Biopolymer Electrolyte for Magnesium-Ion Batteries – Preparation and Evaluation

Thesis submitted in

Partial Fulfillment of the

Degree of Master of Philosophy (M. Phil)

By

D. Nandhini

Roll No. 19MPCHF002

Department of Chemistry

Avinashilingam Institute for Home Science and Higher Education for Women,

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30/1/2021
Signature of the
Supervisor

30/1/21
Signature of the
Head of the Department

DECLARATION

I declare that the dissertation entitled **'Biopolymer Electrolyte for Magnesium-Ion batteries – Preparation and Evaluation'** submitted by me for the degree of Master of Philosophy (M.Phil.) is the record of work carried out by me during the period from July 2019 to January 2021 under the guidance of **Dr. (Mrs.) R. Saratha,** Professor, Department of Chemistry and has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship, Titles in this University or any University or other similar institution of Higher Learning.

30/1/2021
Signature of the Candidate

CERTIFICATE FROM THE SUPERVISOR

This is to certify that the dissertation entitled **'Biopolymer Electrolyte for Magnesium-Ion Batteries – Preparation and Evaluation'** submitted by **Nandhini D** for the degree of Master of Philosophy (M.Phil.) is the record of work carried out by her during the period from July 2019 to January 2021 under the guidance and supervision of **Dr. (Mrs.) R. Saratha,** Professor, Department of Chemistry and that this work has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship, Titles in this University or any University or other similar institution of Higher Learning.

RSaratha 30/1/2021 Prof of Chemistry

Signature of the Supervisor with designation

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF FLOW CHARTS

LIST OF ABBREVATIONS/CODES

EC	Ethylene Carbonate
SN	Succinonitrile
GG	Guar Gum
HFP	Hexafluoro propylene
PVP	Polyvinyl pyrrolidone
PVA	Poly vinyl alcohol
PEO	Polyethylene oxide
PAN	Polyacrylonitrile
PMMA	Polymethyl methacrylate
PVC	Polyvinyl chloride
XRD	X-ray diffraction
FTIR	Fourier transform infrared
SEM	Scanning electron microscope
TGA	Thermal gravimetric analysis
PGMCEC	Pectin/Guar gum/$MgCl_2.6H_2O$/Ethylene carbonate
PGMCSN	Pectin/Guar gum/$MgCl_2.6H_2O$/Succinonitrile
PGMSEC	Pectin/Guar gum/$MgSO_4.7H_2O$/ Ethylene carbonate
PGMSSN	Pectin/Guar gum/$MgSO_4.7H_2O$/Succinonitrile

INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

Nowadays, the environment gets switched towards renewable, clean, healthy, eco-friendly, boundless, and inexhaustible energy sources for living. Energy storage plays a major role in the growing demand for globalization. Among electrical energy storage, batteries have become a vital area in the research. Electrochemical energy storage is a method that is used to store electricity under a chemical form. These devices are the most demanding and long-lasting which has become worldwide attention because of their enormous applications in devices like, sensors and electrochemical cells [1-3].

1.2 BATTERY AND ITS PROCESS

The word “battery” comes from the Old French word “Baterie”, meaning “action of beating”, which is relating to a group of cannons in battle. In order to store the energy by using energy storage devices, scientists in 1700s came with the term “battery” that represented multiple electrochemical cells connected together.

Generally, while charging the battery, ions flow from the cathode to the anode, during discharging, the process is reversed i.e., the ions flow from the anode to the cathode. When the anode becomes devoid of ions, the battery needs to be charged.

When the battery is charging, each ion is extracted from the electrodes and forced to travel through the liquid electrolyte. The separator acts as a checkpoint ensuring only the particular ions pass through to the anode. As the battery’s energy is consumed, the ions travel back to the cathode, until there are none left in the anode. That’s when the battery needs to be charged again [4].

1.3 COMPONENTS OF BATTERY

- Electrodes (anode and cathode)
- A separator (to prevent shorting) and

- An electrolyte (a medium through which charges move between the electrodes)

1.4 CLASSIFICATION OF BATTERIES

All the electrochemical cells and batteries are classified into two types:

I. Primary (non-rechargeable)
II. Secondary (rechargeable)

1.4.1 PRIMARY BATTERIES

Primary batteries are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a particular period of time, rendering them dead. A primary battery cannot be used once the chemicals inside them are exhausted. Some examples of the primary batteries are:

(i) Zinc-Carbon battery:

Zinc anode-based batteries were the predominant primary battery type until 1970's. During the 1940's, the World War II and after the war, Zinc-Carbon based batteries were used. They had an average capacity of 50 Wh/kg.

(ii) Alkaline Manganese battery:

Alkaline manganese batteries are small-sized primary batteries with high performance. Manganese dioxide (MnO_2) is used as the active cathode material, and specially processed fine zinc-alloy powder is used for the active anode material. Potassium hydroxide is used as an electrolyte. They are suitable for various applications such as toys, crime prevention buzzer, medical devices and health appliances.

(iii) Lithium primary battery:

The development of batteries with Lithium as an active anode material is considered a major accomplishment due to the high specific energy and longer shelf life of Lithium batteries. Lithium batteries were manufactured as button and coin cell for a range of applications like watches, memory back up, etc.

1.4.2 SECONDARY BATTERIES

Secondary batteries are batteries that can be recharged after use by passing current through the electrodes in the opposite direction, i.e., from the negative terminal to the positive terminal. They are essentially used as energy storage devices where they are electrically connected to a main energy source and charged by it and also supplying energy when required. Examples of such applications are Hybrid Electric Vehicles (HEV), Uninterrupted Power Supplies (UPS), etc.

Energy density of secondary batteries are relatively lower than that of primary batteries but have other good characteristics like high power density, flat discharge curves, low temperature performance and high discharge rate.

(i) Lead – Acid battery:

The lead-acid batteries are most popular and most used rechargeable batteries. They have been a successful product for more than a century. One of the major applications of lead-acid batteries is in the automobile industry as they are primarily used as SLI Batteries (Starting, Lighting and Ignition). Other applications of lead-acid batteries include energy storage, electric vehicles (hybrid vehicles), emergency power, emergency lighting, communication systems, etc. Electrical efficiency of lead-acid batteries is between 75 to 80%. This efficiency value is suitable for energy storage and electric vehicles.

(ii) Nickel – Cadmium Battery:

Ni-Cd batteries use Nickel Oxyhydroxide (NiOOH) as cathode and cadium metal (Cd) as anode. They have a very long life and are very sturdy and reliable. One of the main advantages of Ni-Cd batteries is that they can be subjected to high discharge rates and they can be operated over a wide range of temperatures.

(iii) Nickel – Metal Hydride Battery:

These are an extended version of Nickel- Hydrogen Electrode batteries are relatively new type of batteries, which are exclusively used in aerospace applications (satellites). The positive electrode is the Nickel Oxyhydroxide (NiOOH) while the negative electrode of the cell is a metal alloy, where hydrogen is stored reversibly. The advantages of Nickel-metal hydride batteries are its higher specific energy and energy density.

(iv) Lithium – ion battery:

Lithium-ion batteries have significantly high energy density, longer cycle life, and high specific energy. Other advantages of lithium-ion batteries are slow self-discharge rate and wide range of operating temperatures.

1.5 SAGA OF BATTERY TECHNOLOGY [5]

Table 1: Battery types, year, parts and its applications

TYPE	YEAR	ANODE	CATHODE	CARRIER	APPLICATIONS	DESCRIPTION
Voltaic pile	1799	Zinc (Zn)	Copper (Cu)	H^+	Not in commercial use	Volta proved to Galvani that electricity was generated by metals, and not from animal spirit.
Lead Acid	1859	Lead (Pb)	Lead dioxide (PbO_2)	H^+ and HSO^{4-}	Gasoline cars, back-up energy storage	It was the world's first rechargeable battery. It is still present in most of the gas-powered cars for ignition and running electronics.
Nickel Cadmium	1899	Cadmium (Cd)	Nickel oxide hydroxide NiO(OH)	OH^-	Electronic devices	Ni-Cd batteries powered portable devices, from camcorders to the first mobile phones. But Cd is a highly toxic element, and hence their uses were reduced after Lithium-ion batteries

						were developed.
Nickel iron	1901	Iron (Fe)	Nickel oxide hydroxide NiO(OH)	OH^-	Railways, back-up energy storage	In the US, Thomas Edison was the first to sell these batteries, but it was invented by a Swede Named Waldemar Jungner. These were sold until the 1970s.
Nickel Zinc	1932	Zinc (Zn)	Nickel oxide hydroxide NiO(OH)	OH^-	Power tools, Tiny portable electronics	Thomas Edison got a patent for this battery in 1901, but it wasn't used in commercial applications until 1932.
Rechargeable alkaline	1950	Zinc (Zn)	Manganese oxide (MnO_2)	OH^-	Electronic devices	These are often called as "pencil cells". Today, some common devices, like TV remote controls and digital clocks, use alkaline batteries.
Nickel hydrogen	1977	Hydrogen (H_2)	Nickel oxide hydroxide NiO(OH)	OH^- /H_2O	Satellites	It can operate at low temperatures i.e., -30 ^{o}C, which is the most important features for the use in space applications.
Vanadium flow battery	1986	V(II)/ V(III) redox couple	V(IV)/V(V) redox couple	H^+	Back-up energy storage	The battery uses large vats of liquids to store the anode and cathode materials, which are brought into electrical

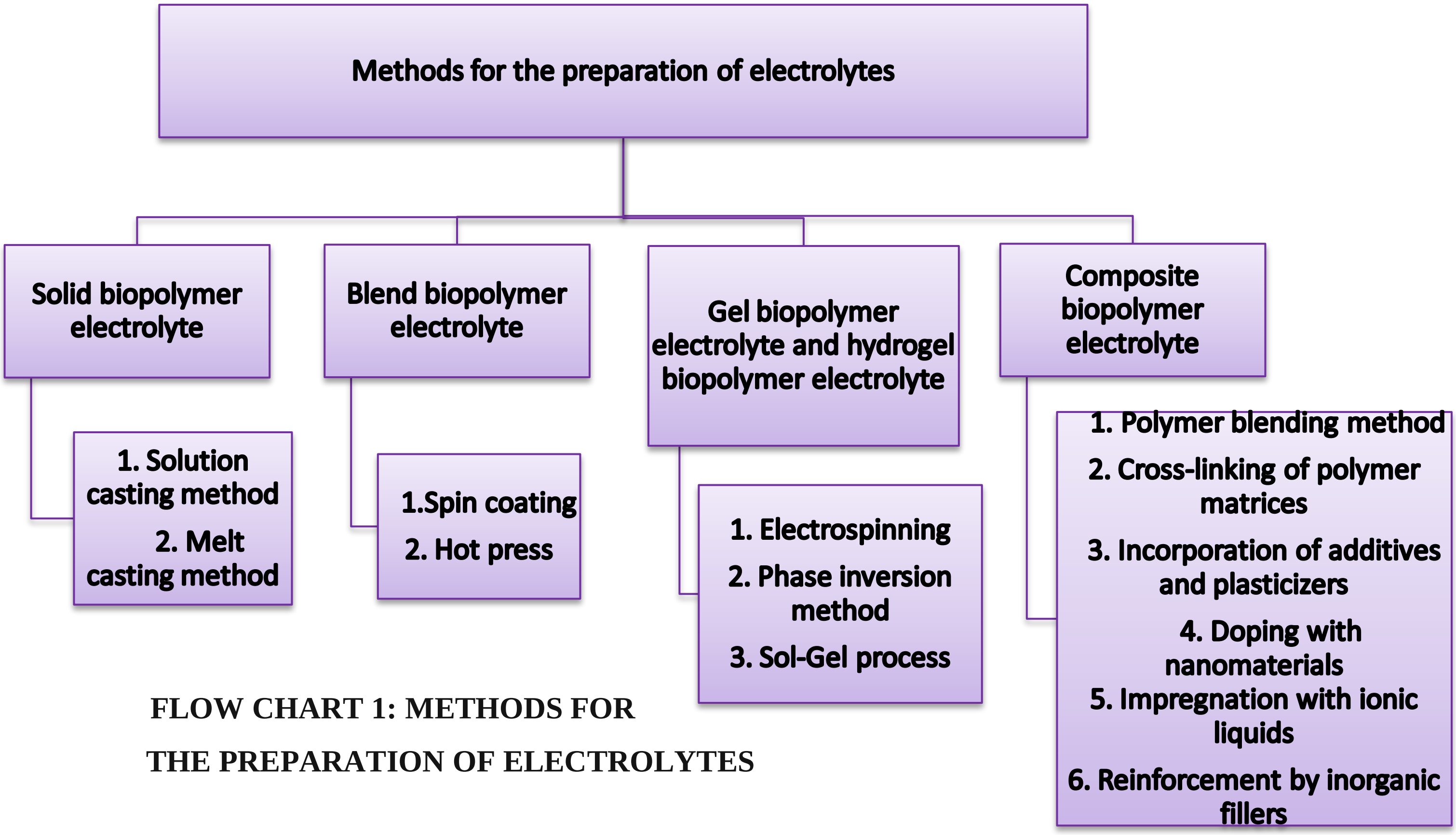
						contact only when the battery is being charged or discharged.
Nickel metal hydride	1990	Metal/water	Nickel oxide hydroxide NiO(OH)	OH^-	Hybrid cars, electronic devices	This battery is present in every Toyota Prius, which is the world's popular hybrid car. It can charge and discharge quickly and do so thousands of times without breaking apart.
Lithium cobalt oxide	1991	Li_aC_6	Li_bCoO_2	Li^+	Electronic devices, all phones and laptops	This type of battery made the smart phone age possible. It is present in billions of smart phones sold so far.
Sodium sulfur	1993	Sodium (Na)	Sulphur (S_8)	Na^+	Back-up energy storage	The sodium sulfur battery operates at a temperature of 300°C. the world's largest virtual battery plant in UAE uses these type of batteries.
Lithium iron phosphate	1996	Li_aC_6	Li_bFePO_4	Li^+	Electric cars, electric buses, electric trucks	This battery is less energy dense but also cheaper to produce other types of lithium ion batteries.
Nickel cobalt aluminium oxide	1999	Li_aC_6	$Li_bNi_{0.8}Co_{0.15}Al_{0.05}O_2$	Li^+	Electric cars	Tesla deploys this type of batteries in its electric vehicles.

Lithium manganese oxide	1999	Li_aC_6	$Li_aMn_2O_4$	Li^+	Power tools, electric cars	These are able to deliver lots of energy in a short time.
Lithium titanate	2008	Li_{4+a} Ti_5O_{12}	Li_bFePO_4	Li^+	Forklifts, fast-charging stations	They are high-power batteries, which is suitable for fast-charging stations.
Nickel manganese cobalt oxide	2008	Li_aC_6	$Li_bNi_{1-x-y}Co_xMn_yO_2$	Li^+	Electric cars	Nowadays, this type of battery is used in electric cars.
Lithium sulfur	2008	Li	Sulphur (S_8)	Li^+	Electric planes	Lithium-sulfur batteries can pack in many times more energy per unit weight and its reliable commercial versions could make electric flight possible.
Zinc bromine		Zinc (Zn)	Bromine (Br)	Zn^{2+} and Br^-	Back-up energy storage	This battery consists of cheap ingredients, which requires a lot of space. That makes it ideal only for use as bulk back-up storage.

1.6 SWITCHING OVER TO GREEN BATTERIES

In 1800, the Italian physicist Alessandro Volta invented the first battery. It consists of stacked discs of copper (Cu) and zinc (Zn) separated by a cloth soaked in salty water which produces 0.76 V. In 1859, the lead-acid battery has been invented and this technology is used in the internal combustion of a car engine. A challenge has been aroused in disposing of these primary batteries. The solution to this problem is to reuse them, by recharging the batteries. So, rechargeable batteries have been developed. For example, a Nickel-cadmium battery uses alkali as an electrolyte. In 1989, nickel-metal hydrogen batteries (NiMH) were developed which had a longer life than Ni-Cd batteries [6]. Liquid electrolytes stated above have disadvantages such as flammability, leakage, poor chemical stability, and poor safety. Solid electrolyte becomes a promising option to mitigate these issues. Among every solid electrolyte, polymer-based solid electrolytes have such advantages as good flexibility, low flammability, high safety, and excellent mechanical, chemical, and thermal stability [7]. But it has one major disadvantage i.e., they are not biodegradable. To overcome this problem, the world is seeking new innovative material which has to be used as the electrolytes. So, the research has been directed towards finding out eco-friendly materials for energy storage devices. Biopolymer electrolyte has certain advantages like low cost, eco-friendly, good film formability, degradability, water-solubility, renewability, adhesive property, and biocompatibility [8].

1.7 PREPARATIVE METHODS FOR THE ELECTROLYTE



FLOW CHART 1: METHODS FOR THE PREPARATION OF ELECTROLYTES

1.8 BIOPOLYMERS USED AS ELECTROLYTES

The following are a few examples that have been used as a component in the battery.

- Agarose/Agar
- Alginate
- Carboxymethyl Cellulose (CMC)
- Carrageenan
- Cellulose
- Chitin and Chitosan
- Gellan Gum
- Gum Arabic
- Guar Gum
- Gum Tragacanth
- Pectin
- Plant Seeds, Plant Tubers, Root and Cereal Starch
- Polysaccharides
- Tamarind seed polysaccharide

Gum Arabic

Cellulose

Carrageenan

Tamarind seed polysaccharide

Guar gum

Chitosan

Fig 1. Pictorial representation of biopolymers

Agarose is a linear polymer made up of beta-D-galactose. The maximum conductivity reported in the literature by using agarose as an electrolyte is around 10^{-2} Scm^{-1}. Carrageenan is obtained from the red seaweed. The ionic conductivity of carrageenan was found to be in the range of 10^{-3} to 10^{-7} S cm^{-1}. Alginate is obtained from the brown seaweed. Gel polymer electrolytes were prepared by the usage of alginate and showed ionic conductivity in the range of 10^{-4} to 10^{-5} S cm^{-1}. Pectin is found in all land-based plants. Commercial pectin is extracted from citrus peels, sugar beets, apple pomace, or sunflower heads. The best ionic conductivity value was found around 10^{-2} S cm^{-1}. Cellulose is the most abundant polymer available worldwide. The best ionic conductivity obtained in this is around 10^{-3} S cm^{-1}. Starch consists of amylose and amylopectin. By adding suitable salts, the conductivity value approaches 10^{-4} S cm^{-1}. Adding the salts in the Sago Palm matrix enhances the ionic conductivity and the maximum value was obtained at 10^{-3} Scm^{-1}. Corn-based biopolymer electrolyte doped with lithium salts exhibits ionic conductive value around 10^{-4} S cm^{-1}. Rice starch complexed with lithium salts achieved a value of ionic conductivity at 10^{-5} S cm^{-1} [9].

1.9 PECTIN

Pectin in the Greek word meaning “congealed and curdled”. It was first isolated by Heneri Bracannot in 1825. Generally, pectin belongs to polysaccharides in nature, which is made up of 35% primary walls in non-graminaceous monocots and dicots, 5% of walls in woody tissue, and 2-10% of grass.

1.10 FUNCTIONS OF PECTIN

Due to the biodegradable and renewable nature of the pectin made the researchers concentrate on the usage of pectin as the polymer electrolyte. It is non-toxic and water-soluble. It is made up of more hydroxyl groups and it has an oxygen atom that aims to form a coordination bond with cations [10-12].

1.11 PECTIN CONTENT OF SOME FRUITS [13]

Table 2: Pectin content of fruits

Fruit	% Pectic substance (wet weight)	Fruit	% Pectic substance (wet weight)
Apple	0.5-2.5	Lychee	0.42
Banana	0.7-1.2	Mango	0.26-0.42
Beet pulp	1.0	Orange peel	3.5-5.5
Carambola	0.66	Papaya	0.66-1.0
Carrot	0.2-2.5	Passion fruit	0.5-3.0
Giant granadilla	0.4	Tamarind	0.6-0.7
Guava	0.77-0.99	Tomato fruit	0.2-0.6
Lemon pulp	2.5-4.0		

1.12 GUAR GUM

The synthesis of Guar-gum based polymer electrolytes improves conducting nature. This type of electrolytes possesses low cost, easy fabrication, high efficiency, biodegradable which are the advantages compared to liquid electrolytes. It is a natural non-ionic polysaccharide extracted from guar beans. It is composed of (1-4)-D mannopyranosyl units with D-galactopyranosyl unit in a ratio of about 1.5:2 at every second mannose, having hydroxyl compounds available for the attachment [14].

1.13 BATTERY MANAGEMENT SYSTEM MARKET GLOBAL FORECAST TO 2023

The battery energy storage system market is expected to grow from 2.0 billion USD in 2018 to reach 8.5 billion USD by 2023, at a Compound annual growth rate (CAGR) of 33.9% between 2018 and 2023. Asia Pacific Accreditation Cooperation (APAC) is gradually becoming a hub for the battery energy storage system industry. The demand from China, India, and Japan for battery energy storage systems is gradually increasing. In China, the electricity demand is at a peak due to the rapid population growth in the country. To fulfill the increasing demand in China, the state-owned State Grid Corporation of China, the world's largest utility, has deployed battery energy storage systems to provide ancillary services throughout its grid [15].

Source: Battery Energy Storage System Market, Updated date - Dec 03, 2019, Markets and markets.

Fig 2. Diagrammatic representation of battery management system market

1.14 COMPARISON OF MAGNESIUM BATTERIES WITH THE LITHIUM-ION BATTERIES

Magnesium batteries are a less expensive and potentially safer alternative to lithium-ion batteries. Researchers from the University of Houston and the Tokyo Research Institute of North America (TRINA) reported in Nature Energy that they produced a new electrolyte and cathode which is capable of operating at room temperature and producing a power density compared to that delivered by lithium-ion batteries. Magnesium is a more readily available alternative to lithium. Magnesium ions have twice the charge of lithium while having a similar ionic radius [16].

Batteries that are made from magnesium metal will have greater stability, higher energy density, and low cost than lithium-ion cells. These are the predictions of scientists at the Department of Energy's National Renewable Energy Laboratory (NREL). Magnesium is common and readily available than lithium. It is the eighth-most abundant element and can be commercially extracted from mineral deposits or seawater. Magnesium atom releases two electrons during battery discharge phase than the lithium which gives one electron. This provides it the potential to deliver almost twice the electrical energy. And also, during the battery charging phase, Magnesium does not grow dendrites on the metal surface. The spiky dendrite crystal formation that formed on the lithium metal surface can cause short-circuiting of the battery. The lack of dendrite formation will make magnesium batteries easier to handle and much safer [17].

