

Chapter 3

CHAPTER III

SYNTHESIS AND CHARACTERIZATION

This chapter provides an overview of the preparation of biopolymer membranes from their corresponding natural sources. This also deals with the characterization of the obtained biopolymer membranes and their respective- bio-electrolytes by various analytical techniques and fabrication of Magnesium, Lithium and Ammonium (H^+) - ion conducting battery.

The preparation of the biopolymer membrane from the biomass includes two different steps.

- Preparation or processing of the Biomass Extract.
- Synthesis of the biopolymer membrane from the Biomass Extract.

3.1 Selection of the biomass:

The biomass selected for the present investigation comprises of three different biomaterials.

- The first biomass, **Corn Silk** is a biowaste and a by-product of the Corn Plant (*Zea Mays*).
- The second biomass is *Sargassum Muticum* which is an invasive Seaweed commonly known as Kadal Paasi in Tamil.
- The third biomass, *Salmalia Malabarica Gum* is a plant exudate commonly known as Ilavam Pisin (Gum) in Tamil.

3.1.1 Materials used for the work

Polyvinyl alcohol (PVA) (mol. wt – 85000 - 1,24,000, Sigma - Aldrich), magnesium chloride ($MgCl_2 \cdot 6H_2O$) (mol. wt – 203.30, Spectrum), lithium chloride (SRL Private ltd, Mumbai), and Ammonium Formate (mol.wt. 63.06, Sigma - Aldrich) are purchased and used as such. Corn silk obtained from the Corn of the local farm has used as the starting material. Similarly, brown seaweed *Sargassum Muticum* (SM), the second biomass, has been obtained from the marine biodiversity area in the Gulf of Mannar, Rameswaram, Tamil Nadu, India. The third biomass, *Salmalia Malabarica Gum*, has been collected from the barks of the tree. Double distilled water and ethanol are used as solvents.

3.1.2 Blending of biomaterials for biopolymer membrane:

The biomaterials are blended with other biopolymer to enhance their film-forming, mechanical, electrical, and thermal properties. Blending is of two types - Physical and Chemical blending.

In the former type, the common technique adopted for preparing them is by melt or solvent blending of the polymers, when both are completely miscible, they are held together by some physical force like Vander Waals force. But the morphology of the obtained polymer blend can be reverted since the thermodynamic tendency is more towards the equilibrium phase there by forming two separate polymer layers once the mechanical stirring is stopped. In the latter case, the practiced method is to synthesize a blend biopolymer by intermixing two different biopolymers at molecular level to form a graft or block copolymer. In this case, the extract of the biomass and the biopolymer are cross-linked by chemical bonding like hydrogen bonding.

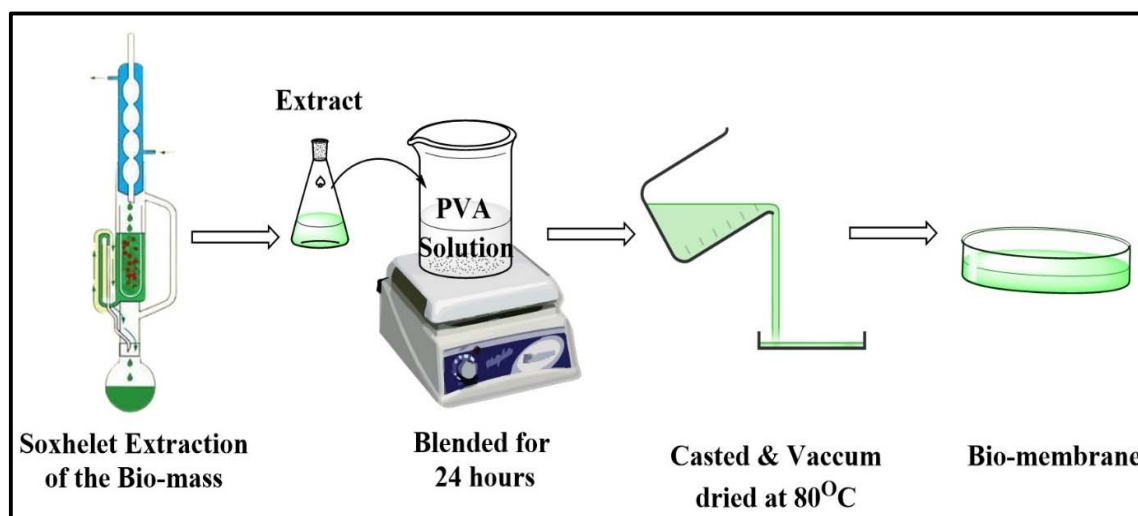


Figure 3.1: Preparation of biopolymer membrane from biomass (Corn Silk/ *Sargassum Muticum*) Extract

In this perspective, a uniform, thin, solid polymer electrolyte has been obtained by **Solution Casting Technique.**

This is an effective and a traditional method widely used to develop thin membranes owing to the ease of preparation. In this technique, appropriate weight ratios of the prepared extract and the biopolymer, polyvinyl alcohol (PVA) are dissolved in double distilled water as the solvent. The solution mixture is magnetically stirred at room temperature for a particular time period, ensuring the complete complexation of the biomass extract and the biopolymer. The obtained clear solution is then transferred to a polypropylene petri dish to obtain a free-standing, flexible membranes as shown in the scheme in Figure 3.1.

