA: Cornstarch blend electrolytes at ambient temperature and different temperature of VA-60 sample respectively. At lower frequencies, the M' value approaches to zero for sample VA-60 and VA-80which is due to the negligible electrode polarization. The non -Debye behavior is confirmed by the long tail at low frequency region and the capacitance effect at the electrodes. [18, 19].

In imaginary part of electric modulus analysis M″ there are two humps are appeared in VA-60 and VA-80 due to the semi crystalline nature of PVA and Cornstarch. At low frequency region, α-crystalline and at high frequency region, β-amorphous regions are present in these two samples.
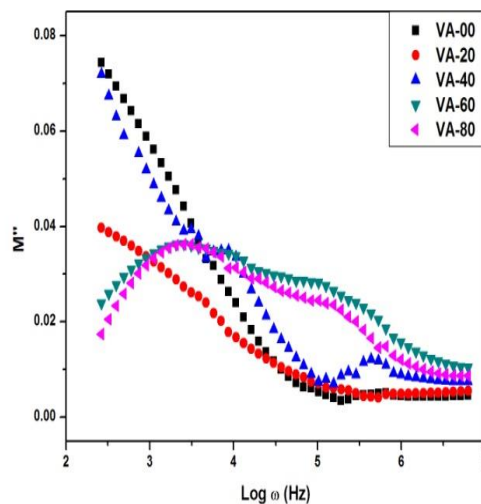

Fig. 8a. Variation of the imaginary part of the modulus (M″) for all composition of PVA: Cornstarch blend electrolytes at ambient temperature
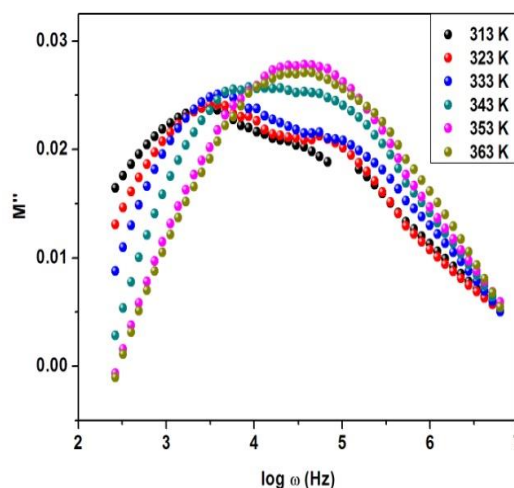

Fig. 8b. The imaginary part of the modulus (M″) for VA-60 sample at different temperature

From fig. 8a, two relaxation times τ_1 and τ_2 are observed. Thus, τ_1 due to α relaxation peaks by dynamic dipole rotation and τ_2 due to β relaxation peaks by dipole orientation in static region respectively. Since, high conducting sample obtain low relaxation time. Improvement of amorphous nature in the polymer matrix by increase of temperature is clearly shown in Fig. 8b. When increase the temperature, two humps in α-crystalline and β-amorphous regions of higher conducting sample VA-60 becomes merging to form a single hump and also shifted towards at high frequency region [20]. Since, the semi crystalline structure of the PVA: Cornstarch blend polymer electrolytes changes into the amorphous structure at high temperature. The electric modulus study is widely used to deduce the bulk dielectric behavior in case of the polymer electrolytes as a function of the frequency.

IV. CONCLUSION

PVA and Cornstarch based blend polymer electrolytes using double distilled water as a solvent have been prepared by technique of solution casting. Conductivity, dielectric (ε_r, ε_i, M′ and M″) and thermal behavior of polymer blend electrolytes have been analyzed in the frequency range of 42 Hz to 1000000 Hz. The higher conductivity observed at ambient temperature and high temperature are found to be 1.56×10^{-9} S cm^{-1} and 4.93×10^{-9} S cm^{-1} for the composition of 60 wt. % of PVA and 40 wt. % of Cornstarch. The plot of composition dependence conductivity shows that all electrolytes obeyed the Arrhenius rule with thermally activated process. Dielectric constant and dielectric loss are increased by increasing the temperature for all the polymer blend electrolytes. When increasing the temperature, two humps in α-crystalline and β-amorphous regions of higher conducting sample VA-60 becomes merging to form a single hump and also shifted towards at high frequency region.The modulus analysis reveals the change in the amorphous nature of the polymer blend at high temperature and denotes the thermally enacted relaxation process and shows the non-Debye nature.

ACKNOWLEDGMENT

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