1.15 ION CONDUCTING POLYMERS

Ion conducting polymers has been obtained by polar polymer-salt complexation which is becoming a trending topic now due to the application in solid-state polymer batteries. "Polymer-Salt complex" is being studied in the polymer electrolytes which denote that a dissociable salt is complexed with the biopolymer (such as pectin and guar gum). To enhance the ionic conductivity, ion-conducting polymers have been developed by

(1) Combining with different ionic salts such as lithium, magnesium and sodium.

(2) Using polymers with different conducting behaviour

Since the present study deals with developing electrolyte using magnesium salts, a review of the previous research study has been concentrated more on studies with magnesium salts such as magnesium chloride ($MgCl_2$), magnesium sulphate ($MgSO_4$), magnesium perchlorate ($MgClO_4$), magnesium nitrate ($Mg(NO_3)_2$), magnesium acetate $Mg(CH_3COO)_2$ which will be discussed with the following session [18].

1.16 TRANSPORT NUMBER

The transport number, t_{ion}, describes the fraction of the total current that is carried by the ion. This number depends on the relative mobility of the ions, and ultimate gives the relative contribution to conductivity of each of the ions. The sum of transport numbers over all the ions in a solution is always equal to 1.

1.17 OBJECTIVES

With the above introductory part, the present study was carried out with the following objectives.

- To prepare solid polymer electrolytes using Pectin, Guar Gum, Magnesium chloride hexahydrate/ Magnesium sulphate heptahydrate, Ethylene carbonate/ Succinonitrile by solution casting technique.
- To characterize the prepared polymer electrolyte by using the techniques such as Fourier Transform-Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), 3-D Laser Profilometry and Thermogravimetric analysis (TG/DTA).
- To measure the ionic conductivity of the prepared solid polymer electrolytes through Electrical Impedance Spectroscopy.
- To determine the transport number for the prepared solid polymer electrolytes.

REVIEW OF LITERATURE

CHAPTER-II

REVIEW OF LITERATURE

This session explains the research work done in the field of solid polymer electrolytes and their related studies.

Objectives

- To find the research gap.
- To get an insight on the biopolymer electrolyte used in batteries.
- To identify the techniques used for the preparation of the solid electrolyte.

2.1CHEMICAL POLYMERS AS ELECTROLYTES

Solid polymer electrolytes using a chemical polymer as a host with different salts were prepared using different combinations of host and salt by the solution casting method are reviewed in the following session.

2.1.1 With Magnesium salts:

The below review tells about the preparation of solid polymer electrolyte by using a chemical polymer as a host with magnesium salt.

- **Anji Reddy Polu *et al.* (2011,2013,2014)** developed polymer electrolytes using magnesium nitrate salt by solution casting method based on (i) blend polymer polyvinyl alcohol (PVA) and polyethylene glycol complexed with magnesium nitrate shows the maximum ionic conductivity at 9.63×10^{-5} S/cm for 35:30:30 ratio of PVA-PEG-$MG(NO_3)_2$ **[19]** (ii) poly(vinyl alcohol) and magnesium nitrate $Mg(NO_3)_2$ shows conductivity at 7.36×10^{-7} S/cm for 70:30 ratio of PVA: $Mg(NO_3)_2$ at 303 K **[20]** (iii) Polyethylene glycol–magnesium nitrate polymer electrolytes with 10 wt% of TiO_2 at room temperature exhibited maximum ionic conductivity at 1.06×10^{-4} S/cm **[21]** and (iv) polyvinyl alcohol and polyvinyl pyrrolidone mixed with magnesium nitrate shows the highest ionic conductivity was obtained for 50PVA-50PVP-30 wt% $Mg(NO_3)_2$ at 3.78×10^{-5} S/cm **[22].**

- **Shahenoor Basha S.K *et al.* (2016,2017)** done their work in producing new Mg^{2+} ion-conducting polymer electrolytes by using polyvinyl pyrrolidone (PVP) with magnesium salts (i) PVP with $MgCl_2$ $6H_2O$ salt has been found polymer film conductivity at 4.03×10^{-6} S/cm for 85:15 ratio at 373 K **[23]**, (ii) for PVP with $MgSO_4.7H_2O$ (85:15), the highest conductivity was found to be 1.05×10^{-5} (S/cm) at room temperature **[24]** and (iii) for PVP with magnesium sulphate heptahydrate ($MgSO_4.7H_2O$), the conductivity of PVP electrolyte is about 7.04×10^{-8} S/cm at R.T, the highest ionic conductivity is found to be 1.75×10^{-5} S/cm at 373 K for a sample with 15% of $MgSO_4.7H_2O$ in PVP polymer **[25]**.

- **Manjuladevi *et al.* (2017,2018)** carried their work by preparing two electrolytes by using blend polymer polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) with magnesium salts (i) The composition of 92.5 PVA: 7.5 PAN: 0.3 mm% $Mg(NO_3)_2$ has 1.71×10^{-3} S/cm at room temperature **[26]** and (ii) The optimized material in the ratio of 92.5:7.5 of PVA: PAN with 0.5 m.m.% of $MgCl_2$ offers a maximum electrical conductivity of 1.01×10^{-3} S cm^{-1} at room temperature **[27].**

- **Ponmani S *et al.* (2018)** developed solid polymer electrolytes by using PVdF-HFP/PVAc with magnesium perchlorate $Mg(ClO_4)_2$ salt by solution casting method. The highest ionic conductivity of 2.93×10^{-4} Scm^{-1} was found for the concentration of 69 Wt% PVdF-HFP: 23 Wt% PVAc: 8 Wt% $Mg(ClO_4)_2$ **[28]** and (ii) Gel polymer electrolyte was done by poly(vinylidene fluoride-co-hexafluoro propylene) and poly(ethyl methacrylate) as a host with $Mg(ClO_4)_2$ as salt and the ionic conductivity was found to be 2.8×10^{-5} S/cm at room temperature **[29].**

- **Ravindran D and Vickraman P (2012)** has prepared a blend polymer electrolyte using $Mg(CH_3COO)_2$ and $Mg(NO_3)_2$ as salt by changing the PEG: [$Mg(CH_3COO)_2$ and $Mg(NO_3)_2$] ratio. The maximum conductivity was observed for the film with the composition PVA-PEG-[$Mg(CH_3COO)_2$+$Mg(NO_3)_2$]: (40-45-7.5-7.5) at 9.852×10^{-6} S/cm **[30].**

- A blend polymer electrolyte made up of poly(ethylene oxide) and poly (vinyl pyrrolidone) with different compositions of $Mg(NO_3)_2$ by **Anil Kumar K.M *et al* (2017).** The highest ion conductivity is 5.8×10^{-4} S/cm at room temperature **[31].**

- **Jingwei Wang *et al.* (2017)** carried out their work by preparing gel polymer electrolyte poly(vinyl alcohol)/magnesium trifluoromethanesulfonate/1-ethyl-3- methylimidazolium trifluoromethanesulfonate (PVA/$Mg(Tf)_2$/EMITf) by solution casting technique. The ion conductivity of 85 PVA:15 $MG(Tf)_2$:15 EMITf gel polymer membrane exhibited a value of 2.10×10^{-4} S/cm **[32].**

- Polymer electrolytes comprised of polyvinyl pyrrolidone and $Mg(ClO_4)_2$ have been prepared by solution casting technique using double-distilled water as solvent by **Mangalam *et. al.* (2017)**. The ionic conductivity and dielectric behavior were explored using AC impedance spectroscopy. Results obtained by cyclic voltammetry on 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ symmetrical cells show evidence for reversibility **[33].**

2.1.2 With lithium salts:

The below review tells about the preparation of solid polymer electrolyte by using a chemical polymer as a host with a lithium salt.

- **Kingslin Mary Genova Francis *et al.* (2016,2017)** prepared blend polymer electrolytes based on (i) poly(vinyl alcohol) and polyacrylonitrile doped with lithium nitrate ($LiNO_3$) using the ratio of 92.5 PVA: 7.5 PAN with 15 wt% $LiNO_3$ gives a maximum conductivity of 1.5×10^{-3} S/cm and **[34]**(ii) PVA-PAN with Lithium triflate ($LiCF_3SO_3$)produces maximum ionic conductivity at 4.0×10^{-5} S/cm for 92.5 PVA: 7.5 PAN: 50 M wt% $LiCF_3SO_3$ **[35].**

- **James Evans *et al.* (1987)** determined the transference numbers in polymer electrolytes by electrochemical methods and the results are given for the measurement of lithium and trifluoromethanesulphonate ions in poly(ethylene oxide) at 90 ^{o}C **[36].**

- **Sundaramahalingam K *et al.* (2018)** have developed a blend polymer consists of polyethylene oxide and polyvinyl pyrrolidone by using the solution casting method with lithium bromide. The maximum conductivity was found to be 1.59×10^{-6} S/cm for PEO (30 wt%) and PVP (70 wt%) with LiBr (4 wt%) at 303 K **[37].**

- **Shih-Hong Wang *et al.* (2014)** used poly- (acrylonitrile-co-vinyl acetate) copolymer blending poly-(methyl methacrylate) as a host which is combined with $LiPF_6$. This composition produced maximum conductivity at 3.5×10-3 S/cm at 30 ^oC **[38].**

- Two systems (plasticized and plasticizer-free) of chitosan and polyvinyl alcohol blend polymer electrolyte complexed with lithium acetate by solution casting method was prepared by **Shukur M.F *et al.* (2018)**. By the composition of 30 wt% LiOAc, a maximum ionic conductivity of 6.46×10^{-5} S/cm is obtained **[39].**

- SPE films were prepared by **Anji Reddy Polu *et al.* (2015)** based on Poly(ethylene oxide) with acetonitrile as a solvent by using a solvent casting method. Here succinonitrile and lithium 4,5-dicyano-2-(trifluoromethyl)imidazole (LiTDI) was used as a plasticizer and doping salt respectively. The conductivity of 9.649×10^{-7} S/cm for undoped PEO-LiTDI and this value gets increased to 2.839×10^{-5} S/cm by the addition of 30 wt% of succinonitrile **[40].**

- **Ravi. M *et al.* (2015)** developed a gel polymer electrolytes consists of poly (e-caprolactone):lithium tetrafluoroborate (PCL: LiBF4) system complexed with the various compositions of 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4) using the solvent casting method. The electrolyte of 85 PCL: 15 $LiBF_4$ + 40 $EMIMBF_4$ exhibited a high conductivity of 2.83×10^{-4} S/cm **[41].**

- **Baskaran. R *et al.* (2006)** synthesized the blend polymer electrolyte which is made up of poly(vinyl acetate) and poly(vinylidene fluoride) with lithium perchlorate ($LiClO_4$) using the solution casting method. The blend ratio 75:25 of PVAc: PVDF has the highest ionic conductivity of 6.4×10^{-4} S/cm. by Wagner's polarization method, the value of ionic transference number of mobile ions is 0.95-0.98 for all the samples **[42].**

- Poly(vinylidene fluoride) and poly(ethylene oxide) are blended with LiClO to form polymer electrolyte membranes by **Jacob M.M.E *et al.* (1997).** The ratio of 80:20 for (PVDF: LiClO): PEO was found to be 2.62×10^{-5} S/cm **[43].**

2.1.3 With Sodium salts:

The below review tells about the preparation of solid polymer electrolyte by using a chemical polymer as a host with sodium salt.

- **Pritam *et al.* (2019)** prepared a novel blended electrolyte consists of polyethylene oxide and polyvinyl pyrrolidine with sodium nitrate ($NaNO_3$) via the solution casting method. A maximum conductivity was found to be 2.92×10^{-5} S/cm at 40 ^{o}C **[44].**

2.1.4 With Ammonium salts:

The following review tells about the development of a solid polymer electrolyte using a chemical polymer as a host with ammonium salts.

- **Subramaniyan *et al.* (2010)** carried out their study using PVA–NH_4NO_3 polymer electrolytes using a solvent casting technique. It was found that there is no significant loss in the voltage up to 3 cycles for the cell Zn + $ZnSO_4 .7H_2O$ |80 PVA: 20 NH_4NO_3 |V_2O_5 + PbO_2 + C + PE **[45].**

- **Mazuki N.F *et al.* (2018)** investigated the abnormal trend of electrochemical properties of solid biopolymer electrolytes system. They blended carboxymethylcellulose with polyvinyl alcohol and then doped with ammonium chloride. It was observed that the decrease in amorphousness and the increase of weight loss demonstrated the abnormal observation of the ionic conductivity when (1-5 wt%) NH_4Cl was added which was lower than the un-doped system. Later, the maximum conductivity at 8.86×10^{-5} S/cm for the sample containing 6 wt % NH_4Cl **[46].**

- **Premalatha *et al.* (2016)** synthesized a blend polymer electrolyte comprising of PVA and PVP doped with ammonium thiocyanate (NH_4SCN) salt by solution casting method. The maximum conductivity was observed at 6.85×10^{-4} S/cm for 50 mol% PVA-50 mol% PVP with 40 mol% NH4SCN. The activation energy was found to be minimum at 0.24 eV **[47].**

- **Hemalatha. R *et al.* (2019)**, carried their work on proton-conducting electrolytes composed of PVA, amino acid i.e., proline and ammonium thiocyanate using the solution casting method. The maximum ionic conductivity for 75 Mwt%: 25 Mwt%: 0.5 Mwt% of PVA/Proline and NH_4SCN is found to be 1.17×10^{-3} S/cm. By using linear sweep voltammetry shows electrochemical stability window is 3.61 V **[48].**

- The blended electrolytes were prepared by **Muthuvinayagam. M *et al.* (2014**), made of poly(vinyledine fluoride):poly(vinyl alcohol) (PVdF: PVA) complexed with ammonium acetate (CH_3COONH_4) by solution casting technique. By the AC impedance spectroscopic analysis, the ionic conductivity was found to be 1.30×10^{-6} S/cm for 5 Wt% $COONH_4$-doped PVdF: PVA polymer blend electrolyte **[49].**

2.2 BIOPOLYMER AS ELECTROLYTES

The following session deals with the various studies on biopolymer as electrolyte using different concentrations of polymer and salt.

2.2.1 With Magnesium salts:

The below review tells about the preparation of solid polymer electrolyte by using biopolymer as a host with magnesium salt.

- **Kiruthika *et al.* (2019)** presented their work by preparing two eco-friendly biopolymer electrolytes (i) pectin with magnesium nitrate salt $Mg(NO_3)_2$ with 50 M.wt%pectin:50 M.wt%$Mg(NO_3)_2$ gives the highest ionic conductivity in the order of 10^{-4} S cm^{-1}. The total ionic transference number of the highest conducting sample is 0.97 and the transference number of Mg^{2+} ion is 0.29. LSV has been used to find the electrochemical stability for the ratio was 3.8 V **[50]** and (ii) pectin with magnesium chloride using the ratio of 30 M wt% pectin:70 M wt% $MgCl_2$ offers the maximum ionic conductivity of 1.14×10^{-3} S/cm **[51].**

- Magnesium ion-conducting polymer electrolyte was done by using the magnesium perchlorate as a salt in the biopolymer host such as (i) tamarind seed polysaccharide (TSP) with magnesium perchlorate ($Mg(ClO_4)_2$) salt by **Perumal *et al.* (2019)** in which the TSP with 0.25 (m.m.%) $Mg(ClO_4)_2$ salt complex exhibited good thermal stability and high electrochemical window. The TSP with 0.25 (m.m.%) of $Mg(ClO_4)_2$ offers a maximum Mg-ion conductivity of 5.66×10^{-4} Scm^{-1} at ambient temperature with maximum ionic transference number of 0.43 **[52]**, (ii) I-carrageenan with different concentration of magnesium perchlorate has been prepared by **Shanmuga Priya *et al.* (2018).** I-carrageenan membrane with 0.6 wt% of magnesium perchlorate has revealed the maximum conductivity of 2.18×10^{-3} S/cm. I-carrageenan with 0.6 wt% of magnesium membrane has shown the highest amorphous nature **[53]** and (iii) cellulose acetate and magnesium perchlorate with DMF as a solvent was done by **Mahalakshmi M *et al.* (2019).** The biopolymer membrane with the ratio of 40:60::CA:$Mg(ClO_4)_2$ has shown the maximum conductivity of 4.05×10^{-4} S/cm at room temperature. Finally, the performance of the battery was studied and the open-circuit voltage of the battery was found to be 1.9 V **[54].**

- **Sangeetha *et.al.* (2019)** have prepared the biopolymer electrolyte based on K-carrageenan with magnesium chloride ($MgCl_2$) by using the solution casting method. The film containing the ratio of 1 g of K-carrageenan: 0.6 Mwt% of $MgCl_2$ exhibited maximum ionic conductivity of 4.76×10^{-3} S cm^{-1} at room temperature which has been analysed by conductivity studies **[55].**

- **Alves *et al.* (2013)** developed the electrolytes made up of agar doped with magnesium triflate ($Mg(CF_3SO_3)_2$) for the fabrication of solid-state devices. The samples were investigated and characterized by conductivity measurements, thermal analysis, cyclic voltammetry, X-ray diffraction, scanning electron microscope **[56].**

- **Hassan M.F *et al.* (2018)** successfully prepared a solid polymer electrolyte based on starch as a polymer and Magnesium Sulphate ($MgSO_4$) as an ionic dopant by using solution casting technique. The highest ionic conductivity (σ) for the sample containing 35 wt% $MgSO_4$ was found to be 8.52×10^{-5} Scm^{-1} **[57].**

2.2.2 With lithium salts:

The below review tells about the preparation of solid polymer electrolyte by using biopolymer as a host with a lithium salt.

- **Perumal *et al.* (2018)** synthesized three biopolymer electrolytes by using (i) pectin-based flexible electrolyte with different compositions of LiCl using solution casting technique. The pectin/LiCl (50:50 M.wt%) exhibited high ionic conductivity in the order of 2.08×10^{-3} S cm^{-1}. The temperature-dependent ionic conductivity obeys Arrhenius behavior. The best performing membrane has been used to construct the primary lithium-ion battery. The open-circuit voltage of the constructed primary lithium-ion battery is found to be 1.93 V **[58]**, (ii) pectin with 50 (m.m.%) LiCl possessed an excellent ionic conductivity of $1.96x10^{-3}$ Scm^{-1} and (iii) pectin with $LiClO_4$ incorporated electrolyte results with an ionic conductivity of $5.38x10^{-5}$ Scm^{-1} for the composition of 60 (m.m.%) pectin: 40 (m.m.%) $LiClO_4$ **[59].**
- **Shilpa R *et al.* (2018, 2019, and 2020)** developed three solid polymer electrolytes by using (i) pectin, lithium salts and plasticizers through solution casting method. Polymer host with different ratios of lithium nitrate ($LiNO_3$) salts, ethylene carbonate (EC) and succinonitrile (SN) were prepared. Electrochemical impedance spectroscopy (EIS) measurements suggest the suitability with 10^{-4} S/cm ionic conductivity **[60]**, (ii) pectin doped with lithium nitrate of different concentrations has been prepared by solution casting technique. The ionic conductivity has been explored using A.C. impedance spectroscopy which reveals that the biopolymer containing 30 wt% Pectin: 70 wt% $LiNO_3$ has highest ionic conductivity of 3.97×10^{-3} S/cm **[61]**, (iii) lithium salt (LiTFSI) doped in pectin and guargum (biopolymers) blended mixture which has low glass transition temperature and good flexibility by the solution casting technique **[62]** and (iv) A review is done based on lithium electrolytes in electrochemical energy storage devices in which the ionic conductivity with increasing voltage is found by doping the salts with the polymers by increasing its conduction for application purpose **[63].**

- **Chitra R *et al.* (2019, 2020)** carried out their work on the synthesis of solid electrolytes by (i) The combination of 1.0 g I-Carrageenan and 0.3 g LiCl displays the highest conductivity value of 5.33×10^{-3} S/cm **[64]** and (ii) I-carrageenan with $LiClO_4$ and Succinonitrile (SN) gives the ionic conductivity for the film composition of 1g I-carrageenan with 0.5 wt% $LiClO_4$ is 3.57×10^{-4} S/cm at room temperature. The inclusion of 0.3 wt% of SN into this system has improved the ionic conductivity to 3.33×10^{-2} S/cm **[65].**

- By using lithium nitrate salts, biopolymer electrolytes were prepared. (i) alginate incorporation with $LiNO_3$ shows the best-conducting nature at 1.14×10^{-4} S cm^{-1} in the sample having 15 wt% $LiNO_3$ **Fuzlin A.F *et al.* (2019) [66],** (ii) pectin doped with lithium nitrate of different concentrations gives the ionic conductivity in which the 30 wt% pectin and 70 wt% $LiNO_3$ has the highest ionic conductivity of 3.97×10^{-3} Scm^{-1} by **Manjuladevi R *et al.* (2018) [67]** and (iii) cellulose acetate with lithium nitrate ($LiNO_3$) was prepared by **Monisha S *et al.* (2017)** gives the highest conductivity at 1.93×10^{-3} S/cm for 50% containing $LiNO_3$ **[68].**

- Gel polymer electrolytes were prepared by using lithium perchlorate salt. (i) pectin-based gel electrolyte in a transparent film form was done by adding glycerol as plasticizer and addition of $LiClO_4$. The film with 68 wt% of glycerol showed the maximum ionic conductivity at 4.7×10^{-4} S/cm at room temperature **Julian R. Andrade *et al.* (2009) [69]** and (ii) gel polymer electrolyte was prepared by **Sudhakar Y.N *et al.* (2014)** using guar gum as the polymer host, $LiClO_4$ as doping salt and glycerol as the plasticizer. Impedance studies reveal that the highest ionic conductivity was found to be 2.2×10^{-3} Scm^{-1} **[70].**

- **Sampath Kumar *et al.* (2018)** developed the polymer electrolytes due to their biocompatibility, film-forming nature, and non-toxicity. So, the biopolymer membrane has been prepared using tamarind seed polysaccharide (TSP) and lithium chloride (LiCl) salt by solution casting technique. XRD analysis has been done to investigate the highest amorphous nature which has been found for 1 g of TSP with 0.4 g LiCl. FTIR spectrum analysis confirmed the complex formation between TSP biopolymer with LiCl. The maximum ionic conductivity is of the order of 6.7×10^{-3} S cm^{-1} at room temperature has been proved by AC impedance conductivity analysis. The glass transition temperature for the highest conducting biopolymer membrane is 44.25 °C using the DSC technique **[71].**

- **Nursyahida Binti Sahli and Ab Malik Marwan Bin Ali (2102)** formed a solid polymer electrolyte film containing methylcellulose that plays the role of polymer host and lithium triflate ($LiCF_3SO_3$) as a doping salt was prepared by solution casting technique. The sample with 30 wt% of LiCF3SO3 exhibited the highest conductivity of 2.1342×10^{-5} S/cm **[72].**

- Biodegradable corn starch–lithium hexafluorophosphate ($LiPF_6$) based biopolymer electrolytes were prepared via solution casting technique by **Ramesh S *et al.* (2011)**. The polymer matrix was doped by using an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($BmImPF_6$). Upon addition of 50 wt.% $BmImPF_6$, the maximum ionic conductivity of $(1.47 \pm 0.02) \times 10^{-4}$ Scm^{-1} was achieved because of its higher amorphous region **[73].**

- **Ahmad Danial Azzahari *et al.* (2018)** prepared the guar gum succinate (GGS) by chemically modified by reacting guar gum with succinic anhydride. GGS was used as a polymer host and incorporated a blend of ethylene carbonate (EC), carboxymethyl cellulose (CMC), lithium triflate (LiTf) and lithium iodide (LiI). The electrolyte system for GGS:EC (1:0.6) with 30 wt% LiTf showed highest conductivity of 6.29×10^{-5} S/cm and for GGS:CMC:EC (0.5:0.5:0.6) with 25 wt% LiI showed 2.10×10^{-4} S/cm **[74].**

- **Arockia Mary I *et al.* (2019)** made an effort to prepare the environment-friendly electrolyte by using K-carrageenan with different concentrations of lithium bromide (LiBr). One gram of K-carrageenan with 0.5 wt% LiBr has the highest conductivity as 3.43×10^{-3} S/cm at ambient temperature **[75].**

2.2.3 With ammonium salts:

The below review tells about the preparation of solid polymer electrolyte by using biopolymer as a host with an ammonium salt.