3.2 Preparation of corn silk extract (CSE) and corn silk biopolymer membrane (CSBP) from corn silk biomass

The corn silk extract is prepared from corn silk obtained from local farm. At first the corn silk is dried in shade and cut into pieces. It is then washed well with distilled water and then with ethanol. The solution is then heated with mechanical stirring and allowed to cool to room temperature. The extract thus obtained is brown in colour and is now filtered and stored in an air tight container at 4°C which can be used upto 6 months.

To enhance the free film-forming tendency of the prepared extract CSE, it is blended with PVA, due to its non-toxic, water-soluble, eco-friendly and its good film-forming nature. It is to be noted that the ionic conductivity of the semicrystalline, pure PVA is $2.5 \times 10^{-10} \text{ Scm}^{-1}$ [1] which has been considerably increased to $1.747 \times 10^{-5} \text{ Scm}^{-1}$ when the biomaterial is blended with 1g PVA. This enunciates the fact that the biomass CSE has a significant contribution to the conductivity of the biopolymer membrane. Figure 3.2 and 3.3 shows the Cole-Cole plot for the pure blend i.e., 0.9g CSE + 1g PVA, and for the other biopolymer membranes 0.5g CSE + 1g PVA, 0.75g CSE + 1g PVA, and 1g CSE + 1g PVA respectively. Figure 3.4 is the equivalent circuit for the former Cole-Cole plots with only a semicircle.

The biopolymer membranes have been prepared as in Figure 3.1, using CSE and PVA. 1gm of PVA is dissolved in double distilled water to get a homogenous solution. CSE of different quantities (0.5g, 0.75g, 0.9g) has been added to the PVA solution and is stirred well. The resulting solution is vacuum dried at 80°C to remove the solvent.

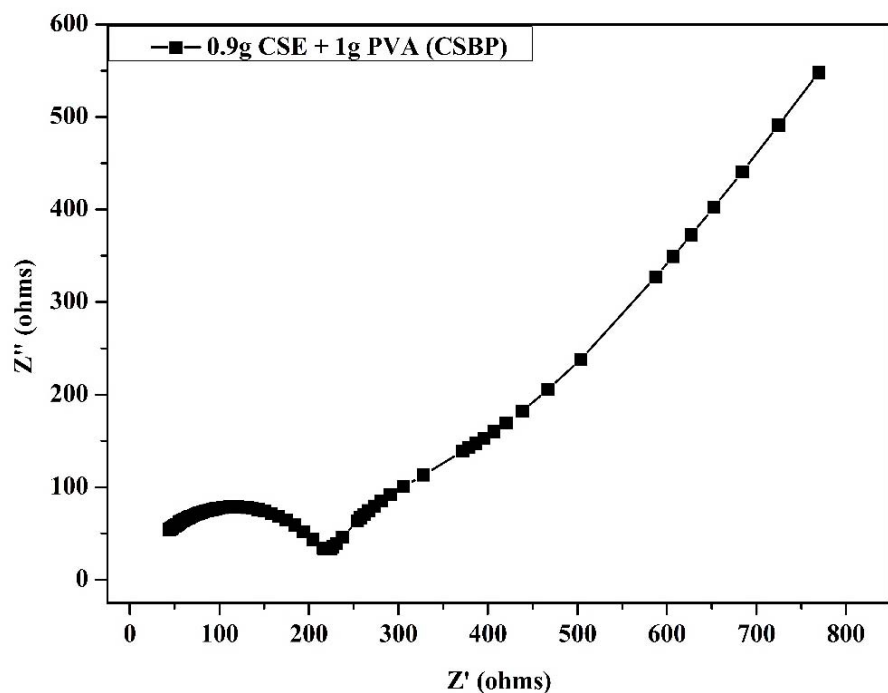


Figure 3.2: Cole-Cole plot for the pure CSBP (1g PVA + 0.9g CSE)