- Ammonium nitrate has been used as a salt for the preparation of biopolymer electrolytes such as (i) cellulose acetate and ammonium nitrate which have been prepared as films by **Monisha S *et al.* (2016).** The ratio of 50mol% Cellulose acetate and 50mol% NH_4NO_3 complex has the highest ionic conductivity of 1.02×10^{-3} S/cm **[76],** (ii) alginate complexed with the salt

NH_4NO_3 gives the ionic conductivity at a maximum value of 5.56×10^{-5} S/cm for the sample having 25 wt% NH_4NO_3 **Rasali N.M.J *et al.* (2018) [77], (iii)** iota-carrageenan with ammonium nitrate (NH_4NO_3) by the solution-casting method was prepared by **Moniha V *et al.* (2018)**. From the AC impedance spectroscopic analysis, the ionic conductivity value is 1.46×10^{-3} S/cm at room temperature for the mixture of 1.0 g I-carrageenan with 0.4 wt% NH_4NO_3 **[78]** and (iv) starch and ammonium nitrate (NH_4NO_3) was carried out by **Ahmad Khiar A.S and Arof A.K (2010).** Impedance analysis has been done and the results proved that the sample with 25 wt% NH_4NO_3 has a smaller bulk resistance compared to that of the pure sample. The highest obtainable room temperature conductivity was 2.83×10^{-5} S/cm, while at 100 °C, the conductivity was found to be 2.09×10^{-4} S/cm **[79].**

- An attempt to synthesize polymer electrolytes with ammonium thiocyanate salt is as follows: (i) **Muthukrishnan *et al.* (2019)** done their work by using pectin with ammonium thiocyanate (NH_4SCN) salt via solution casting technique. The highest conductivity of 1.5×10^{-3} S cm^{-1} was observed for 40 mol% pectin: 60 mol% NH_4SCN sample **[80],** (ii) **Zulkefli F.N *et al.* (2015)** prepared an electrolyte using corn starch with 30 wt% NH_4SCN salt which exhibited the highest ionic conductivity of 5.54×10^{-3} S/cm **[81],** (iii) kappa-carrageenan incorporated with 0.5% ammonium thiocyanate (NH_4SCN) achieved a highest ionic conductivity of 6.83×10^{-4} S/cm from AC impedance analysis **Christopher Selvin *P et al.* (2018) [82]** and (iv) **Nirmala Devi G *et al.* (2017)** prepared dextrin doped with ammonium thiocyanate salt via solution casting process. AC impedance analyser showed that the ionic conductivity increases with an increase in salt concentration up to 40%. The highest ionic conductivity was found to be 4.05×10^{-4} S/cm for the polymer electrolyte having dextrin complexed with 40 mol% of NH_4SCN **[83].**

- **Vijaya *et al.* (2017)** focused their present study on the proton-conducting polymer electrolytes based on the biopolymer pectin doped with ammonium chloride (NH_4Cl) and ammonium bromide (NH_4Br) prepared by solution casting technique. The conductivity of the pure pectin membrane is 9.41×10^{-7} S cm^{-1}. The polymer systems with 30 mol% NH_4Cl-doped pectin and 40 mol% NH_4Br-doped pectin have been found to have maximum ionic conductivity of 4.52×10^{-4} and 1.07×10^{-3} S cm^{-1} respectively **[84].**

- **Samsudin A S *et al.* (2014),** gone through the research by incorporating various NH_4Br composition with carboxymethyl cellulose (CMC). The ratio containing 25wt% NH_4Br has the highest ionic conductivity was shown at 1.12×10^{-4} S/cm **[85].**

- **Rani M.S.A *et al.* (2015)** undertaken their work to study the conductivity of a biopolymer electrolyte as carboxymethyl cellulose with ammonium acetate. The highest conductivity was found to be 2.18×10^{-3} S/cm with 20 wt% NH_4CH_3COO **[86].**

- **Rudhziah S *et al.* (2015)** done their work by preparing a biopolymer blend salt film by adding different weight percentages of NH_4I to solutions containing 1g of Carboxymethyl kappa-carrageenan/Carboxymethyl cellulose of mass ratio 60:40%. The highest ionic conductivity achieved was 2.41×10^{-3} S/cm at 30% of the salt **[87].**

- **Manindra Kumar *et al.* (2012)** synthesized a new biopolymer electrolyte system by mixing NH_4I with potato starch. It has an ionic conductivity maximum at 2.4×10^{-4} S/cm **[88].**

- **Nik Aziz N.A *et al.* (2010)** made their work by preparing polymer electrolytes of methylcellulose as a polymer host and ammonium fluoride (NH_4F) as a dopant by the solution casting method. The highest ionic conductivity value was found to be 6.40×10^{-7} S/cm for the sample containing 18 wt% of NH_4F **[89].**

- A biopolymer-based electrolyte was prepared by **Mohd Saiful Asmal Rani *et al.* (2014)** by using cellulose from kenaf bast fiber which is carboxymethyl cellulose with ammonium acetate. The ionic conductivity was found to be 5.77×10^{-4} S/cm for the film containing 20 wt% of CH_3COONH_4 **[90].**

2.2.4 With other salts:

The below review tells about the preparation of solid polymer electrolyte by using biopolymer as a host with other salts.

- **Ellen Raphael *et al.* (2010)** formed a new type of polymer electrolyte based on agar as a biopolymer. The best ionic conductivity was obtained at 1.1×10^{-4} S/cm for the samples containing a concentration of 50 wt % of acetic acid **[91].**

- **Mishra R.K *et al.* (2009)** presented their work by synthesizing amidated pectin crosslinked with glutaraldehyde. The prepared polymer electrolyte membrane has a maximum conductivity of 1.098×10^{-3} Scm^{-1}**[92].**

- **Alves R *et al.* (2017)** made a green solid polymer electrolyte containing Er^{3+} ions by using a solvent casting process. The trivalent cations as erbium triflate ($Er(CF_3SO_3)_3$) have been blended with the chitosan which acts as a host polymer. The most conducting electrolyte displayed 2.06×10^{-5} at 30 °C and 5.91×10^{-4} at 90 °C **[93].**

- **Majid S.R and Arof A.K (2007)** carried out their work on chitosan-based proton-conducting electrolytes. Chitosan-phosphoric acid electrolytes were prepared using the solution casting process. In this reaction, more protons are supplied as the acid content increases. This has been continued up to 50 vol% acid. In that concentration, there exhibited a maximum conductivity of $(4.9\pm1.7)\times10^{-4}$ Scm^{-1}**[94].**

- **Xiaoteng Jia *et al.* (2014)** demonstrated a biocompatible magnesium-air battery device. It is made up of bioresorable magnesium alloy anode and polypyrrole-para (toluene sulfonic acid) cathode. The electrolyte used here is made up of choline nitrate embedded in chitosan. This device offers a maximum ionic conductivity of 8.9×10^{-3} S/cm. the assembled battery delivered a volumetric power density of 3.9 WL^{-1}**[95].**

- **Shujahadeen B *et al.* (2010)** done their work on solid polymer electrolyte which is composed of chitosan and silver triflate ($AgCF_3SO_3$). Their conductivity was found to increase when the concentration of silver triflate increases **[96].**

- **Nurhaziqah A.M.S *et al.* (2018)** made a study by using different compositions of calcium nitrate $Ca(NO_3)_2$ salt with methylcellulose (MC). MC-$Ca(NO_3)_2$ solid biopolymer electrolyte was prepared by using the solution casting technique. The highest conductivity among the samples was found to be 2.21×10^{-7} Scm^{-1} for 25 wt% of the salt **[97].**

MATERIALS AND METHODOLOGY

CHAPTER III

MATERIALS AND METHODOLOGY

The chapter deals with the materials used and methods adopted and characterized to prepare the biopolymer solid electrolytes.

3.1 Materials used

The materials used for the preparation of the polymer electrolytes were listed below:

- Pectin
- Guar Gum
- Magnesium Chloride hexahydrate
- Magnesium sulphate heptahydrate
- Ethylene carbonate
- Succinonitrile

3.2 Properties and Structure of Pectin

Host polymer : Pectin
Chemical name : poly-D-galacturonic acid methyl ester
Molecular formula : $C_6H_{10}O_7$
Molecular weight : 194.14 kg/mol
Appearance : Fine powder
Color : Yellowish white

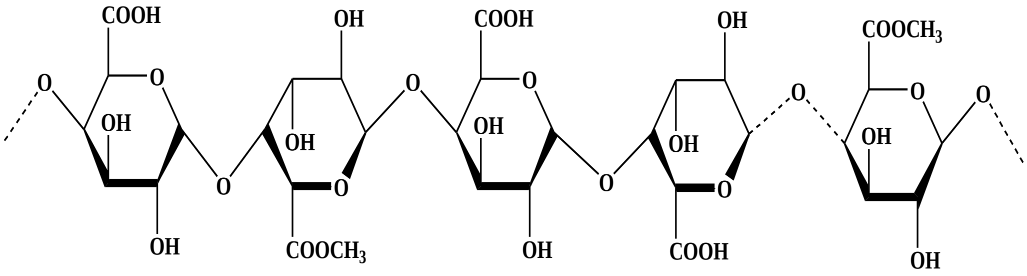


Fig 3. Structure of Pectin

Fig 4. Appearance of pectin

3.3 Properties and Structure of Guar gum

Host polymer : Guar Gum

Molecular formula : $C_{18}H_{32}O_{16}$

Molecular weight : 535.15 kg/mol

Appearance : Coarse powder

Color : Dirty white

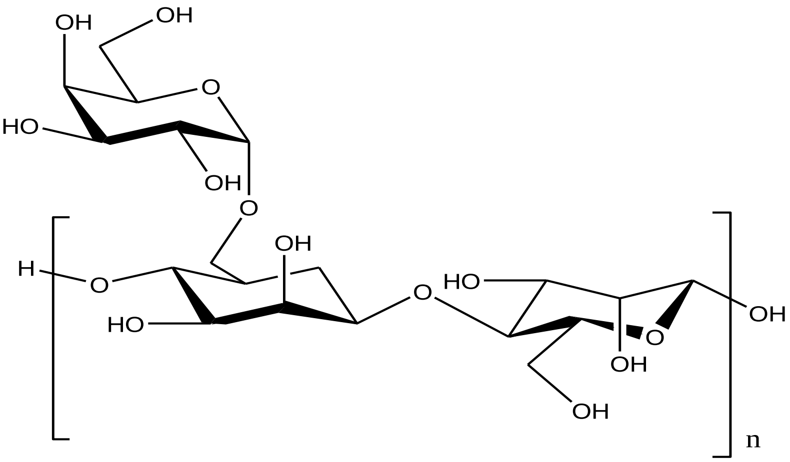


Fig 5. Structure of Guar Gum

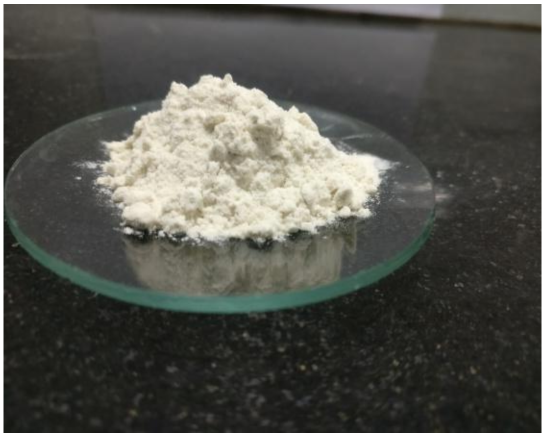


Fig 6. Appearance of Guar gum

3.4 Properties of Magnesium chloride hexahydrate

Ionic salt : Magnesium chloride hexahydrate

Chemical formula : $MgCl_2 .6H_2O$

Molecular weight : 203.31 g/mol

Appearance : Crystalline solid

Color : Colorless

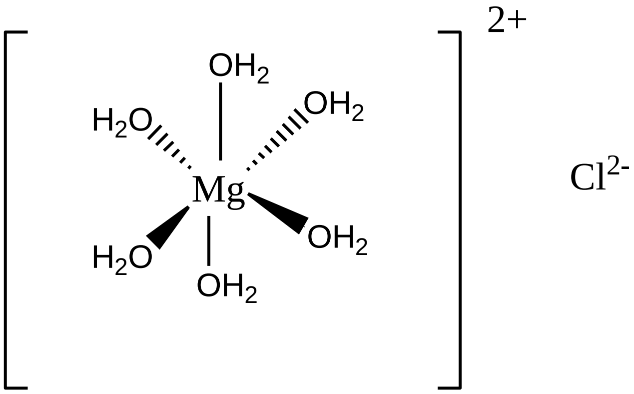


Fig 7. Structure of $MgCl_2.6H_2O$

Fig 8. Appearance of $MgCl_2.6H_2O$

3.5 Properties and structure of Magnesium sulphate heptahydrate

Ionic salt : Magnesium sulphate heptahydrate
Chemical formula : $MgSO_4.7H_2O$
Molecular weight : 246.48 g/mol
Appearance : Crystalline powder
Color : White

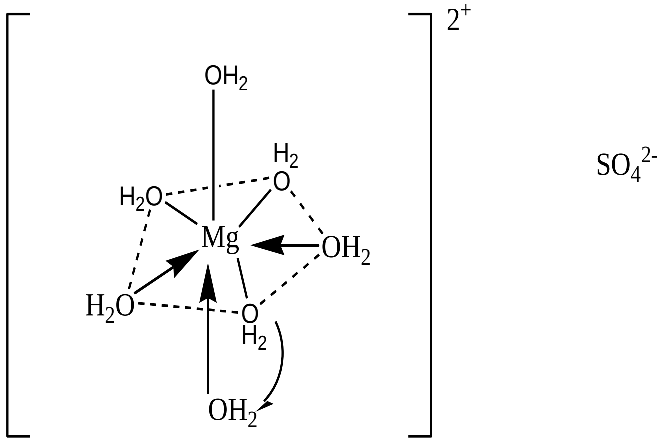


Fig 9. Structure of $MgSO_4.7H_2O$

Fig 10. Appearance of $MgSO_4.7H_2O$

3.6 Properties and structure of ethylene carbonate

Plasticizer : Ethylene carbonate

Molecular formula : $(CH_2O)_2CO$

Molecular weight : 88.06 g/mol

Appearance : Crystalline solid

Color : Colourless

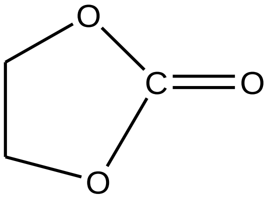


Fig 11. Structure of ethylene carbonate

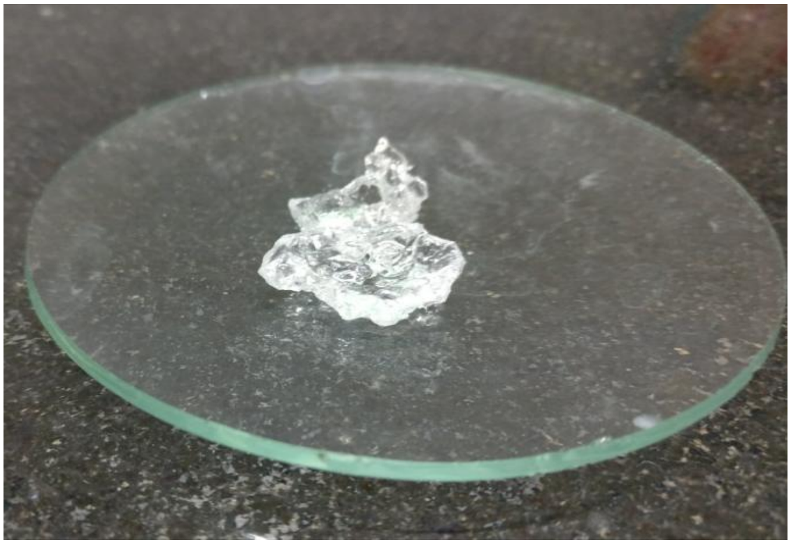


Fig 12. Appearance of ethylene carbonate

3.7 Properties and structure of succinonitrile

Plasticizer : Succinonitrile
Molecular formula : $C_2H_4\,(CN)_2$
Molecular weight : 80.09 g/mol
Appearance : Waxy crystals
Color : Colourless

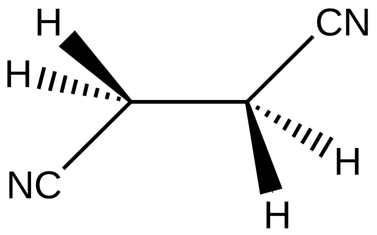


Fig 13. Structure of succinonitrile

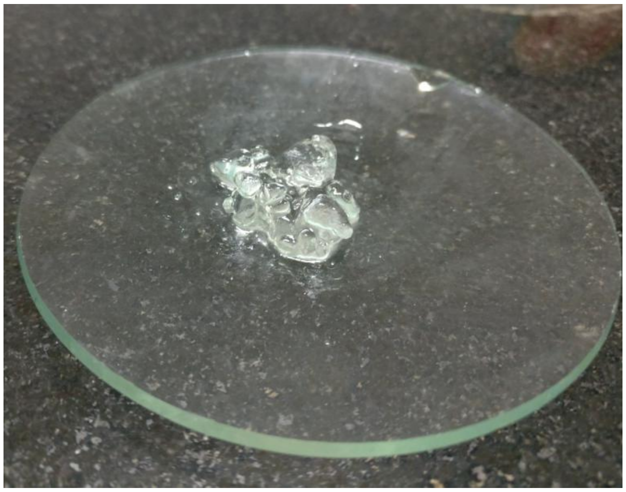


Fig 14. Appearance of succinonitrile

3.8 Methodology

The blend polymer pectin and guar gum have been complexed with two different ionic salts namely magnesium chloride and magnesium sulphate to prepare four ion-conducting biopolymer electrolytes with two plasticizers like ethyl carbonate and succinonitrile. The polymer electrolyte has been prepared by using the solution casting method. Among the other methods of electrolyte preparation, the solution casting technique is the worldwide used method due to ease of preparation. Hence, the above method is used for the preparation of electrolyte.

3.9 Preparation of polymer electrolytes

3.9.1 Pectin/Guar gum/$MgCl_2.6H_2O$/Ethylene carbonate:

The biopolymers pectin and guar gum have been blended with 40 ml distilled water for an hour in a magnetic stirrer, then magnesium chloride hexahydrate salt and ethylene carbonate as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous mixture. The mixture was poured onto the Petri-dishes and kept in an air-oven for 24 hours at 40 ^{o}C. The concentrations (M wt %) of Pectin/Guar gum/$MgCl_2.6H_2O$/Ethylene carbonate were taken in the following ratio

(i) 45:25:25:5
(ii) 40:20:35:5
(iii) 35:15:45:5
(iv) 30:10:55:5

3.9.2 Pectin/Guar gum/$MgCl_2.6H_2O$/Succinonitrile:

The biopolymers pectin and guar gum have been blended with 40 ml distilled water for an hour in a magnetic stirrer, then magnesium chloride hexahydrate salt and succinonitrile as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous mixture. The mixture was poured onto the Petri-dishes and kept in an air-oven for 24 hours at 40 ^{o}C. The concentrations (M wt %) of Pectin/Guar gum/$MgCl_2.6H_2O$/Succinonitrile were taken in the following ratio

(i) 45:25:25:5
(ii) 40:20:35:5
(iii) 35:15:45:5
(iv) 30:10:55:5

3.9.3 Pectin/Guar gum/$MgSO_4.7H_2O$/Ethylene carbonate:

The biopolymers pectin and guar gum have been blended with 40 ml distilled water for an hour in a magnetic stirrer, then magnesium sulphate heptahydrate salt and succinonitrile as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous mixture. The mixture was poured onto the Petri-dishes and kept in an air-oven for 24 hours at 40 ^oC. The concentrations (M wt %) of Pectin/Guar gum/$MgSO_4.7H_2O$/Ethylene carbonate were taken in the following ratio

(i) 45:25:25:5
(ii) 40:20:35:5
(iii) 35:15:45:5
(iv) 30:10:55:5

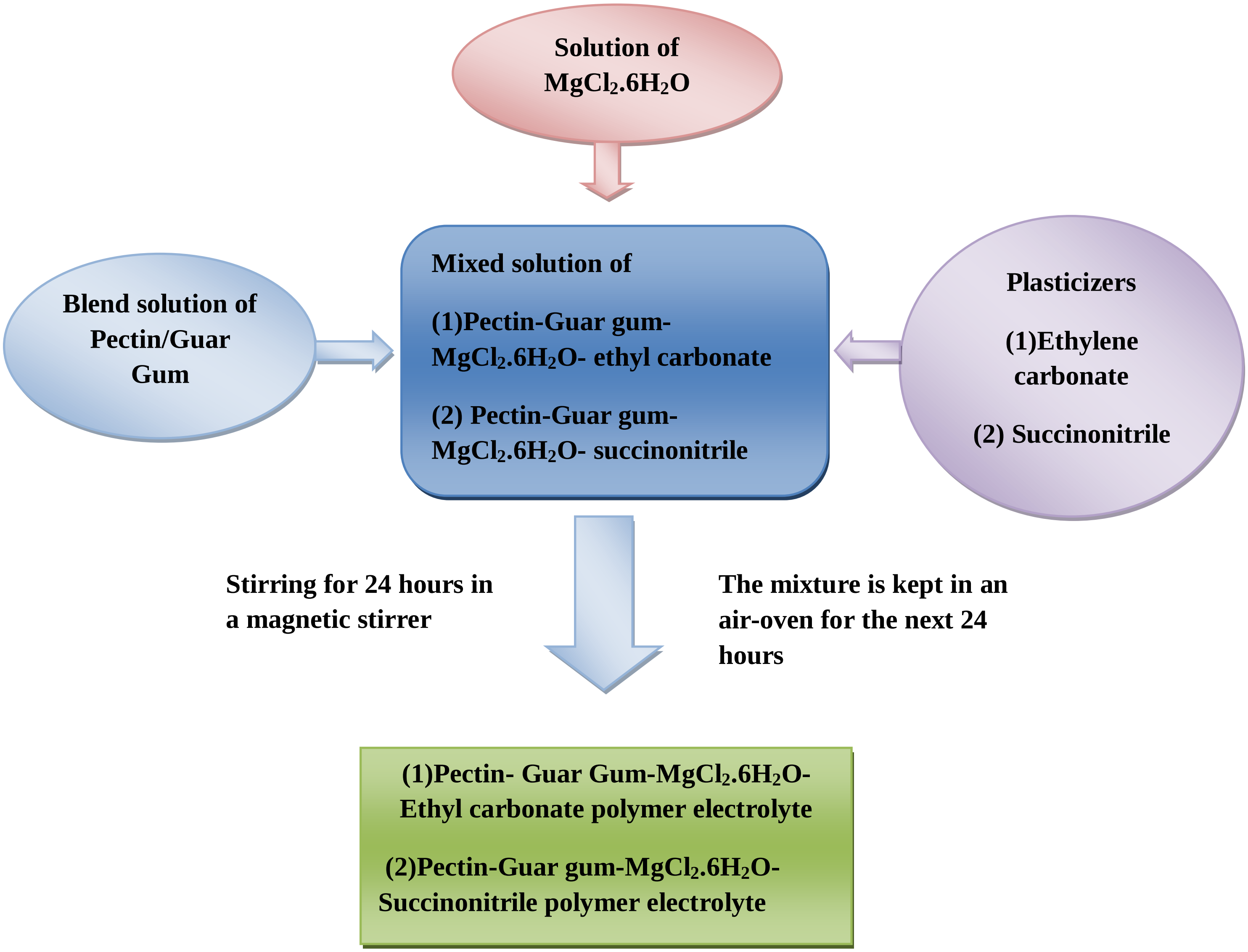
3.9.4 Pectin/Guar gum/$MgSO_4.7H_2O$/Succinonitrile:

The biopolymers pectin and guar gum have been blended with 40 ml distilled water for an hour in a magnetic stirrer, then magnesium sulphate heptahydrate salt and succinonitrile as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous mixture. The mixture was poured onto the Petri-dishes and kept in an air-oven for 24 hours at 40 ^oC. The concentrations (M wt %) of Pectin/Guar gum/$MgSO_4.7H_2O$/Succinonitrile were taken in the following ratio

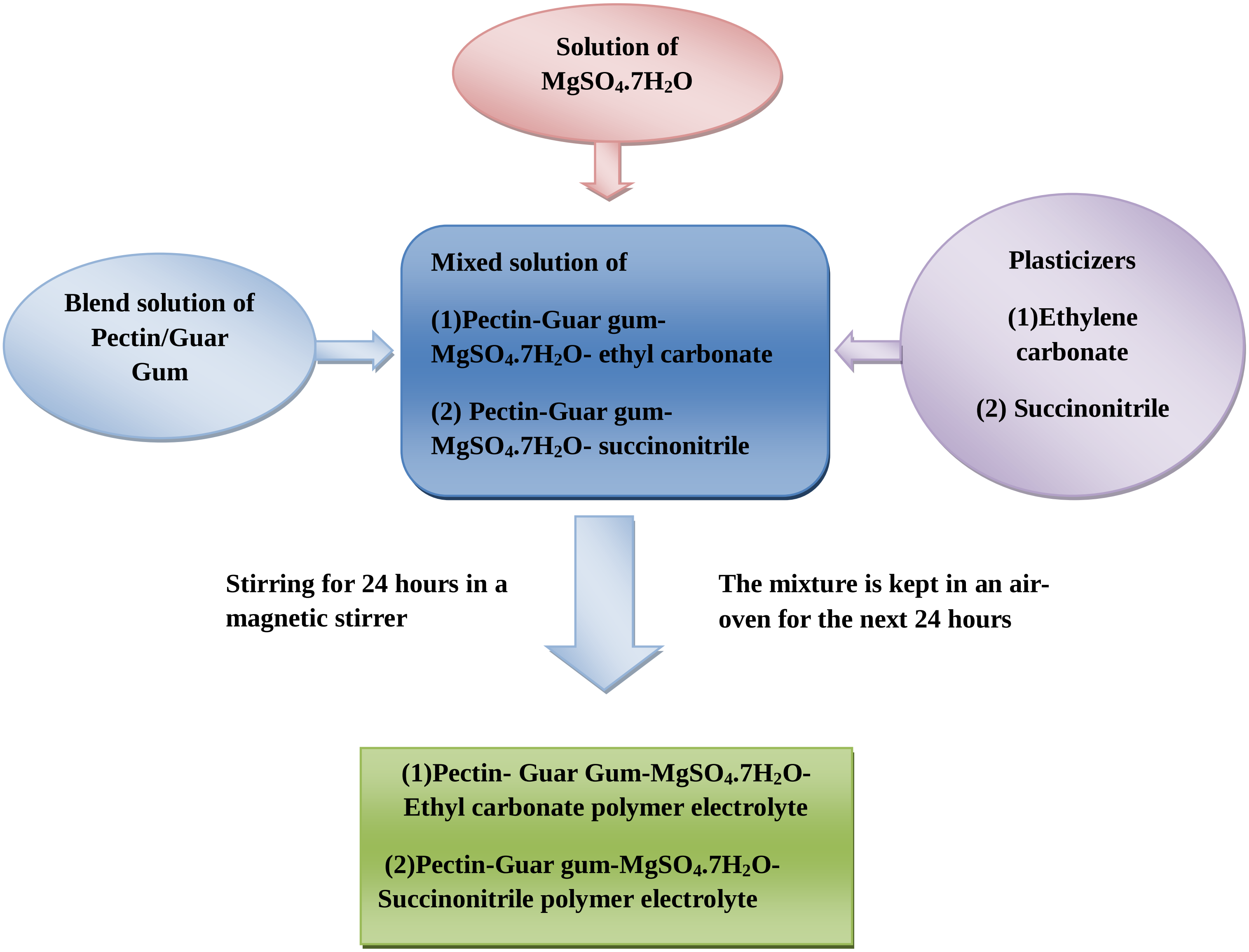
(i) 45:25:25:5
(ii) 40:20:35:5
(iii) 35:15:45:5
(iv) 30:10:55:5

3.10 Experimental flow charts/photographs

Various electrolytes are shown in flow chart 2 and 3.



Flow chart 2. Pectin/Guar Gum with magnesium chloride salts



Flow chart 3. Pectin/Guar Gum with magnesium sulphate salts

The stepwise process for the preparation of the solid biopolymer electrolytes were shown in the Figure 15 (a-e).

Fig 15 a. stirring for 24 hours in a magnetic stirrer (Individual)

Fig 15 b. stirring for 24 hours in a magnetic stirrer (Group)

Fig 15 c. The homogeneous solution transferred to the petri dish

Fig 15 d. The Petri dishes with the homogeneous solution were kept in hot air- oven

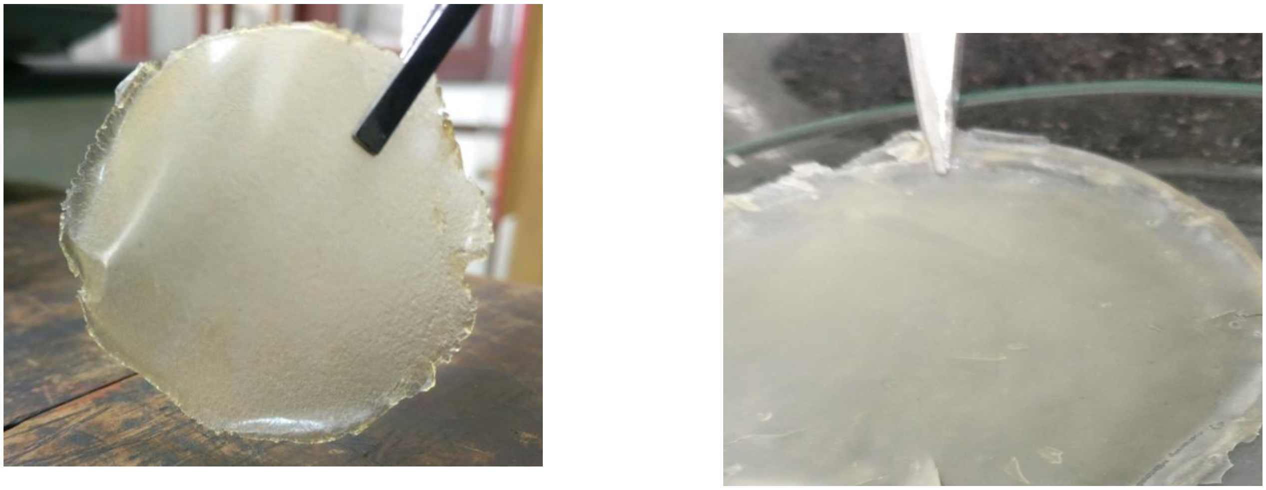


Fig 15 e. Solid polymer film of PGMCSN7

3.11 Characterization

The prepared biopolymer blend solid electrolytes have been characterized by the following techniques/analysis:

3.11.1 Fourier Transform Infrared (FTIR)

The FTIR spectra of the blend polymer pectin-Guar gum and $MgCl_2$ doped blend polymer samples were done in the frequency range of 4000-400 cm^{-1} using FT-IR (Miracle 10 SHIMADZU) spectrophotometer at ambient temperature.

The basic principle of FTIR is that it is an analytical technique that is used to identify polymeric, organic and inorganic substances. This method uses infrared light to scan test samples and observe physical and chemical properties. Fig 16 shows the pictorial representation of the FTIR instrument.

The instrument sends Infrared (IR) radiation of about 10,000 to 100 cm^{-1} through the sample, in which some of them get absorbed and some passed through. The absorbed radiation is converted into vibrational and rotational energy by the molecules of the sample. The resulting signal at the detector gives a spectrum in which the wave number from 4000 to 400 cm^{-1} represents the molecular fingerprint of the sample. Each molecule will produce a unique fingerprint, making FTIR analysis a great tool for chemical identification.

Fig 16. FT-IR (Miracle 10 SHIMADZU)

Courtesy: Google

3.11.2 Thermal Gravimetric/Differential Thermal Analysis (TG/DTA)

The Thermal Gravimetric/Differential Thermal Analysis (TG/DTA) 6300 Model instrument (EXSTAR) perform thermogravimetric measurements. Figure 17 shows the pictorial representation of TG/DTA 6300. A TGA analysis was performed by gradually raising the temperature of a sample in a furnace as its weight was measured on an analytical balance that remains outside of the furnace. In TGA, mass loss was found if there loss of a volatile component.

Fig 17. TG/DTA 6300 Model instrument (EXSTAR)

Courtesy: Google

3.11.3 3-D Optical Profilometer

The sample’s roughness was determined by 3-D Optical Profilometer (Zeta-20). Figure 18 shows the pictorial representation of the 3-D Optical Profilometer. Profilometry is a technique used to extract topographical data from a surface. The work of profilometry is to get step heights, surface morphology, and surface roughness. The key role of this technique is to direct the light in such a manner that it can detect the surface in three dimensions.

Fig 18. 3-D Optical Profilometer (Zeta-20)

Courtesy: Google

3.11.4 X-ray diffraction Analysis

XRD patterns of the polymer films were displayed in the range of $2\theta = 10^{o}$ - 90^{o} using XPERT PRO Diffractometer at ambient temperature. Figure 19 shows the pictorial representation of the XPERT PRO Diffractometer. XRD works on the principle of constructive interference of a sample and monochromatic X-rays. These X-rays were generated by a cathode ray tube, filtered to monochromatic (single wavelength) radiation, collimated to concentrate, and directed towards the sample. The interaction of the incident rays with sample produces constructive interference which should satisfy Bragg’s law. The diffracted X-rays were detected, processed, and counted. By scanning the sample through a range of 2θ angles, all the possible diffraction directions of the lattice should be attained due to the random orientation of the film material. An important component of all diffraction is the angle between the incident and the diffracted rays.

Fig 19. XPERT PRO Diffractometer

Courtesy: Google

3.11.5 Impedance studies

Using Ametek PARSTAT MC – 1000, the impedance measurements were done in the frequency range of 1 Hz to 1 MHz at ambient temperature. Figure 20 shows the pictorial representation of Ametek PARSTAT MC-1000. Impedance spectroscopy is a powerful device for the analysis of the electrical properties of the solid electrolyte material and their interfaces. The ionic conductivity depends on their mobility and the conducting species. This method is used to establish the mechanism of conductivity, observing the polymer chain participation and carrier generation processes. The blend solid polymer film was kept between the two aluminium electrodes. The values of real and imaginary impedance were taken. A plot of real impedance on the X-axis versus negative imaginary impedance on the Y-axis was drawn. In the graph, two well-defined regions can be seen, a semicircle that is in the high- frequency range and an inclined spike at the low-frequency region. From the complex impedance plot, the (R_b) bulk resistance can be calculated from the point of intersection of the semicircle and the inclined spike.

By knowing the bulk resistance, the conductivity of the sample can be determined using the relation

$\sigma = L/R_b A$

Where A and L are the area and thickness of the film respectively.

Fig 20. Ametek PARSTAT MC – 1000

3.11.6 Transport number measurement

Chronoamperometry technique

Chronoamperometry technique is used to measure transference number which identifies whether the conductivity in the polymer electrolyte is due to presence of ions or electrons. Transference number is calculated using Wager's polarization formula

$$t_{ion} = (I_f - I_i)/I_i$$

where t_{ion} is the transfer of ions
I_i is the initial current and
I_f is the final current.

The DC potential of 0.1 V is applied across the cell in the Al electrode/PGMCEC/Al electrode configuration, and the polarization current is monitored as a function of time. The initial total current has been found to decrease with respect to time due to the depletion of the ionic species in the electrolyte and reaches constant state in the fully depleted situation. The cell is polarized at the steady state, and due to the migration of electrons, the current flows across the electrolyte and interfaces. Figure 21 shows the Ametek PARSTAT MC 1000 instrument running chronoamperometry.

Fig 21 a. Ametek PARSTAT MC – 1000 (Chronoamperometry)

Fig 21 b. Thin film probe set up

RESULTS AND DISCUSSION

CHAPTER IV

RESULTS AND DISCUSSION

The following four sets of biopolymer solid electrolytes with different compositions of Pectin, Guar gum, $MgCl_2.6H_2O/MgSO_4.7H_2O$, EC/SN were prepared for the present work.

(i) Pectin/Guar gum/$MgCl_2.6H_2O$/Ethylene carbonate

(ii) Pectin/Guar gum/$MgCl_2.6H_2O$/Succinonitrile

(iii) Pectin/Guar gum/$MgSO_4.7H_2O$/ Ethylene carbonate

(iv) Pectin/Guar gum/$MgSO_4.7H_2O$/Succinonitrile

Out of four electrolytes prepared, the two electrolytes (iii) and (iv) prepared from $MgSO_4.7H_2O$ were not good enough for the characterization (Figure 22), because of the opaque and rigid nature of the films of pectin/guar gum prepared with the magnesium sulphate salts. Hence, further characterizations for these two polymer electrolytes were not carried out. Figure 23 (a-d) shows the picture of Pectin/Guar gum/$MgCl_2.6H_2O$/EC and figure 24 (a-d) shows the picture of Pectin/Guar gum/$MgCl_2.6H_2O$/SN.

Fig 22. Film of Pectin/Guar gum/$MgSO_4.7H_2O$/EC

Fig 23 a. Film of PGMCEC7

Fig 23 b. Film of PGMCEC6

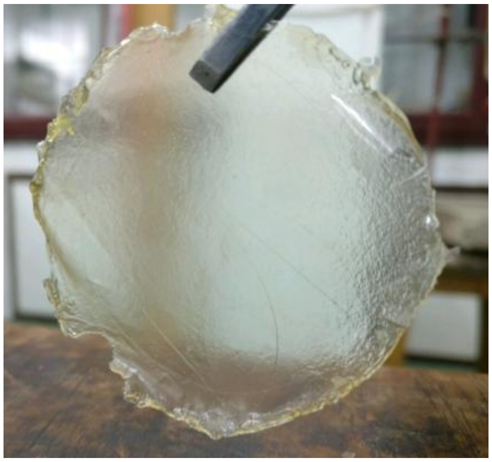


Fig 23 c. Film of PGMCEC5

Fig 23 d. Film of PGMCEC4

Fig 23. Pictorial representation of the film of Pectin/Guar gum/$MgCl_2.6H_2O$/EC

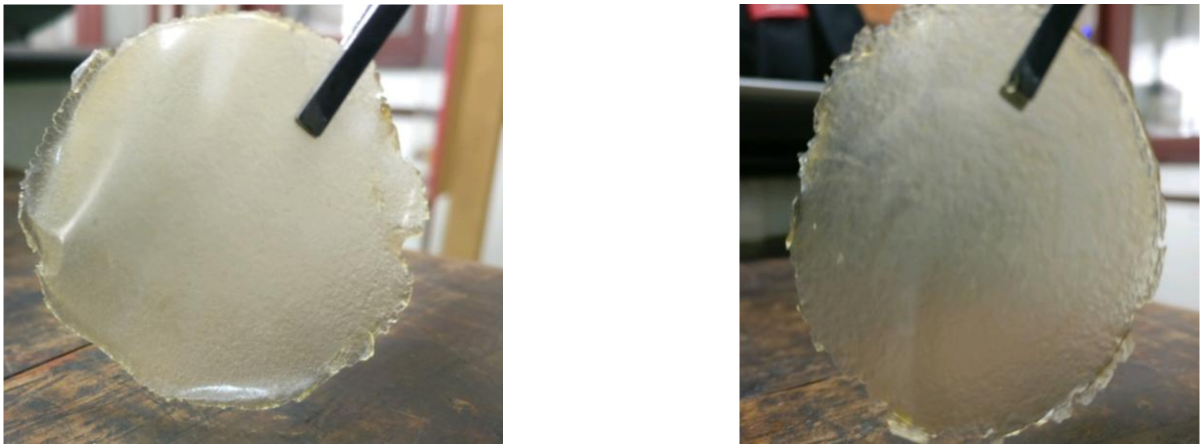


Fig 24 a. Film of PGMCSN7 **Fig 24 b. Film of PGMCSN6**

Fig 24 c. Film of PGMCSN5 **Fig 24 d. Film of PGMCSN4**

Fig 24. Pictorial representation of the film of Pectin/Guar gum/$MgCl_2.6H_2O$/SN

The code and composition chosen for the solid biopolymer electrolytes for Magnesium ion batteries were given in tables 3 and 4. The thin transparent films obtained were characterized by Fourier Transform-Infrared Spectroscopy (FT-IR), X-ray Diffraction

(XRD), Thermogravimetric analysis (TGA/DTA), 3-D Laser Profilometry, and Electrical Impedance Spectroscopy.

Table 3. Pectin/Guar gum/$MgCl_2.6H_2O$/EC blend electrolytes

Code	Composition (M wt %)
PGMCEC7	Pectin (45): guar gum (25): $MgCl_2.6H_2O$ (25): EC (5)
PGMCEC6	Pectin (40): guar gum (20): $MgCl_2.6H_2O$ (35): EC (5)
PGMCEC5	Pectin (35): guar gum (15): $MgCl_2.6H_2O$ (45): EC (5)
PGMCEC4	Pectin (30): guar gum (10): $MgCl_2.6H_2O$ (55): EC (5)

Table 4. Pectin/Guar gum/$MgCl_2.6H_2O$/SN blend electrolytes

Code	Composition (M wt %)
PGMCSN7	Pectin (45): guar gum (25): $MgCl_2.6H_2O$ (25): SN (5)
PGMCSN6	Pectin (40): guar gum (20): $MgCl_2.6H_2O$ (35): SN (5)
PGMCSN5	Pectin (35): guar gum (15): $MgCl_2.6H_2O$ (45): SN (5)
PGMCSN4	Pectin (30): guar gum (10): $MgCl_2.6H_2O$ (55): SN (5)

4.1 FT-IR Analysis

FT-IR spectra of PGMCEC blend biopolymer electrolytes are shown in Fig 25(a-d) and the values are given in the table 5. In the pure blend pectin-GG, a broad peak at 3394.72 cm^{-1} corresponds to the O-H stretching vibration mode which gets shifted and broadened at 3300 cm^{-1} for the doped samples. A medium peak at 1743.65 cm^{-1} is allotted to the stretching vibrations of the C=O bond of the biopolymer. This peak gets submerged for the biopolymers added with ionic salt. The vibration peak at 1635.64 cm^{-1} is assigned to the carbonyl group of

COO^- for the biopolymer. The O-H bending is observed at 1373.32 cm^{-1} for the blend polymer and gets shifted to 1396.46 cm^{-1} for the samples with the ionic salt. The blend polymer electrolyte exhibits peak at 1234.44 cm^{-1} gets shifted to 1226.73 cm^{-1} for PGMCEC7. It is assigned as C-O-C stretching and 1242.16 cm^{-1} for other compositions [51]. The C-Cl stretching mode of $MgCl_2$ is achieved at 678.94 cm^{-1} for PGMCEC7 and PGMCEC5 and at 671.23 cm^{-1} for PGMCEC6 and PGMCEC4[27].