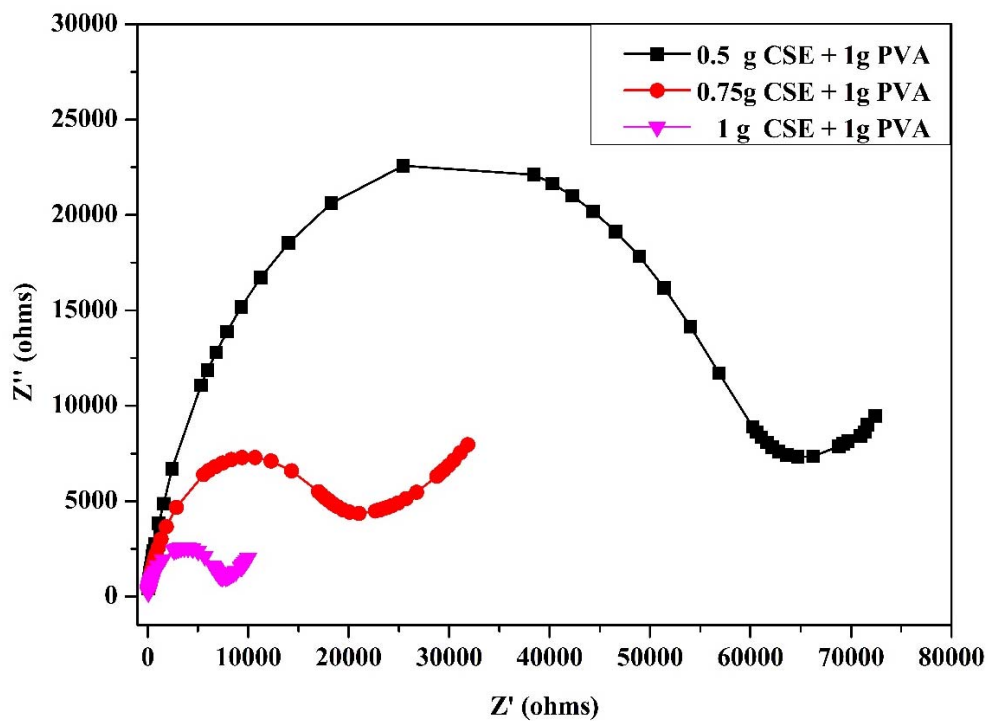


Figure 3.3: Cole-Cole plot for the biopolymer membrane 1g PVA + 0.5g CSE, 1g PVA+ 0.75g CSE and 1g PVA + 1g CSE

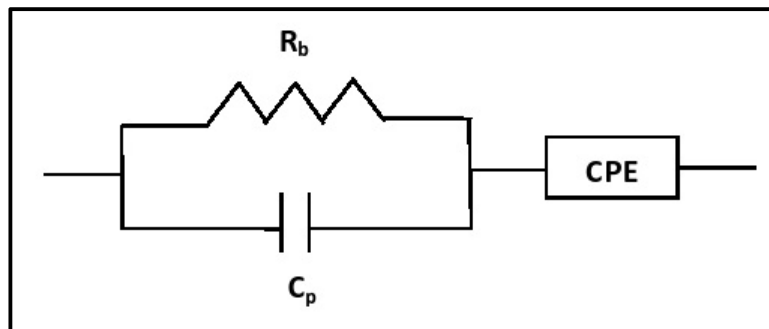


Figure 3.4: Equivalent circuit for the Cole-Cole plot containing a semicircle

After, complete evaporation of the solvent, free-standing membranes are obtained. The prepared biopolymer film with different concentrations of CSE was optimized from their conductivity values in Table 3.1 from AC Impedance Analysis and 0.9g CSE + 1g PVA has been chosen as the pure biopolymer membrane for further synthesis of the respective Mg, Li, and Ammonium bio-electrolytes.

Table 3.1: Ionic conductivity (σ) values of the biopolymer membranes at 303K

Composition	σ (S cm ⁻¹)	R_b (Ohms)
1g PVA + 0.5g CSE	5.91×10^{-8}	64708.94
1g PVA + 0.75g CSE	4.64×10^{-7}	21071.82
1g PVA + 0.9g CSE	1.74×10^{-5}	220.13
1g PVA + 1g CSE	5.79×10^{-7}	7440.69

3.3 Preparation of Sargassum Muticum Extract (SME) and Sargassum Muticum biopolymer membrane (SMBP) from seaweed biomass

Brown seaweed *Sargassum Muticum* (SM) has been collected from the marine biodiversity area in the Gulf of Mannar, Rameswaram, Tamil Nadu, India. The seaweed

samples were cleaned with distilled water and dried in shade at room temperature. The seaweed extract is prepared from *Sargassum Muticum* as mentioned for the former biomass. The extract (SME) thus obtained is green and was filtered using Whatman No.1 filter and stored in an air-tight container and refrigerated to 4°C and can be used for further work. Similarly, to augment the ionic conductivity of the membrane and to improve its film-forming capacity, the prepared extract SME has been blended with PVA, a non-toxic, water-soluble, and biodegradable biopolymer. The components of the SME are given in Figure 3.5. The seaweed extract has contributed substantially to the ionic conductivity of the biopolymer membrane. This is understood by considering the ionic conductivity of the semicrystalline, pure PVA is $2.5 \times 10^{-10} \text{ Scm}^{-1}$ [1] which then increased to $1.57 \times 10^{-6} \text{ S cm}^{-1}$ when the extract SME is blended with 0.8 g PVA.