Table 5. Peak assignments of pectin/guar gum/$MgCl_2.6H_2O$/EC polymer electrolytes

20% Pectin:20% Guar Gum	**PGMCEC7 (45:25:25:5 M wt%)**	**PGMCEC6 (40:20:35:5 M wt%)**	**PGMCEC5 (35:15:45:5 M wt%)**	**PGMCEC4 (30:10:55:5 M wt%)**	**Characteristic groups**
Wave number(cm^{-1})					
3394.72	3279.41	3279.41	3279.41	3279.41	OH-stretching vibration
2947.23	-	-	-	-	C-H stretching of CH_2 group
1373.32	1396.46	-	-	1327.08	-OH bending
1234.44	1226.73	1242.16	1242.16	1242.16	C-O-C stretching
1149.57	1141.86	1149.57	1149.57	1149.57	C-OH and primary alcoholic CH_2OH stretching
1041.56	1018.41	1026.13	1018.41	1010.70	CH_2 twisting vibration
678.94	678.94	671.23	678.94	671.23	C-Cl stretching

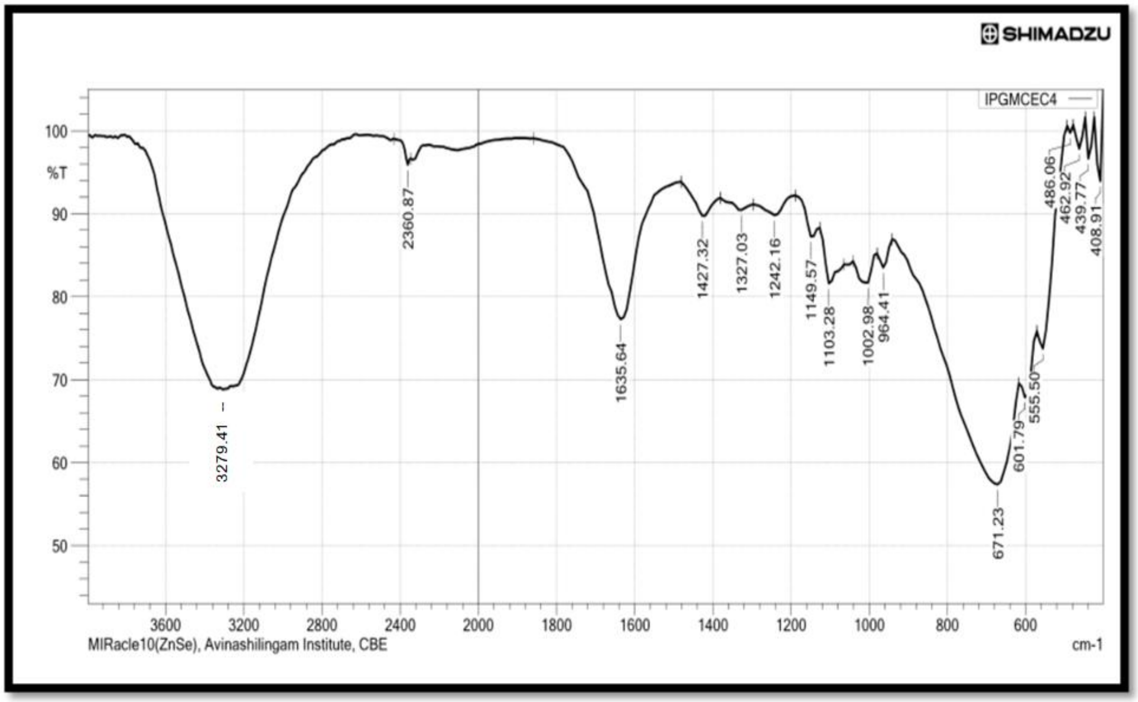


Fig 25 a. FTIR spectra of PGMCEC4

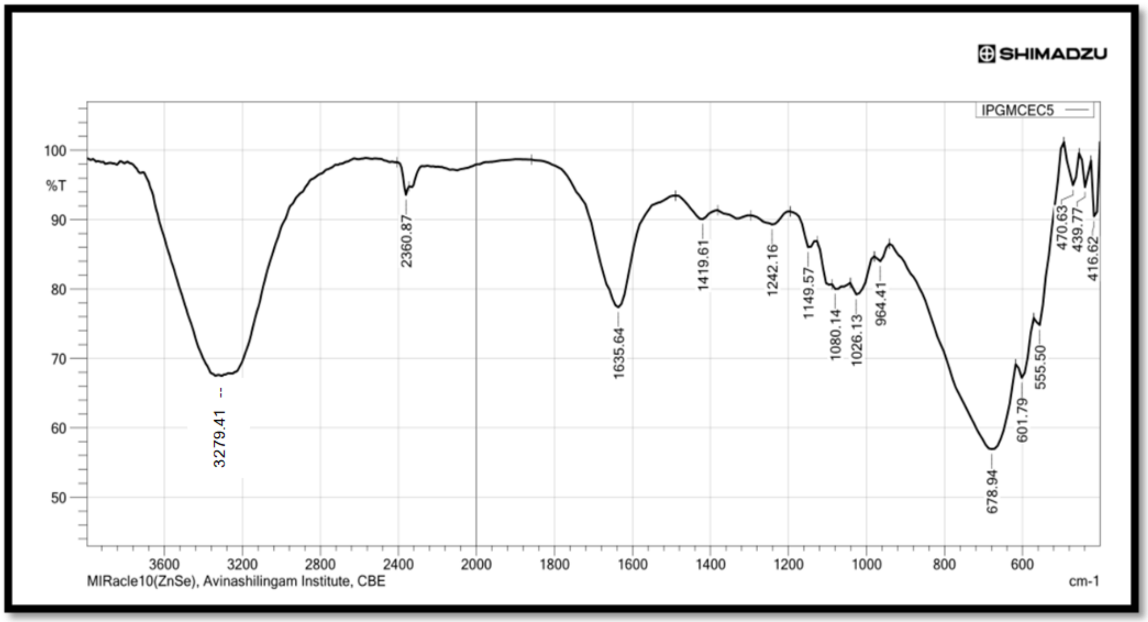


Fig 25 b. FTIR spectra of PGMCEC5

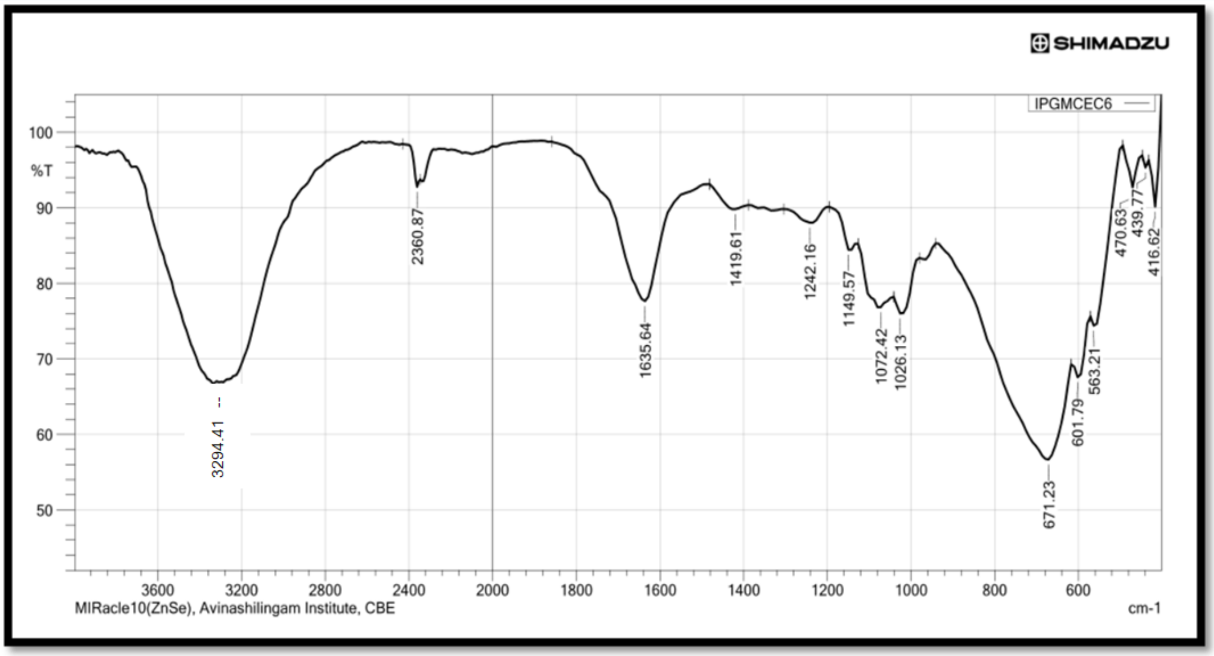


Fig 25 c. FTIR spectra of PGMCEC6

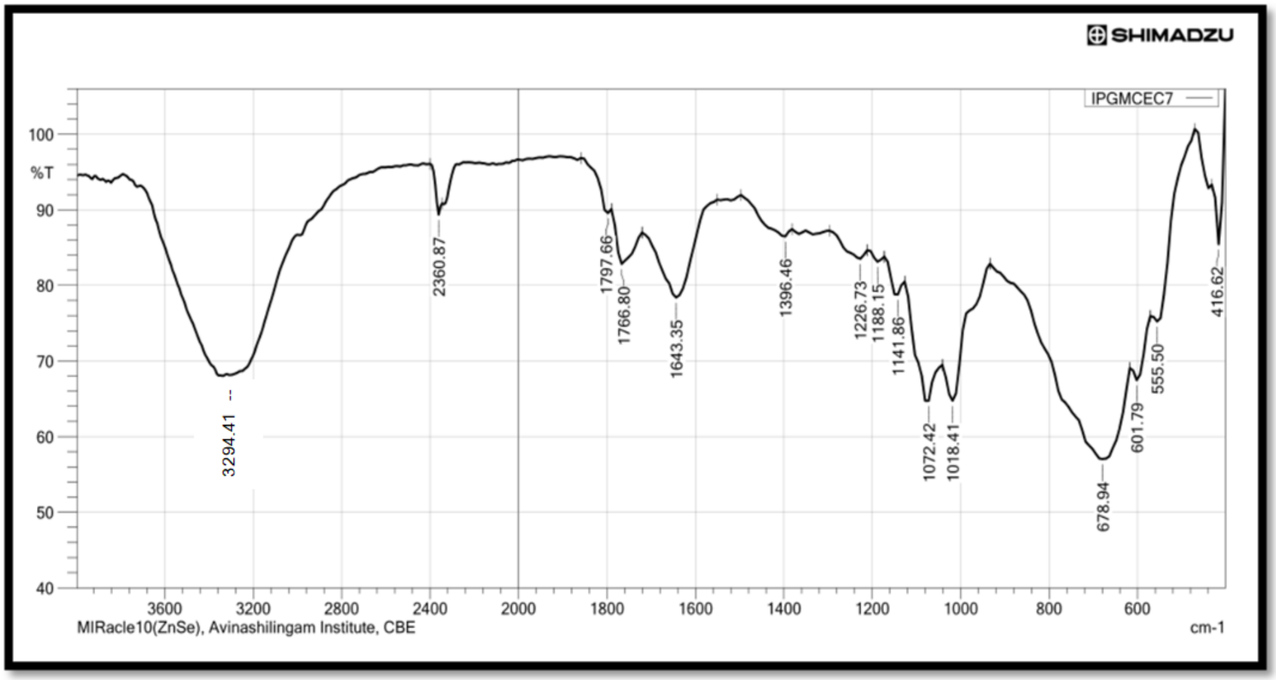


Fig 25 d. FTIR spectra of PGMCEC7

Fig 24. FT-IR spectra of Pectin-GG-$MgCl_2.6H_2O$-EC blend biopolymer electrolytes

Figure 26(a-d) shows the FTIR spectra of Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes and those values are given in Table 6. A broad peak around 3394.72 cm^{-1} represents stretching of O-H bond for pure blend polymer which gets switched to 3718.16 cm^{-1} for PGMCSN4, PGMCSN6, and 3726.47 cm^{-1} for PGMCSN5, PGMCSN7. The C-H bond stretching observed at 2947.23 cm^{-1} for the blend sample gets shifted to 2978.09 cm^{-1} for all the ionic salt-containing samples. A medium peak at 1072.42 cm^{-1} represents C-N bond stretching present in all the doped samples.

Table 6. Peak assignments of pectin/guar gum/$MgCl_2.6H_2O$/SN polymer electrolytes

20% Pectin:20% Guar Gum	**PGMCSN7 (45:25:25:5 M wt%)**	**PGMCSN6 (40:20:35:5 M wt%)**	**PGMCSN5 (35:15:45:5 M wt%)**	**PGMCSN4 (30:10:55:5 M wt%)**	**Characteristic groups**
Wavenumber(cm^{-1})					
3394.72	3271.27	3271.27	3271.27	3271.27	OH-stretching vibration
2947.23	2978.09	2978.09	2978.09	2978.09	C-H stretching of CH_2 group
1373.32	1388.75	1388.75	1388.75	1404.18	-OH bending
1234.44	1234.44	1242.16	1249.87	1242.16	C-O-C stretching
-	1072.42	1072.42	1072.42	1072.42	C-N stretching
1041.56	1026.13	1026.13	1026.13	1018.41	CH_2 twisting vibration
678.94	678.94	686.66	678.94	671.23	C-Cl stretching

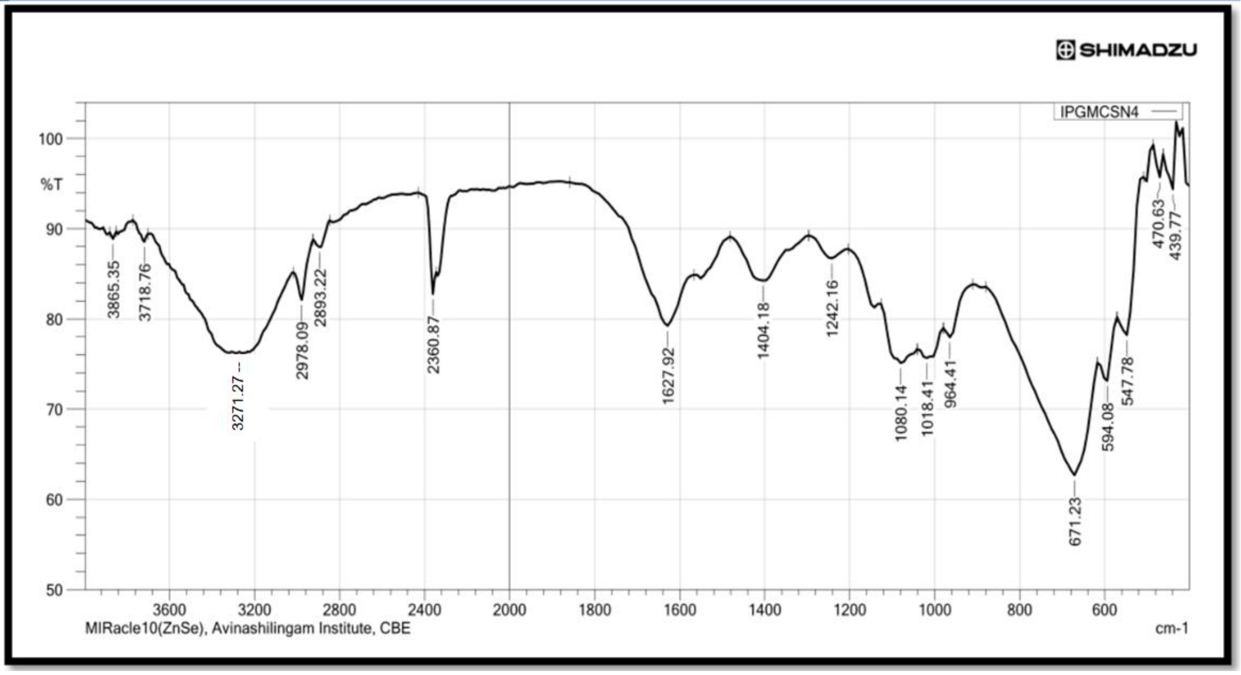


Fig 26 a. FTIR spectra of PGMCSN4

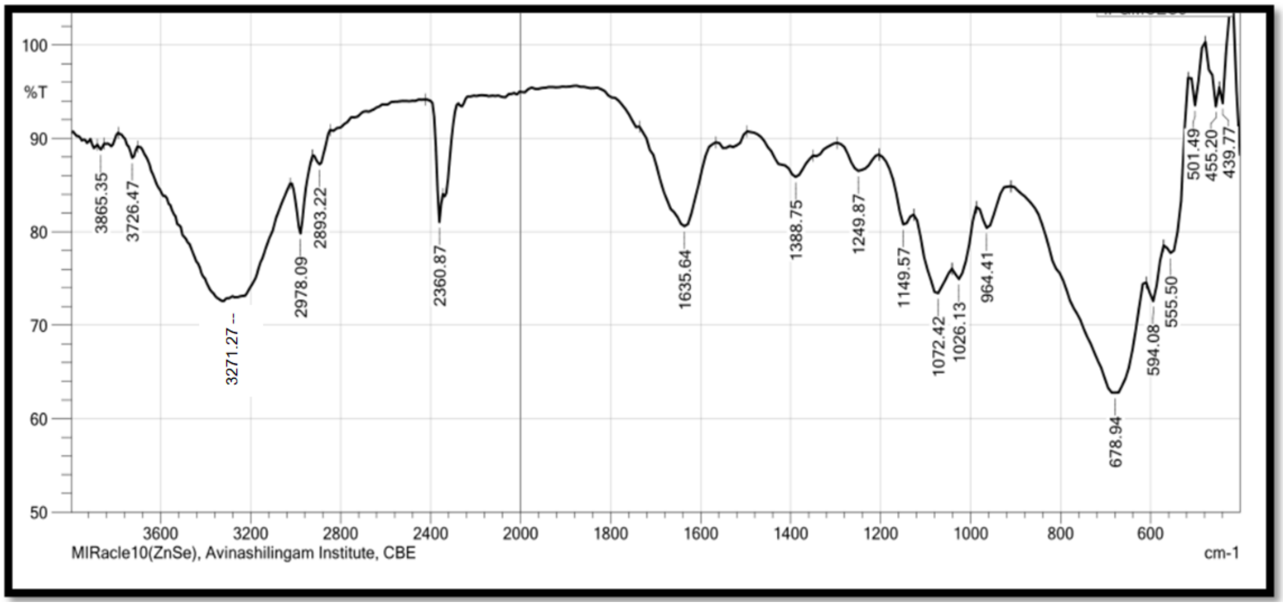


Fig 26 b. FTIR spectra of PGMCSN5

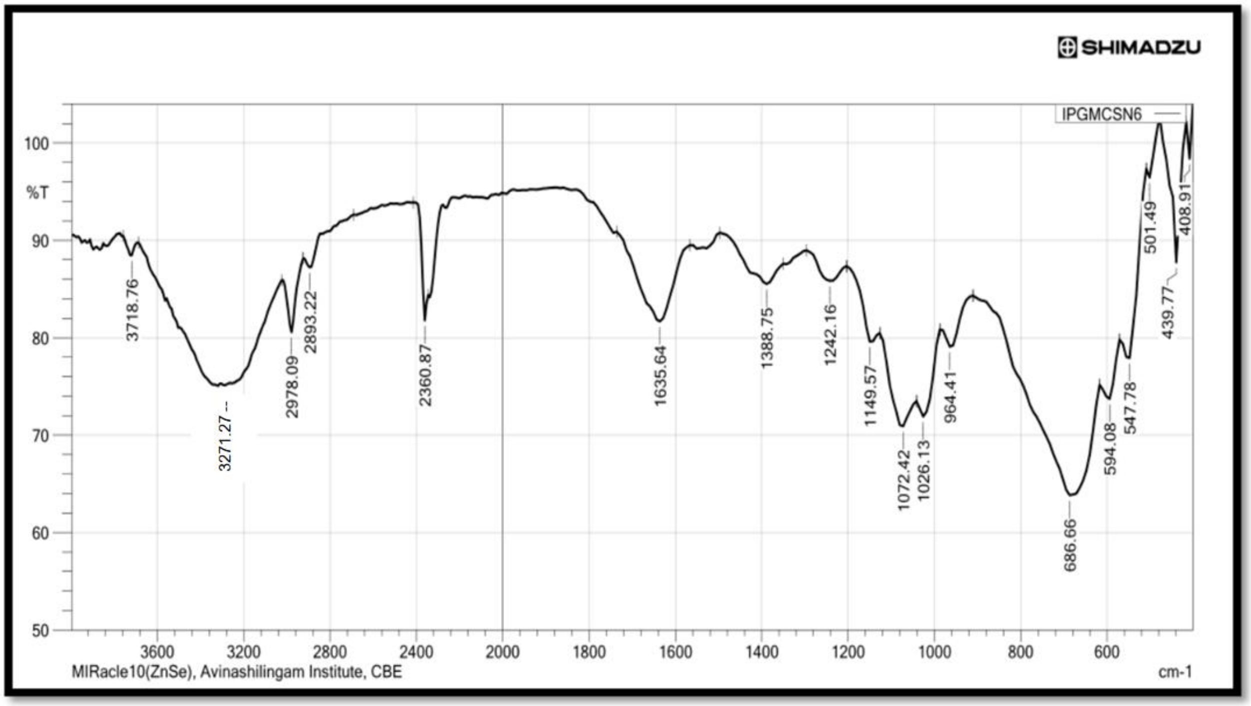


Fig 26 c. FTIR spectra of PGMCSN6

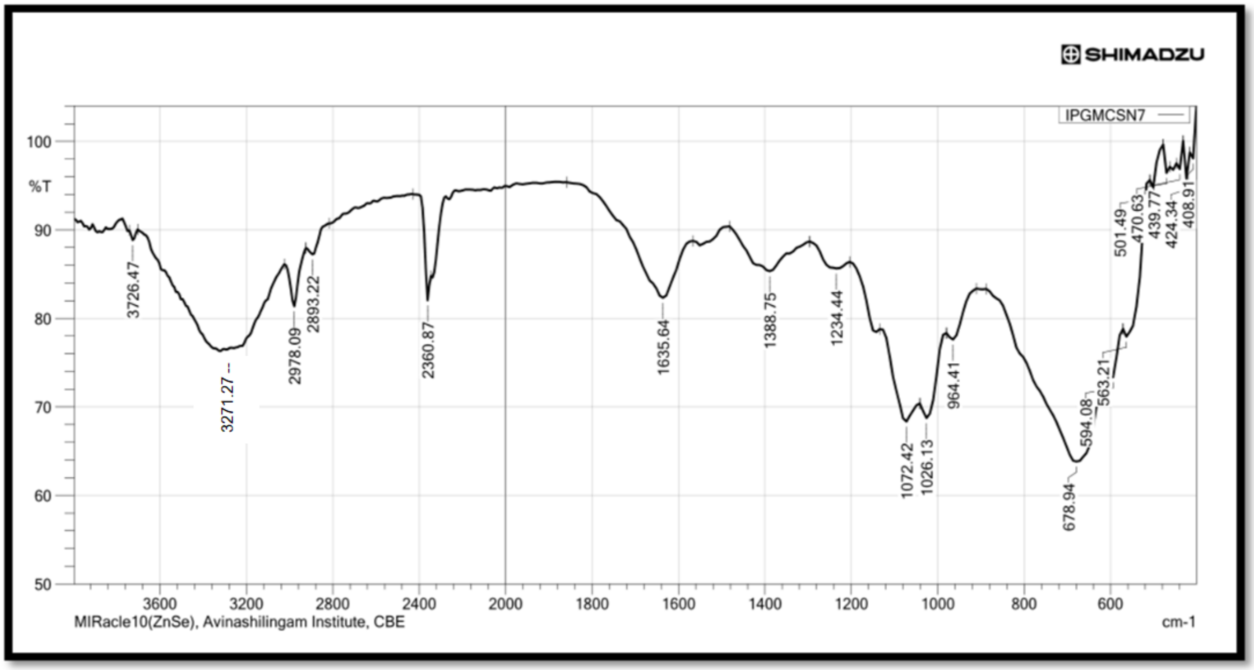


Fig 26 d. FTIR spectra of PGMCSN7

Fig 26. FTIR spectra of Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

4.2 XRD Analysis

Figure 27 shows the XRD spectra of pectin-guar gum blend polymer complexed with various concentrations of $MgCl_2.6H_2O$ and plasticizer ethylene carbonate. For the pure pectin-guar gum, the crystalline region is located at an angle $2\theta = 10, 20, 44.6^{\circ}$ [99]. This type of peak was observed between 20° and 35° in the study of characterization of blend polymer PVA-PVP complexed with ammonium thiocyanate [47]. For PGMCEC4, the peaks were observed at 22° and 29°. For PGMCEC5, the peaks were at 22° and 31°. For PGMCEC6, a broad peak was observed between 15° and 45° and for PGMCEC7, the peak was observed at 23°. An increase in the concentration of ionic salt $MgCl_2$ $.6H_2O$, (45:25:25:5, 40:20:35:5, 35:15:45:5 and 30:10:55:5) decreases the intensity which results in a broad peak. This might be feasible only if there is a complete interaction of salt with the polymer matrix. As a result, conductivity and amorphous nature get increased in the polymer films. The polymer electrolyte of PGMCEC6 exhibits maximum amorphous nature [55].

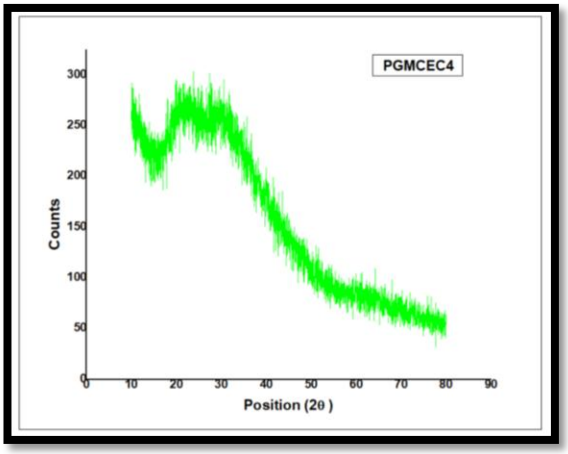


Fig 27 a. XRD spectra of PGMCEC4

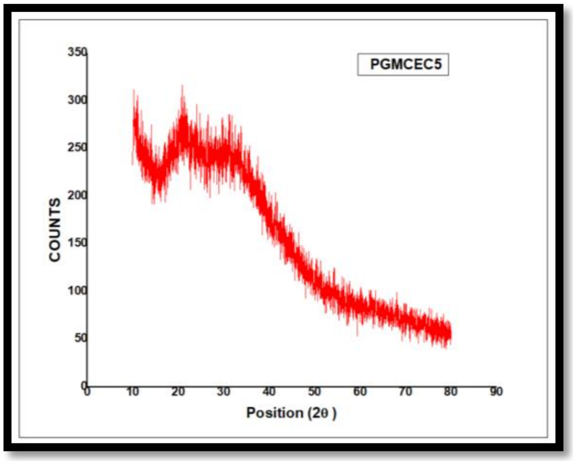


Fig 27 b. XRD spectra of PGMCEC5

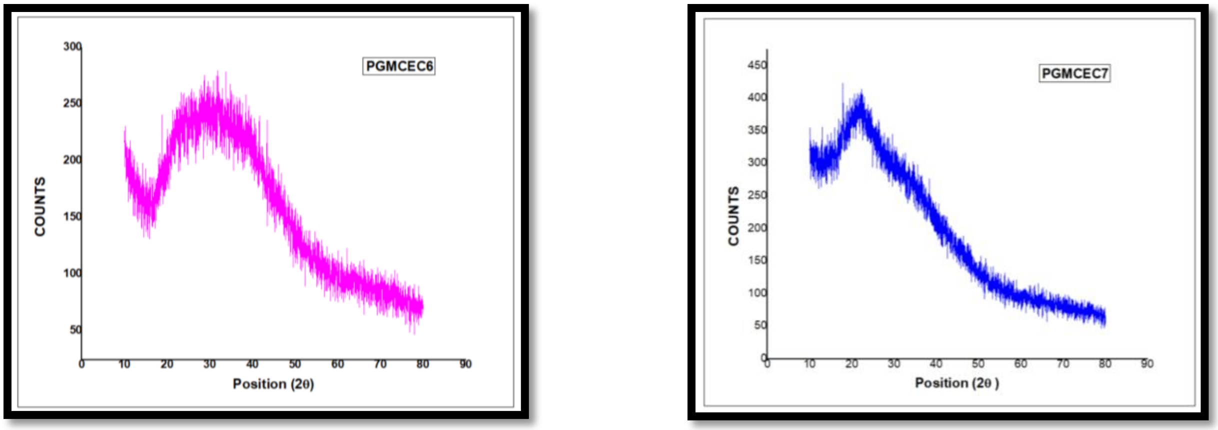


Fig 27 c. XRD spectra of PGMCEC6 **Fig 27 d. XRD spectra of PGMCEC7**

Fig 27. XRD spectra of Pectin-GG-$MgCl_2.6H_2O$-EC blend polymer electrolytes

Figure 28, deals with the XRD patterns of pure pectin-GG blend polymer with various concentrations of $MgCl_2.6H_2O$ and plasticizer succinonitrile. For PGMCSN4, the peak is at 29° and for PGMCSN5, the peak is observed at 33°. For PGMCSN7, the sharp peak is at 23°. The polymer electrolyte of PGMCSN6 exhibits maximum amorphous nature having a broad peak between 15° and 30°.

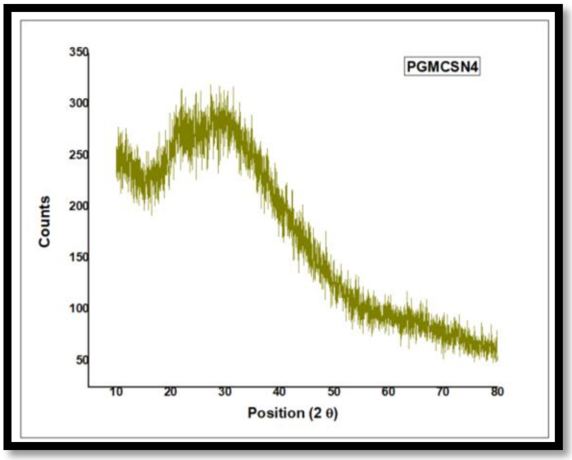


Fig 28 a. XRD spectra of PGMCSN4

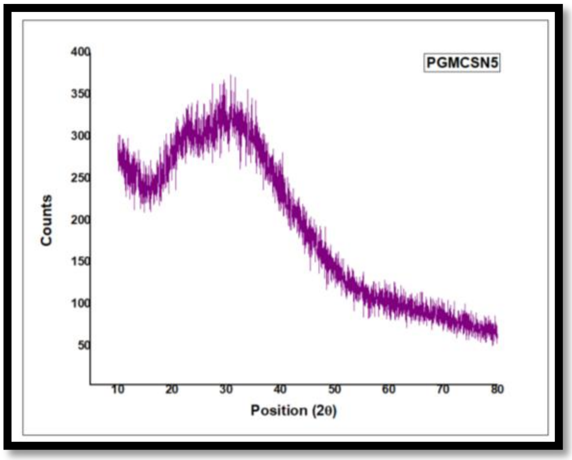
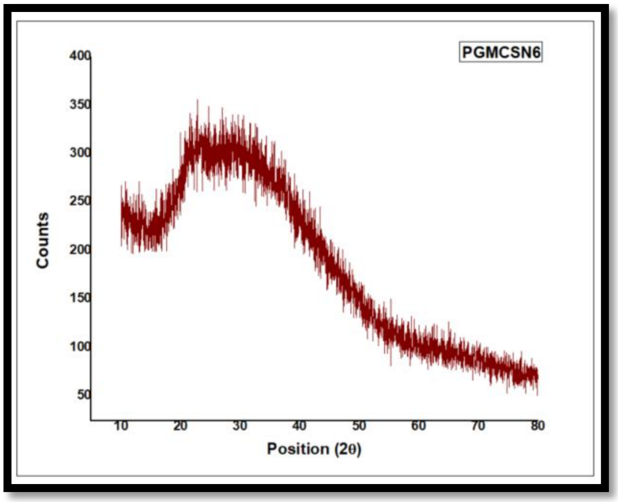


Fig 28 b. XRD spectra of PGMCSN5



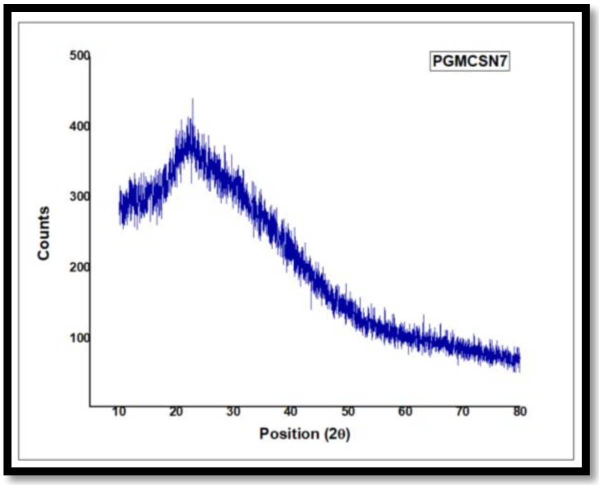


Fig 28 c. XRD spectra of PGMCSN6

Fig 28 d. XRD spectra of PGMCSN7

Fig 28 XRD spectra of Pectin-GG-MgCl$_2$.6H$_2$O-SN blend polymer electrolytes

4.3 TG/DTA Analysis

Figure 29 shows a thermogravimetric curve of different compositions of pectin-guar gum-MgCl$_2$.6H$_2$O-EC blend biopolymer electrolytes and the values are given in Table 7. For pure Pectin-Guar gum, the first weight loss of 18% at 120^{o}C is may be due to the breakdown of trapped moisture content. On further increase in temperature, a major weight loss of 65% was observed at 250^{o}C.

For PGMCEC7 blend polymer electrolytes, the loss of weight with 27% at 117^{o}C takes place in the first zone. The reason is due to the vaporization of residual moisture in the sample. Beyond this zone, a major loss of 81.3% at 321^{o}C was observed. The depletion can be assigned to the breakage of C-O-C bonds in mannose and galactose backbones, results in CO$_2$ expulsion from the guar gum backbone [98]. Similar weight loss was observed in the second zone for PGMCEC6, PGMCEC5, and PGMCEC4 blend polymer electrolytes such as 70, 84, 81.5 % at 293^{o}C, 305^{o}C, 299.5^{o}C respectively due to the breakage of C-O-C bonds. The residue of 10.3% was left for PGMCEC4. It was confirmed from TGA results that on adding ionic salt and plasticizer have significantly affected the thermal stability of polymer film [100].

Figure 30 shows the TG curve of various compositions of pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes and the values are given in Table 8. For PGMCSN7 blend polymer electrolytes, the loss of weight with 52.7 % at 140 °C takes place in the first zone. The reason is due to the vaporization of moisture in the sample. Beyond this zone, a major loss of 51.5 % around 150-350°C was observed. The depletion can be assigned to the breakage of C-O-C bonds in mannose and galactose backbones, results in CO_2 expulsion from the guar gum backbone. Similar weight loss was observed in the second zone for PGMCSN6, PGMCSN5, and PGMCSN4 blend polymer electrolytes such as 92.5, 98.6 and 72.7 % at 450°C, 255°C, 550°C respectively due to the breakage of C-O-C bonds.

Table 7. Percentage weight loss of Pectin-GG-$MgCl_2.6H_2O$-EC polymer electrolytes

S. No	Code	Composition of Pectin-GG-$MgCl_2.6H_2O$-EC polymer electrolytes (M wt %)	Total weight loss (%)
1	Pure Pectin/GG	20%Pectin/ 20%GG	98.9
2	PGMCEC7	45:25:25:5	80.3
3	PGMCEC6	40:20:35:5	86.4
4	PGMCEC5	35:15:45:5	89.1
5	PGMCEC4	30:10:55:5	88.9

Table 8. Percentage weight loss of Pectin-GG-$MgCl_2.6H_2O$-SN polymer electrolytes

S. No	Code	Composition of Pectin-GG-$MgCl_2.6H_2O$-SN polymer electrolytes (M wt %)	Total weight loss (%)
1	Pure Pectin/GG	20%Pectin/ 20%GG	98.9
2	PGMCSN7	45:25:25:5	75.3
3	PGMCSN6	40:20:35:5	92.5
4	PGMCSN5	35:15:45:5	98.6
5	PGMCSN4	30:10:55:5	72.7

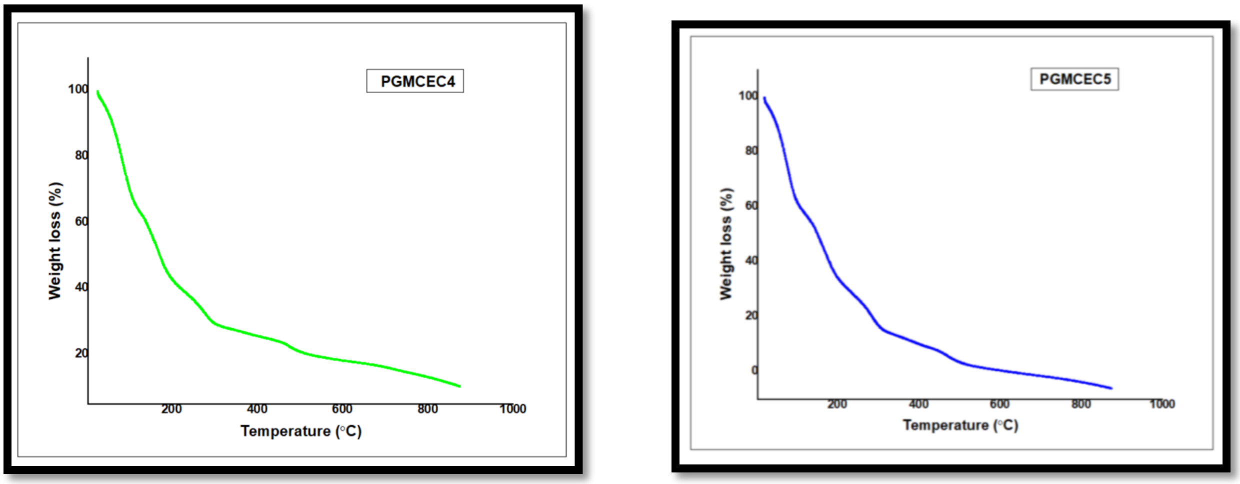


Fig 29 a. TG curve of PGMCEC4

Fig 29 b. TG curve of PGMCEC5

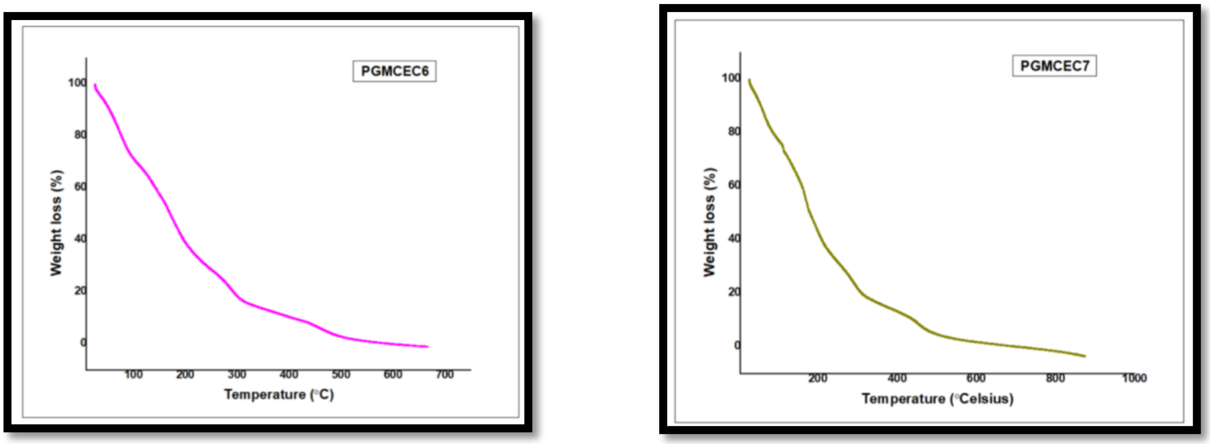


Fig 29 c. TG curve of PGMCEC6

Fig 29 d. TG curve of PGMCEC7

Fig 29. TG curve of Pectin-GG-$MgCl_2.6H_2O$-EC blend polymer electrolytes

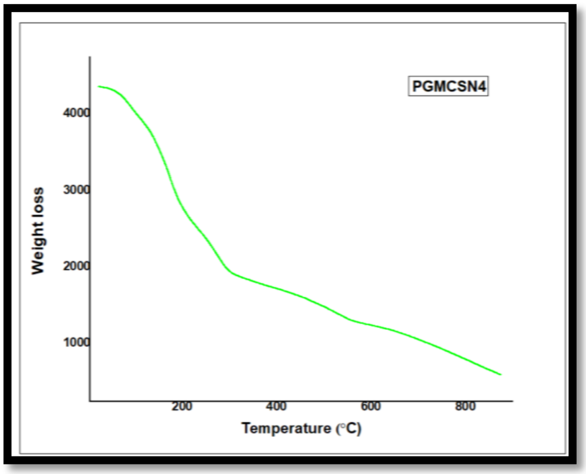


Fig 30 a. TG curve of PGMCSN4

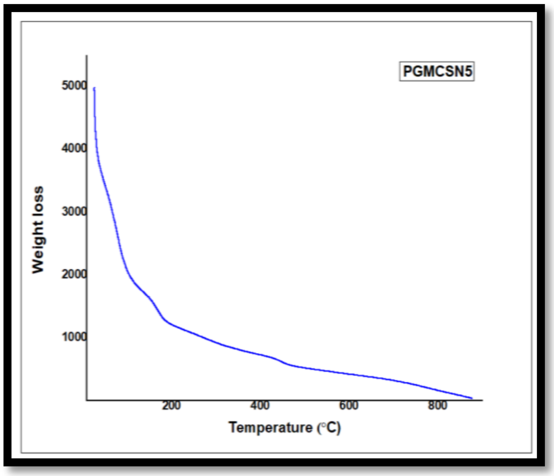


Fig 30 b. TG curve of PGMCSN5

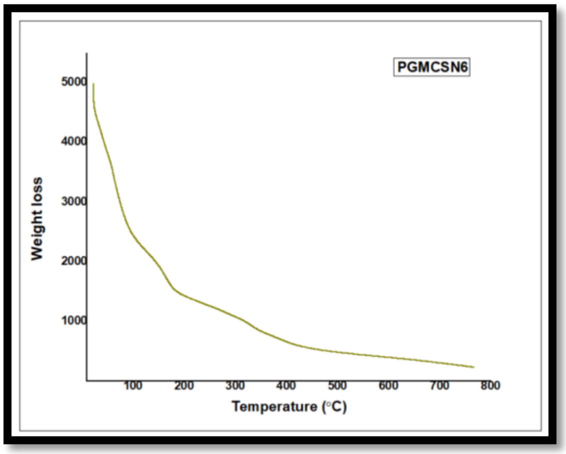


Fig 30 c. TG curve of PGMCSN6

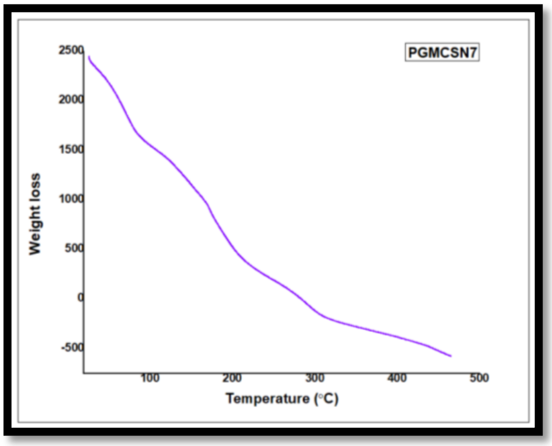
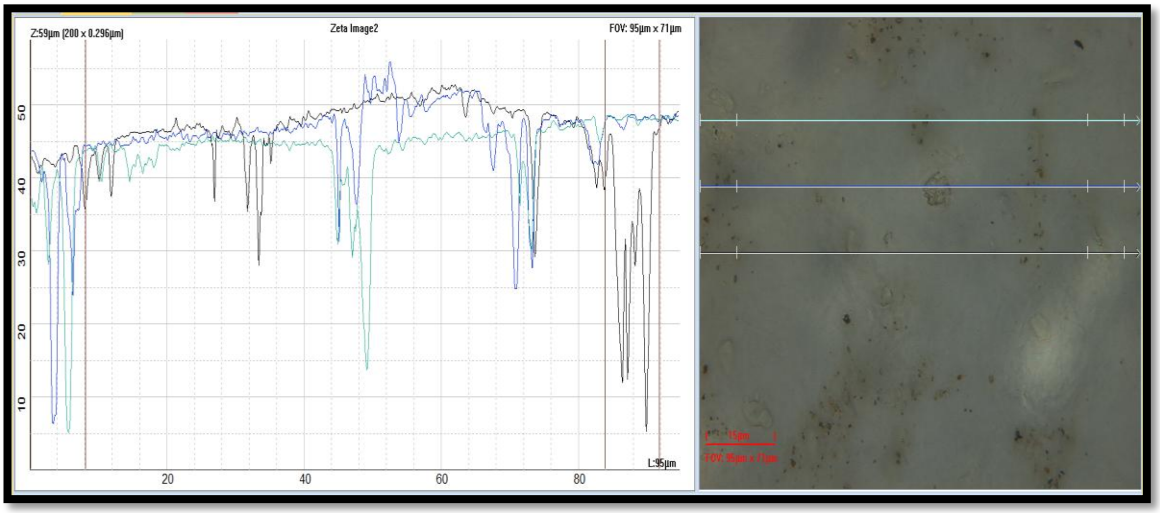


Fig 30 d. TG curve of PGMCSN7

Fig 30. TG curve of Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

4.4 3-D Laser Profilometry Analysis

Profilometry is the measurement of surface topography. It is used to measure surface thickness, flatness, texture, thin film coating stress, surface curvature, etc. The morphology of the film surface was studied using 3-D Laser Profilometer. An increase in the roughness of the surface of the film, the average roughness (Ra) value increases. The topographical representation of surface features and 3D zeta images of the polymer electrolytes were shown in fig 31 a (PGMCEC4), 31 b (PGMCEC5), 31 c (PGMCEC6), 31 d (PGMCEC7) and 32 a (PGMCSN4), 32 b (PGMCSN5), 32 c (PGMCSN6) and 32 d (PGMCSN7). The Ra values for the various concentrations of the blend biopolymer films are given in Tables 9 and 10.