Table 3.2: Ionic conductivity (σ) values of the blend biopolymer membrane of seaweed at 303K

Composition	σ (S cm ⁻¹)	R _b (Ohms)
1g SME + 0.4g PVA	3.13×10^{-9}	1440000
1g SME + 0.6g PVA	2.83×10^{-8}	239000
1g SME + 0.8g PVA	1.57×10^{-6}	6200
1g SME + 1g PVA	1.45×10^{-7}	26817

Thus, the biopolymer membrane has been prepared, using SME and different ratios of PVA. 1gm of SME is maintained as the host solution. Different quantities of polyvinyl alcohol (0.4g, 0.6g, 0.8g, and 1g) are used to prepare the biopolymer membranes. The prepared biopolymer membranes with different concentrations of PVA were optimized from their AC Impedance studies. Their respective Cole-Cole plots are shown in Figure 3.6 and 3.7 and its ionic conductivity values in Table 3.2. The biopolymer membrane composition of 1g SME + 0.8g PVA (SMBP) which possess the highest ionic conductivity has been chosen for the bio-electrolyte preparation.

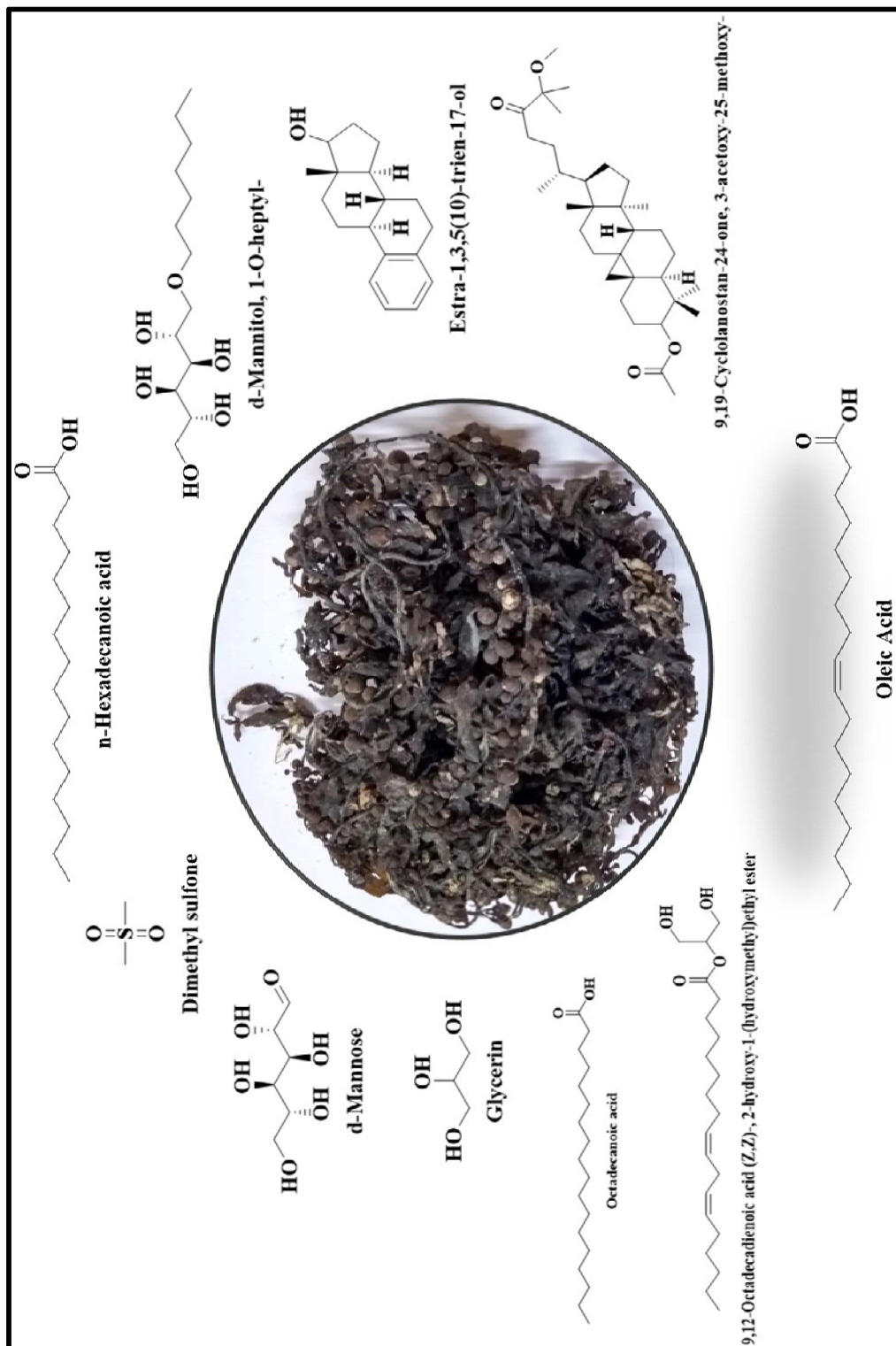


Fig 3.5: Components present in the *Sargassum Muticum* Extract (SME) from Gas Chromatography- Mass Spectroscopy (GC-MS)

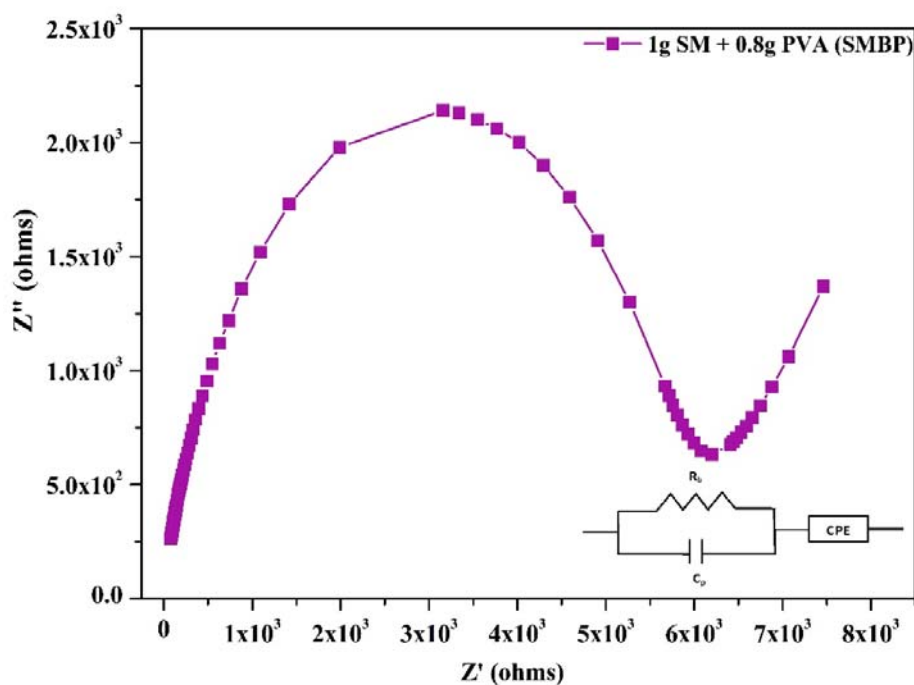


Figure 3.6: Cole-Cole plot for the biopolymer membrane SMBP (1g SME + 0.8g PVA)

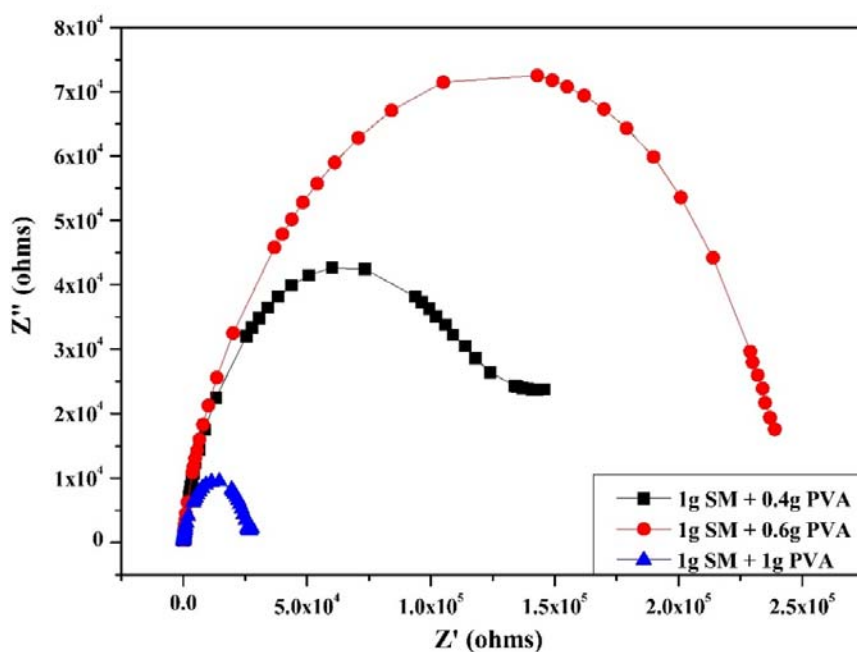


Figure 3.7: Cole-Cole plot for the biopolymer membranes 1g SME + 0.4g PVA, 1g SME + 0.6g PVA, 1g SME + 0.1g PVA