Topographical representation of surface features of PGMCEC4

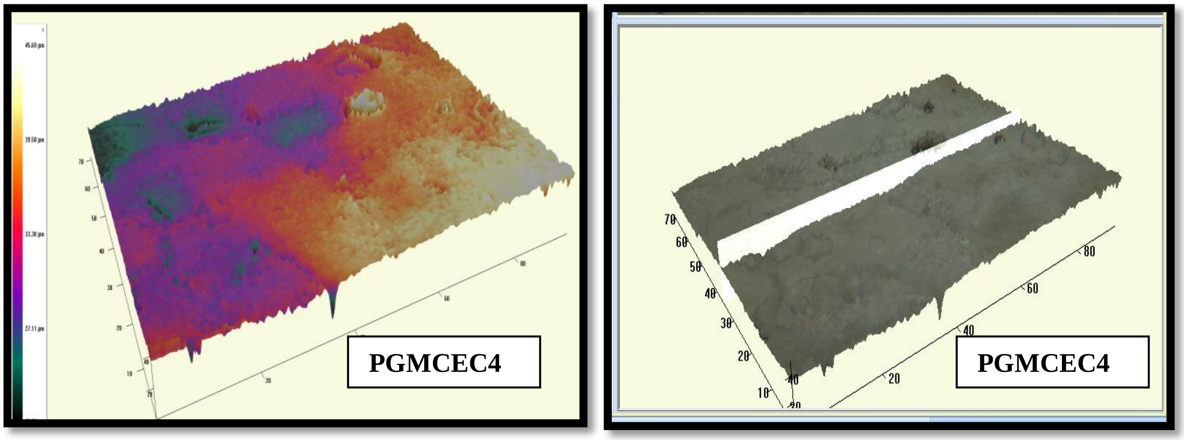
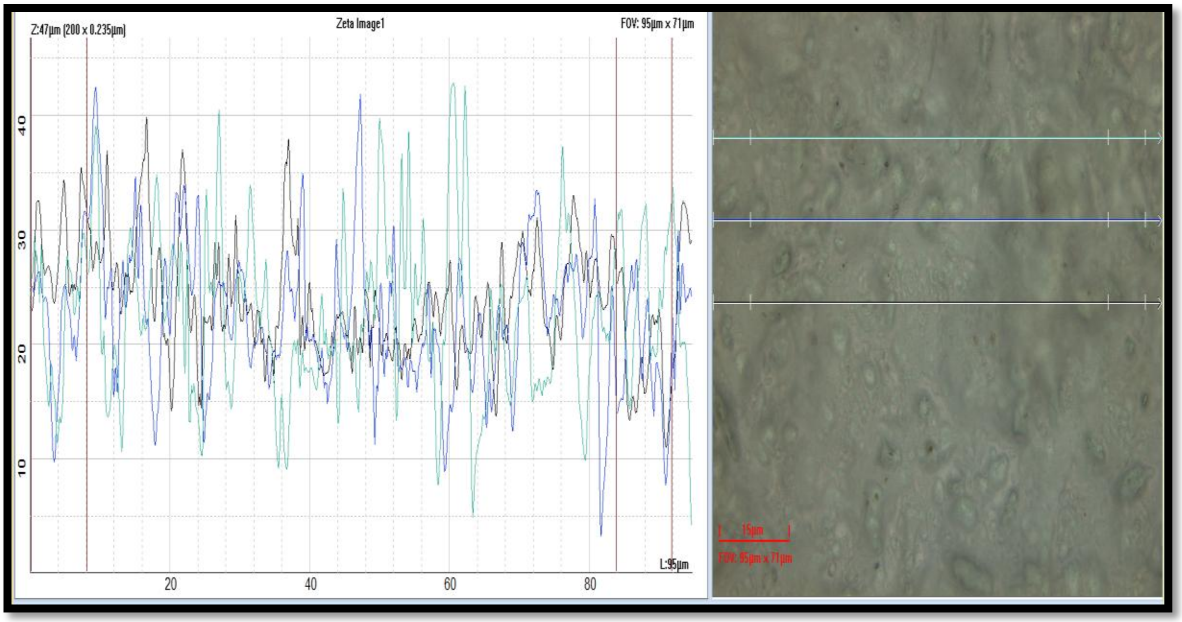


Fig 31 a. Zeta images of PGMCEC4



Topographical representation of surface features of PGMCEC5

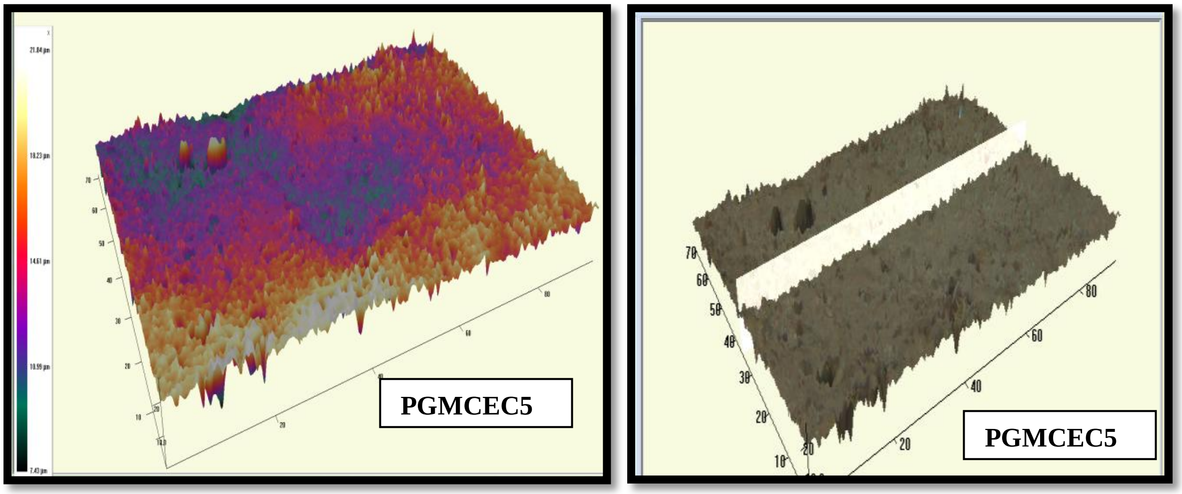
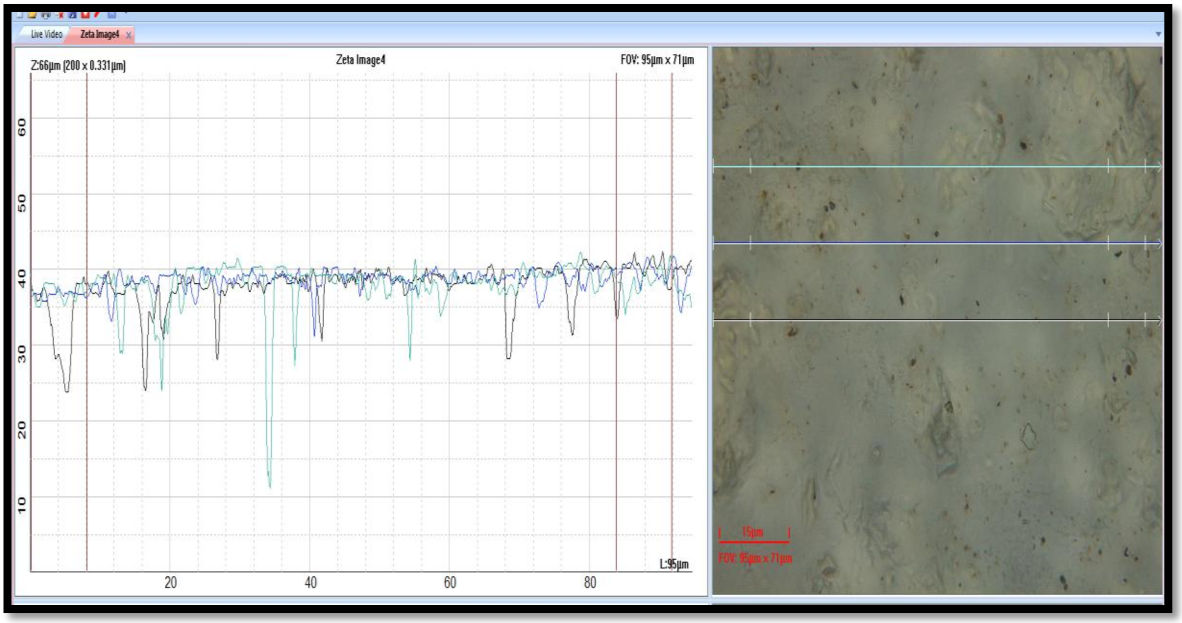


Fig 31 b. Zeta images of PGMCEC5



Topographical representation of surface features of PGMCEC6

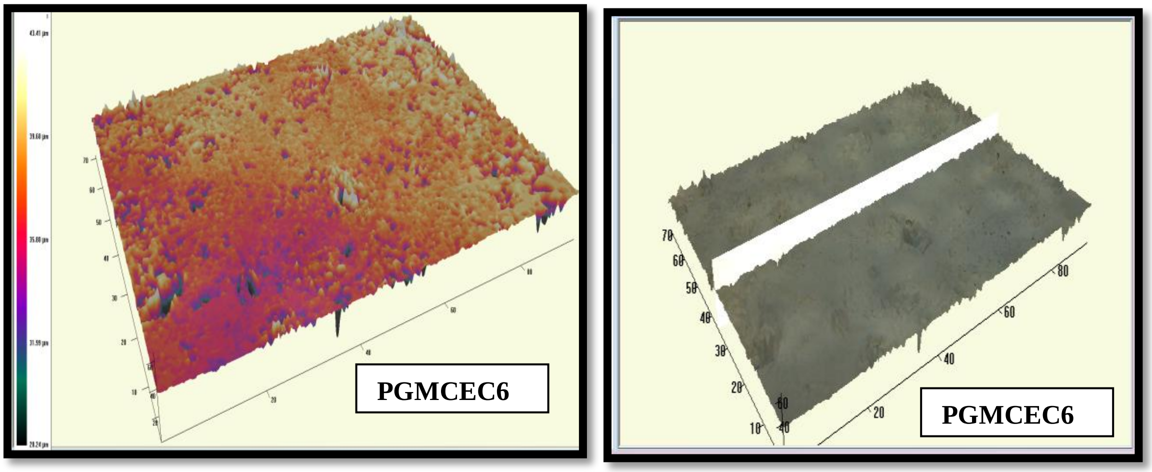
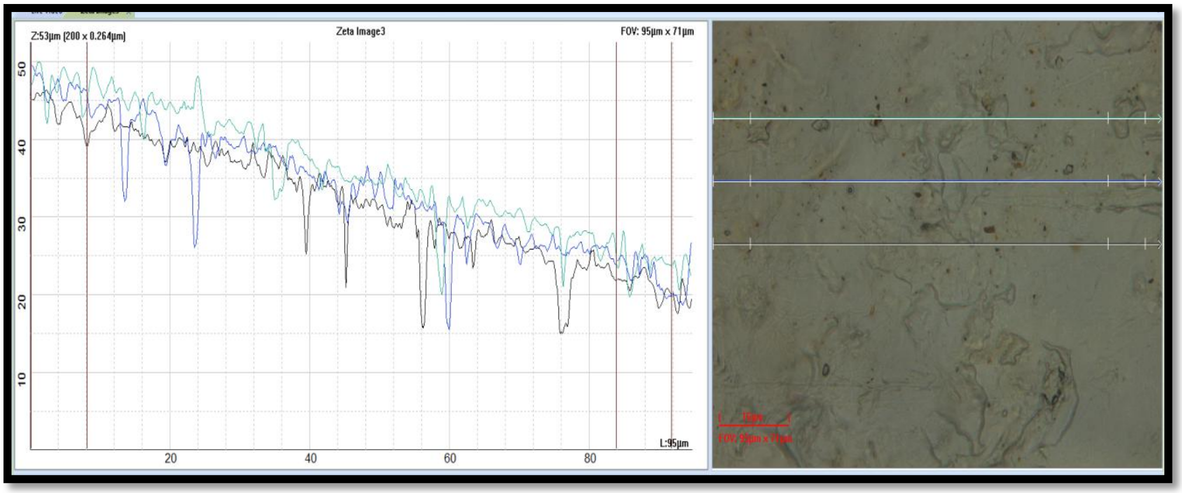


Fig 31 c. Zeta 3D images of PGMCEC6



Topographical representation of surface features of PGMCEC7

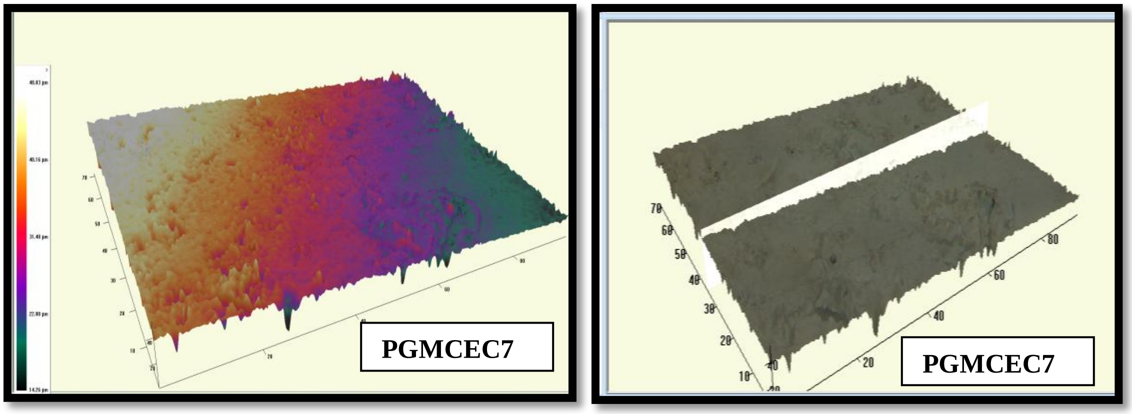
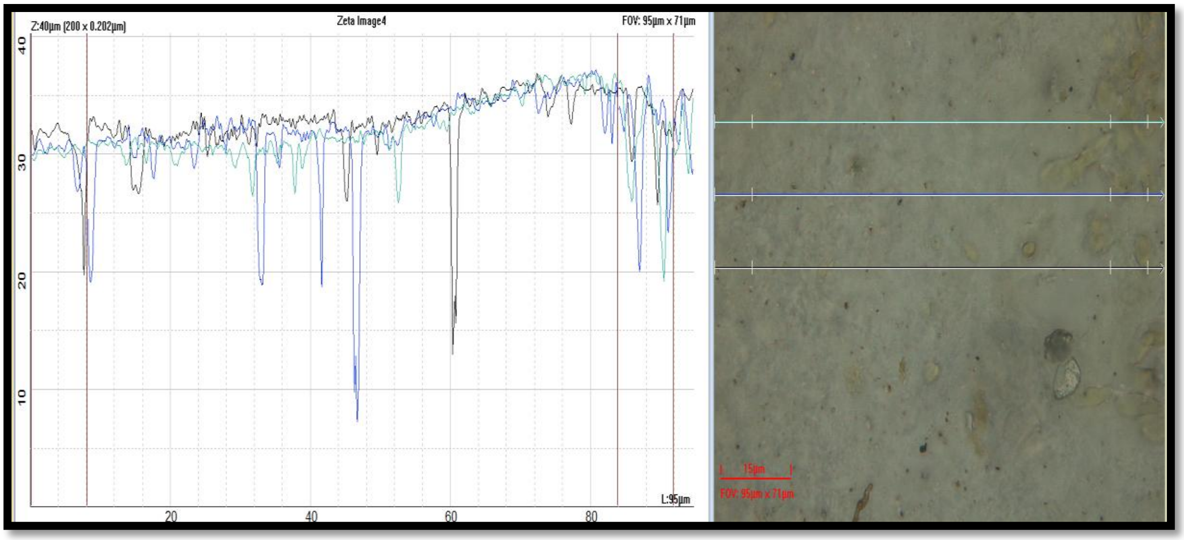


Fig 31 d. Zeta 3D images of PGMCEC7

Fig 31. Zeta 3D images of Pectin-GG-$MgCl_2$-EC blend polymer electrolytes

Table 9. Average roughness values of Pectin-GG-$MgCl_2.6H_2O$-EC blend polymer electrolytes

Code	Composition of Pectin-GG-$MgCl_2.6H_2O$-EC (M wt %)	Average roughness (Ra) values (%)
PGMCEC7	45:25:25:5	2.88
PGMCEC6	40:20:35:5	26.3
PGMCEC5	35:15:45:5	11.8
PGMCEC4	30:10:55:5	22.7



Topographical representation of surface features of PGMCSN4

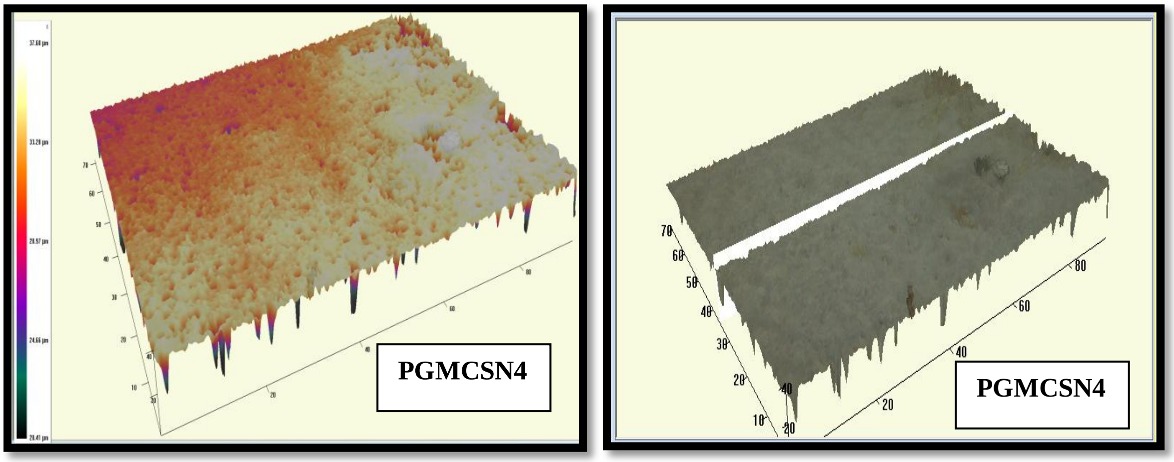
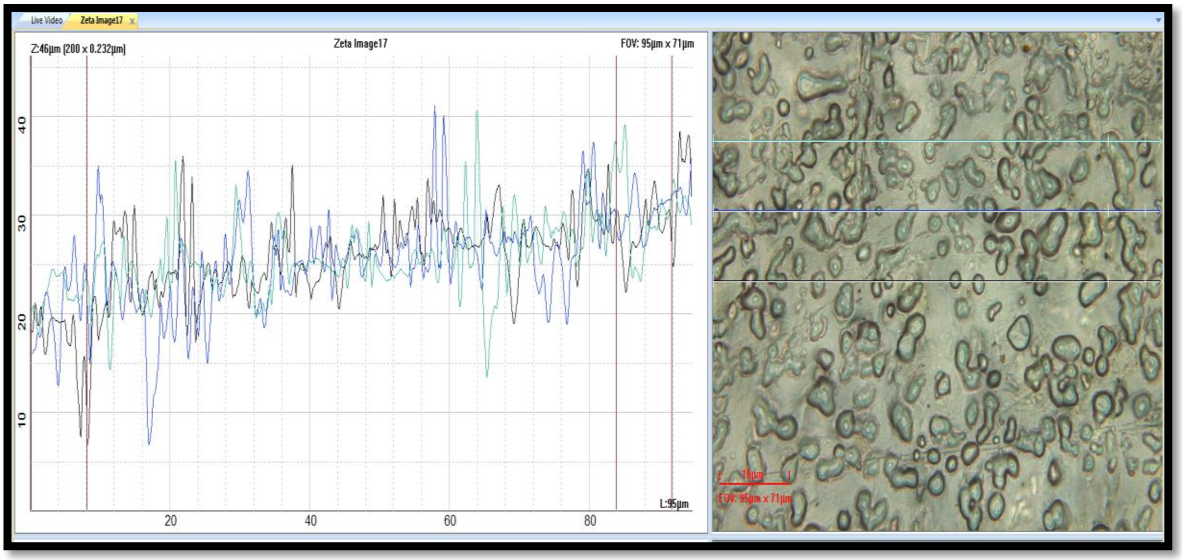