3.4 Preparation of Salmalia Malabarica gum (SG) and Salmalia gum biopolymer membrane (SGBP) from plant exudate as biomass

Salmalia Malabarica Gum, commonly known as Ilavam Pisin was collected from the bark of the tree. This gum is washed and extracted over ethanol and then obtained as a clean dry brown powder. Similarly, to the former biopolymer membrane preparation, 1g of SG is added with different ratios of PVA to prepare various composition of biopolymer membranes. In order to enhance the ionic conductivity of the membrane and to improve its film-forming capacity, the prepared SG powder has been blended with PVA, a non-toxic, water-soluble, and biodegradable biopolymer to improve the ionic conductivity and to improve the film-forming ability of the biopolymer membrane. The ionic conductivity of the prepared Salmalia Gum Biopolymer membrane (SGBP) has been found to be to $3.11 \times 10^{-5} \text{ S cm}^{-1}$ when the extract SG is blended with 0.8 g PVA.

The biopolymer membranes have been prepared with 1gm of SG and various quantities of (0.4g, 0.6g, 0.8g, and 1g) polyvinyl alcohol. The prepared biopolymer membranes with different concentrations of PVA has been optimized by the AC Impedance technique. The Cole-Cole plots for 1g SG + 0.8g PVA are shown in Figure 3.8 and Cole-Cole plots for the biopolymer membranes 1g SME + 0.6g PVA, 1g SME + 0.7g PVA, 1g SME + 0.9g PVA are shown in Figure 3.9. The respective ionic conductivity values of the prepared membranes are tabulated in Table 3.3. Henceforth, the biopolymer membrane composition of 1g SME + 0.8g PVA (SMBP) which possess the highest ionic conductivity has been chosen for the bio-electrolyte preparation.

Table 3.3: Ionic conductivity (σ) values of the blend biopolymer membranes of Salmalia Gum at 303K

Composition	σ (S cm ⁻¹)	R _b (Ohms)
1g SG + 0.6g PVA	2.38×10^{-8}	134000
1g SG + 0.7g PVA	6.46×10^{-7}	5314
1g SG + 0.8g PVA	3.11×10^{-5}	2567
1g SG + 0.9g PVA	1.01×10^{-6}	6380

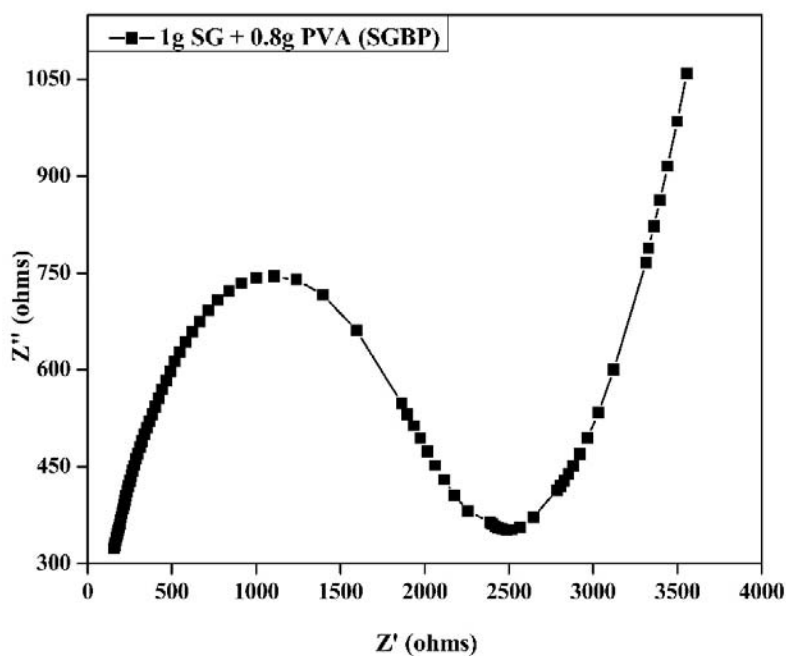


Figure 3.8: Cole-Cole plot for the biopolymer membrane SGBP (1g SG + 0.8g PVA)

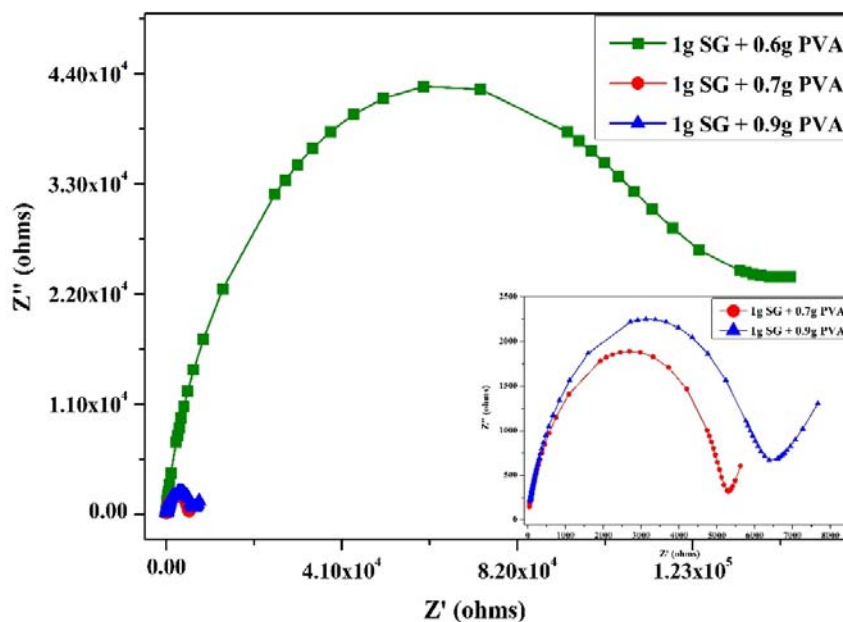


Figure 3.9: Cole-Cole plot for the biopolymer membranes 1g SG + 0.6g PVA, 1g SG + 0.7g PVA, 1g SG + 0.9g PVA

3.5 Characterization Techniques

3.5.1 Gas chromatography-mass spectrometry analysis:

3.5.1.1 Instrumentation

The Clarus SQ 8C Gas Chromatography-Mass Spectrometer from Perkin Elmer was engaged for analysis. The instrument was set as follows, Injector port temperature set to 220°C, Interface temperature set as 250°C, source kept at 220°C. The oven temperature-programmed as available, 75°C for 2 mins, 150°C @ 10°C/min, up to 250°C @ 10°C/min. The split ratio set as 1:12 and the injector used was spitless mode. The DB-5 MS capillary standard non - polar column was used whose dimensions were 0.25mm OD x 0.25µm ID x 30 meters length procured from Agilent Co., USA. Helium was used as the carrier gas at 1 ml/min. The MS was set to scan from 50 to 550 Da. The source was maintained at 220°C and 4.5e⁻⁶ m torr vacuum pressure. The ionization energy was -70eV. The MS was also having an inbuilt pre-filter which reduced the neutral particles. The data system has inbuilt libraries for searching and matching the spectrum. NIST MS Search 2.2v contains more than five lakh references.

3.5.1.2 Identification of compounds:

Interpretation of mass spectrum of GC – MS was done using the database of National Institute Standard and Technology (NIST14). The spectrum of the known component was compared with the spectrum of the known components stored in the inbuilt library. The GC-MS analysis of the ethanolic extract of corn silk and *Sargassum Muticum* was performed. This analysis was carried out to determine the possible chemical components in the ethanolic extract of the biomass.

3.5.2 X-ray diffraction (XRD) studies

XRD – Analysis is a versatile technique to identify the structural properties of the membranes specifically their crystalline/amorphous nature. This technique, aids in supporting the trend of ionic conductivity in the prepared membranes [2]. X-ray diffraction analysis has been performed to establish the effect of the ionic salt in the crystalline or amorphous nature of the bio-electrolyte membrane of the analysed samples.

The crystalline lattice provides a diffraction maxima at well defined ‘ θ ’ values which is characteristic for a particular material as explained by Bragg’s law

$$n\lambda = 2d \sin \theta \quad (3.1)$$

Where λ is the wavelength of incident x-rays used and n is an integer

d is the interplanar distance (\square) and θ is the angle of incidence of the x-ray beam ($^\circ$)

Typically, crystalline materials produce well-defined and sharp peaks while amorphous materials produce broad peaks. The percentage of crystallinity of the prepared membranes is calculated using the formula given below [3]:

$$\% \text{ Crystallinity} = \left(\frac{\% \text{ area under the crystalline peak}}{\text{The total area of the peak}} \right) \times 100 \quad (3.2)$$

In the present study, the amorphousity of the sample has been analyzed using Rigaku Ultima IV diffractometer with Cu – K α (1.54 \square) radiation in the range of $2\theta = 10$ to 80° at a rate of 2° per min at room temperature. The diffractogram of the prepared biopolymer films shows a broadening in the peak along with a decrease in intensity of peak with the addition of the ionic salt. This enhances the amorphous nature of the membranes thus favoring an increase in the ionic conductivity [4].

3.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is an efficient tool used to analyse the functional groups in the biopolymer membrane samples through frequency shifts and change in intensities of the absorption band. These changes occur due to the interactions of the biopolymer with the added ionic salt [5]. The association and dissociation of the salt with the biopolymer membrane and the electrolyte system have been obtained from the FTIR spectrum [6]. The infrared spectra for the solid electrolyte systems depends on the composition of the host material composition and their interaction with the added ionic salts which thereby initiates changes in the vibrational modes of the molecules in the host matrix. This enables the identification of the functional groups present in the moiety and the complex formation between the host molecule and the salt, which are generally a finger print for individual molecules [7].

In our present study the coordination site between the biopolymer and the salt was scanned using FTIR analysis in the frequency range 4000 cm^{-1} to 400 cm^{-1} with the resolution of 1 cm^{-1} at room temperature.

3.5.4 Differential scanning Calorimetry (DSC)

DSC is a thermal analysis technique which provides a perception into the physical properties of the material like their thermal stability, glass transition temperature (T_g) with their response to heat. The change in glass transition temperature provides valuable insight into the flexibility and the intermolecular interactions of the host matrix. This is because of the dependence of the T_g value on the molecular weight, chain flexibility, their cross-linking of the membrane matrix. T_g is the critical temperature at which the material changes from its glassy to a rubbery state [8,9].

In the current investigation, Glass transition temperature (T_g) of the biopolymer electrolyte has been studied using DSC technique with DSC Q20 V24.11 Build 124 under nitrogen atmosphere in the temperature range from 20 to 200 °C at the heating rate of 10 °C/min.

3.5.5 Linear Sweep Voltammetry (LSV)

LSV is used to study the electrochemical stability of the material and their electrochemical working potential. The electrochemical potential window is studied to estimate the exact working potential of the prepared biopolymer electrolytes where neither reduction nor oxidation take place. In this technique the current at the working electrode is noted by linearly sweeping the potential between the reference and working electrode. In our work the measurement was performed by Biologic VSP – 300, with a two-electrode system at the scan rate of 1 mVs^{-1} in the 0 - 5V potential range at room temperature.

3.5.6 Transference number measurement (TNM)

Transference number also called ionic transport number reveals the ionic or electronic contribution of the electrolyte system and is dimensionless [10]. In this measurement, this approach has been adopted to establish the fact that the conductance is due to the presence of ions. Wagner's dc- polarization technique: dc voltage 1.5V is applied across the electrolyte CSBP of highest conducting film loaded between the stainless-steel electrodes (SS/Biopolymer film/SS), in which current is observed as a function of time. The transference number has been

calculated from the polarization current curve Vs time plot and using the equation below as equation 3.4 and 3.4 [11].

$$t_+ = \frac{I_i - I_f}{I_i} \quad (3.3)$$

$$t_{elec} = \frac{I_f}{I_i} \quad (3.4)$$

where t_+ and t_{elec} are the transference number of cation and electrons and I_i and I_f are the initial and final residual current respectively [12]. It is enviable that the transference number reaches unity to substantiate the ionic conductivity of the electrolyte membrane. The plot of the polarization current versus time gives a suggestion about the polarization at the electrode-electrolyte interface.

Thus, it is observed that the total current due to ions, decreases with time which is because of the depletion of ions in the electrolyte and then the current becomes steady once it is completely exhausted of all the ions [13,14].

3.5.7 Electrochemical Impedance Spectroscopy (EIS)

EIS also known as AC Impedance spectroscopy is a versatile technique to determine the electrical and electrochemical properties of the prepared samples by providing an insight to the polarization phenomenon occurring at the electrode interface of the cell.

In this work, the conductance properties of the prepared samples were measured employing the HIOKI-IM 3532 LCR metre Hi-tester in the frequency range about 42 to 1 MHz at room temperature. The biopolymer electrolyte is loaded between the blocking stainless-steel electrodes. The ionic conductivity of the blend biopolymeric material is evaluated by AC Impedance spectroscopy and the respective plots are called Nyquist plot or Cole-Cole plot.

Basically, an impedance plot consists of a semicircle at the high frequency region and an incline spike at the low frequency region. The semicircle is due to the bulk resistance caused by the free movement of ions in the host matrix and the inclined spike is due to the polarization effect at the electrode-electrolyte interface represented as Constant Phase Element (CPE) if it is inclined to 45° and estimated by using the below equation 3.5 [15].

$$\sigma = \frac{t}{AR_b} \text{ Scm}^{-1} \quad (3.5)$$

Where σ is the ionic conductivity, A is the contact area of the sample, t is the thickness and R_b is the bulk resistance of the polymer membrane calculated from the EQ software developed by B A Boukamp [16,17].

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