Fig 32 a. Zeta 3D images of PGMCSN4



Topographical representation of surface features of PGMCSN5

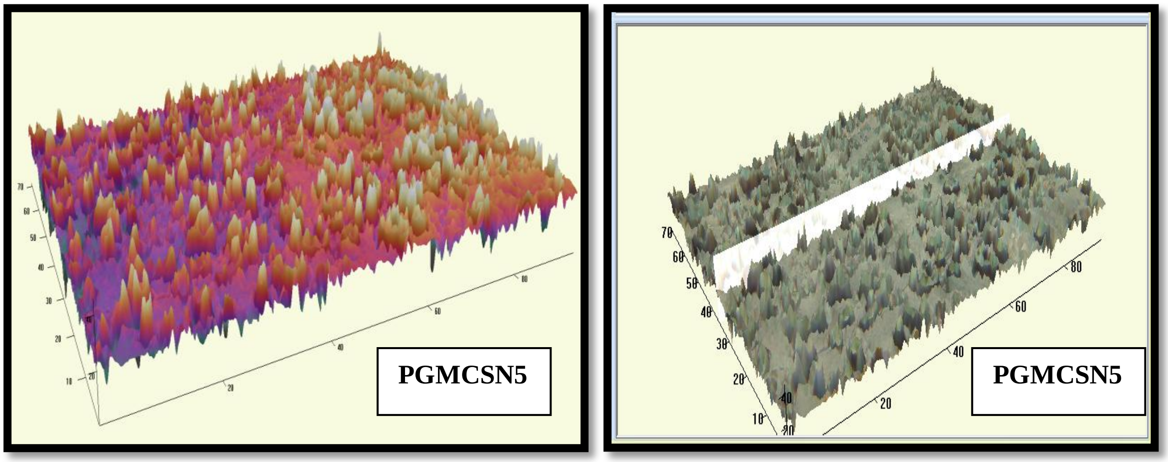
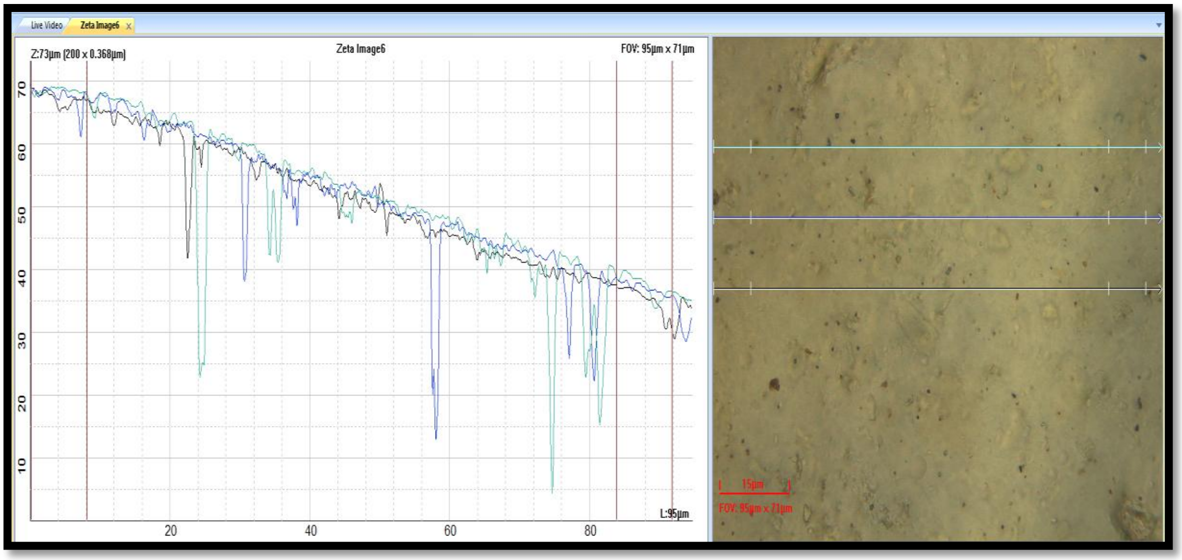


Fig 32 b. Zeta 3D images of PGMCSN5



Topographical representation of surface features of PGMCSN6

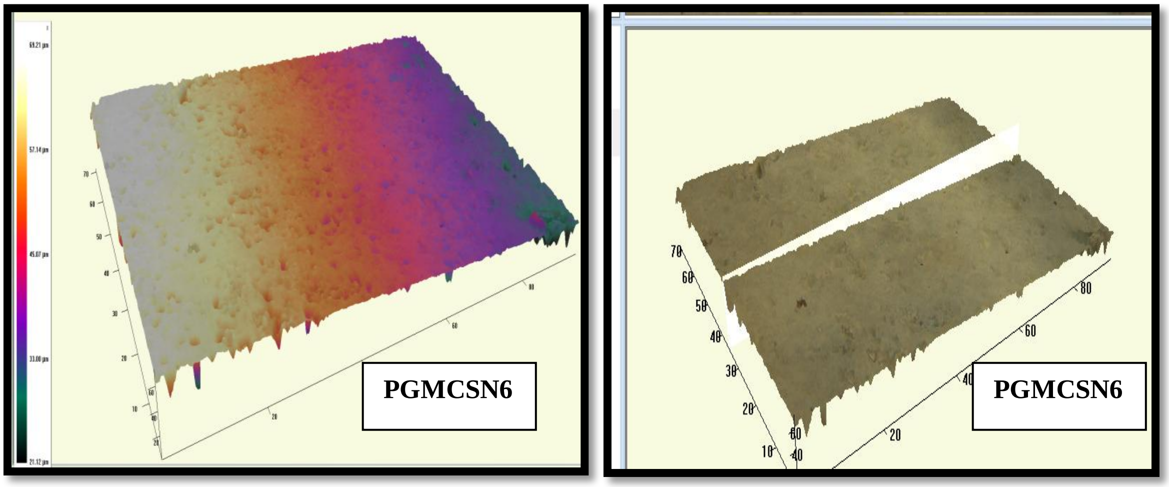
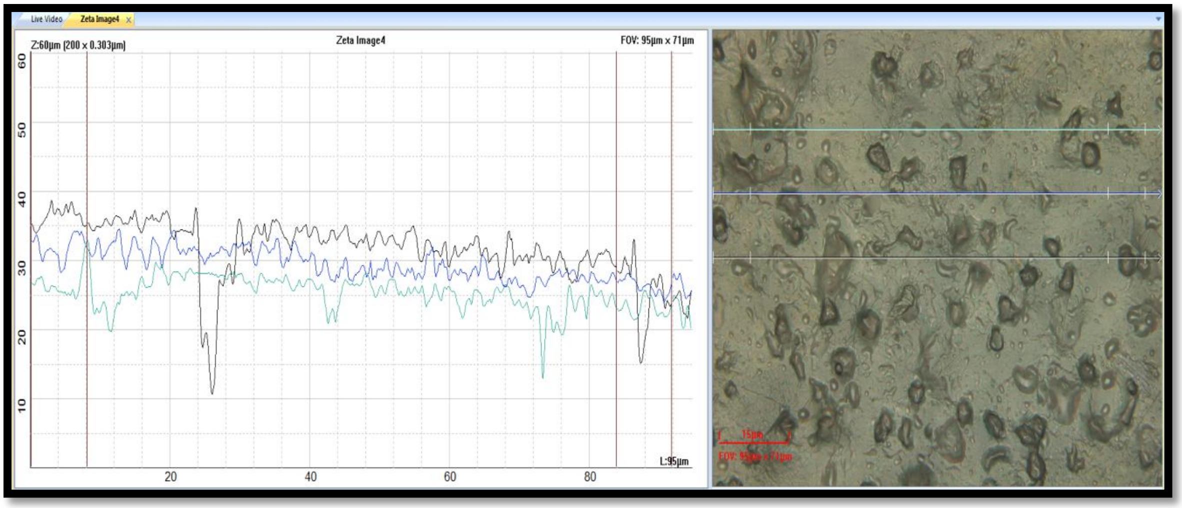


Fig 32 c. Zeta 3D images of PGMCSN6



Topographical representation of surface features of PGMCSN7

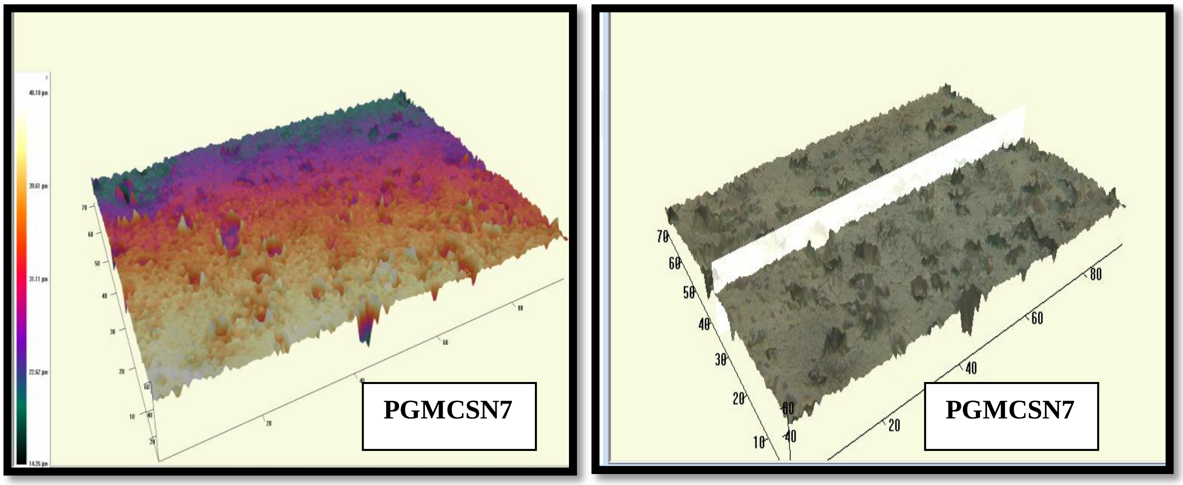


Fig 32 d. Zeta 3D images of PGMCSN7

Fig 32. Zeta 3D images of Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

Table 10. Average roughness values of Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

Code	Composition of Pectin-GG-$MgCl_2.6H_2O$-SN (M wt %)	Average roughness (Ra) values (%)
PGMCSN7	45:25:25:5	5.00
PGMCSN6	40:20:35:5	9.37
PGMCSN5	35:15:45:5	7.03
PGMCSN4	30:10:55:5	15.7

Among all four biopolymer thin films of Pectin-GG-$MgCl_2$-EC, PGMCEC7 and PGMCEC5 exhibit lesser average roughness values (R_a) of 2.88% and 11.8% respectively. Hence, the above two compositions of biopolymer films were comparatively smoother than the other two compositions PGMCEC6 and PGMCEC4 which exhibit a higher R_a values of 26.3% and 22.7% respectively.

In Pectin-GG-$MgCl_2$-SN, PGMCSN7 and PGMCSN5 have R_a values of 5.00% and 7.03% respectively. These two films were smoother than PGMCSN6 and PGMCSN4 having R_a values of 9.37% and 15.7% respectively.

4.5 Impedance studies:

The conductivity values for various compositions of ionic salt $MgCl_2.6H_2O$ doped with blend polymer Pectin-Guar Gum at room temperature (303K) with different plasticizers EC/SN are given in Tables 11 and 12 respectively.

Table 11. Conductivity values of Pectin/Guar gum/$MgCl_2.6H_2O$/EC blend polymer electrolytes

Code	Composition	Conductivity (S/cm)
PGMCEC7	45:25:25:5	7.87×10^{-5}
PGMCEC6	40:20:35:5	2.71×10^{-3}
PGMCEC5	35:15:45:5	**3.51×10^{-3}**
PGMCEC4	30:10:55:5	9.225×10^{-4}

Table 12. Conductivity values of Pectin/ Guar gum /$MgCl_2.6H_2O$/ SN blend polymer electrolytes

Code	Composition	Conductivity (S/cm)
PGMCSN7	45:25:25:5	2.28×10^{-4}
PGMCSN6	40:20:35:5	3.15×10^{-6}
PGMCSN5	35:15:45:5	6.13×10^{-5}
PGMCSN4	30:10:55:5	**2.63×10^{-3}**

Nyquist plots for Pectin-Guar Gum doped with various concentrations of $MgCl_2.6H_2O$ with different plasticizers EC/SN at ambient temperature (303K) were shown in fig 33 (a-d) and 34 (a-d) respectively. It is evident from the table 10, that the film containing 35:15:45:5 M wt% of PGMCEC5 exhibits higher conductivity of 3.51×10^{-3} S/cm. On further addition of salt, the conductivity is found to be decreased for PGMCEC4 (9.225×10^{-4} S/cm). This may be due to the aggregate formation which is blocking the ion motion [101]. From the table 11, it is clear that the film PGMCSN4 containing 30:10:55:5 M wt% exhibits higher conductivity of 2.63×10^{-3} S/cm.

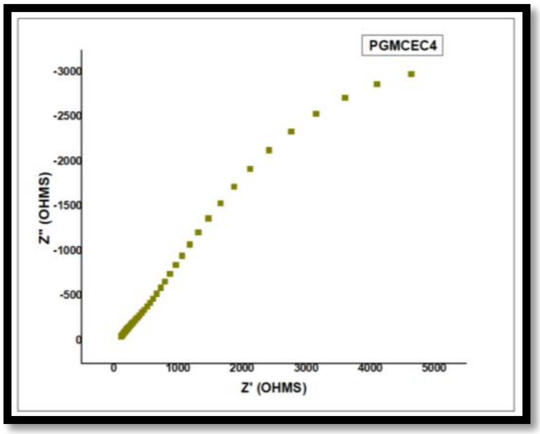


Fig 33 a. Nyquist plot of PGMCEC4

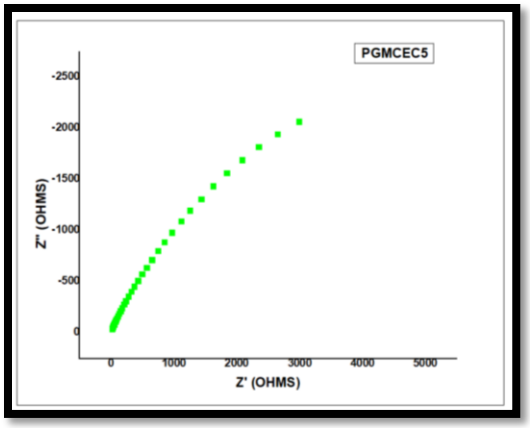


Fig 33 b. Nyquist plot of PGMCEC5

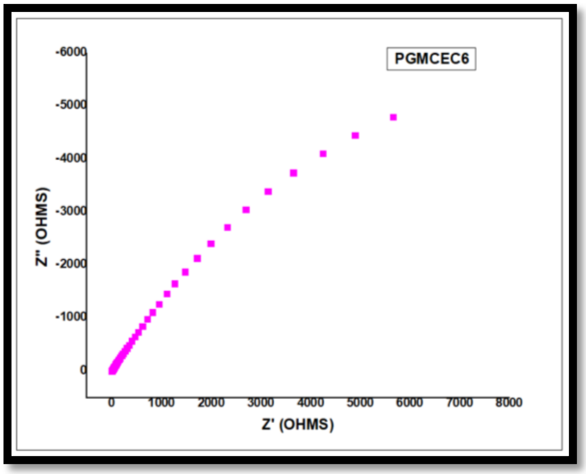


Fig 33 c. Nyquist plot of PGMCEC6

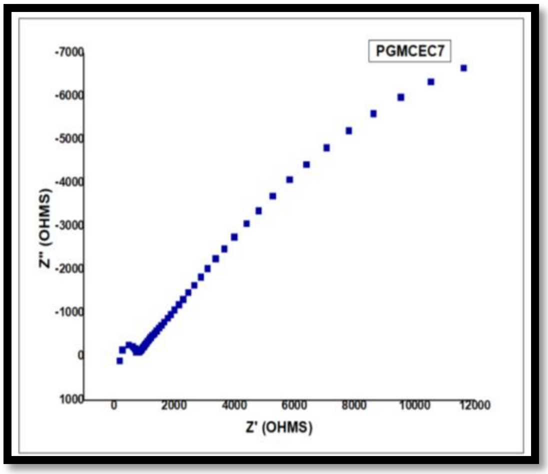


Fig 33 d. Nyquist plot of PGMCEC7

Fig 33. Nyquist plot for Pectin-GG-$MgCl_2.6H_2O$-EC blend polymer electrolytes

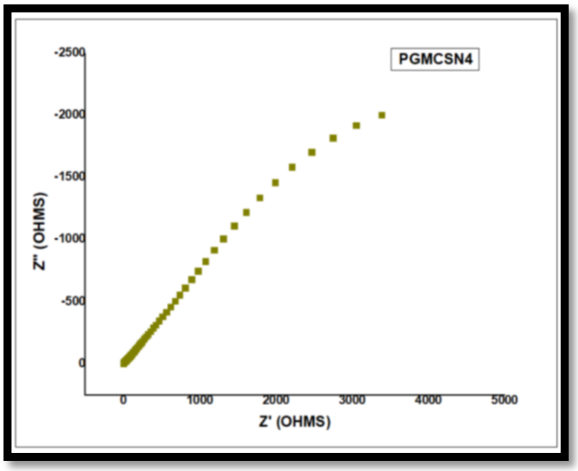


Fig 34 a. Nyquist plot of PGMCSN4

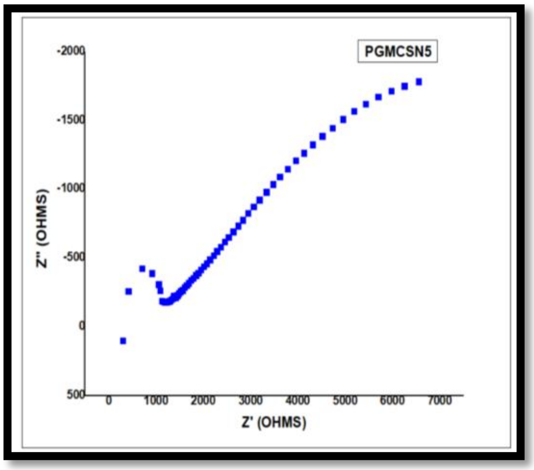


Fig 34 b. Nyquist plot of PGMCSN5

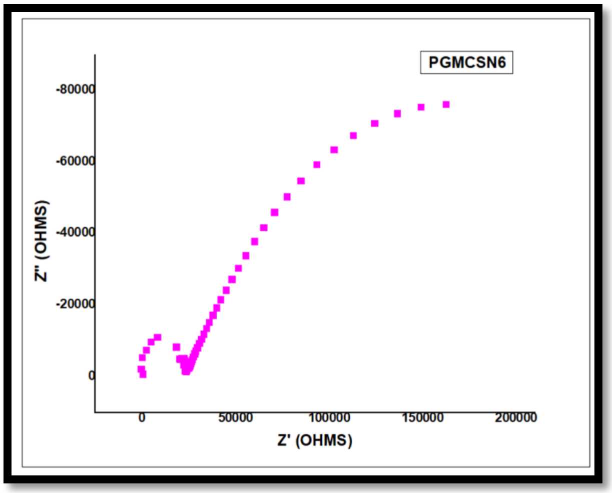


Fig 34 c. Nyquist plot of PGMCSN6

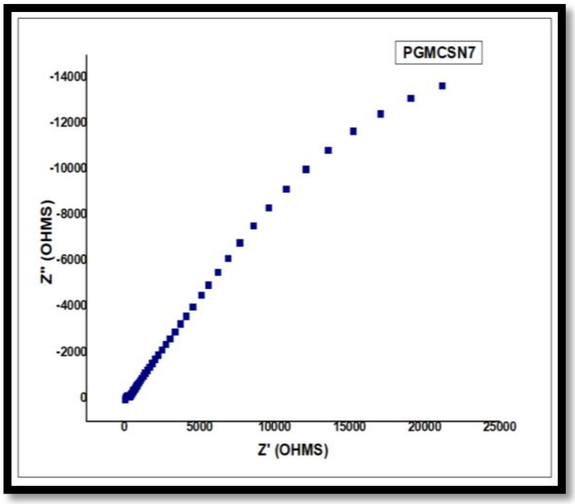


Fig 34 d. Nyquist plot of PGMCSN7

Fig 34. Nyquist plot for Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

4.6 Transport number measurement

The transport number was measured using chronoamperometry technique and the figure 35 (a-d) shows the transport number curve for Pectin/Guar gum/$MgCl_2.6H_2O$/EC and 36 (a-d) shows the transport number curve for Pectin/Guar gum/$MgCl_2.6H_2O$/SN. The transport number values for Pectin/Guar gum/$MgCl_2.6H_2O$/EC and Pectin/Guar gum/$MgCl_2.6H_2O$/SN are given in the Tables 13 and 14 respectively.

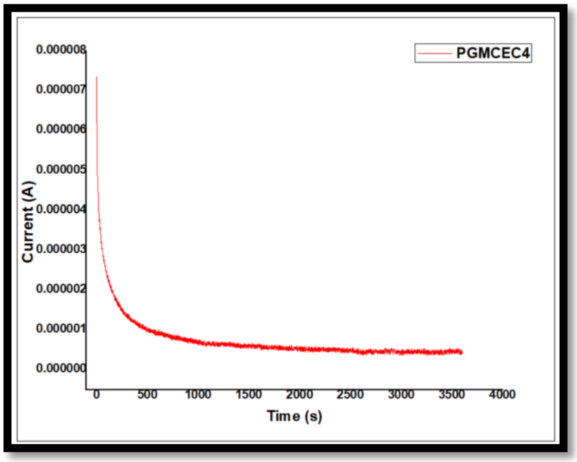


Fig 35 a. Transport number curve of PGMCEC4

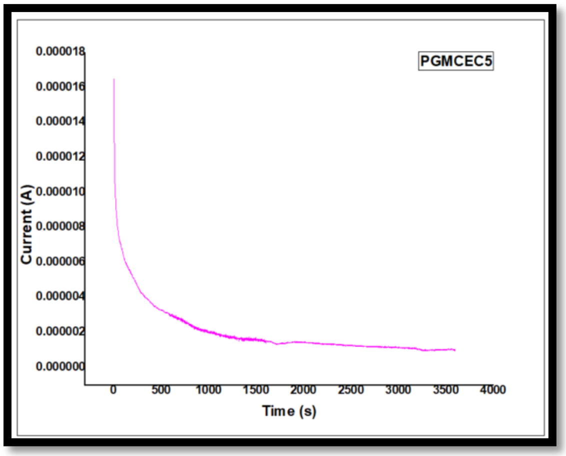


Fig 35 b. Transport number curve of PGMCEC5

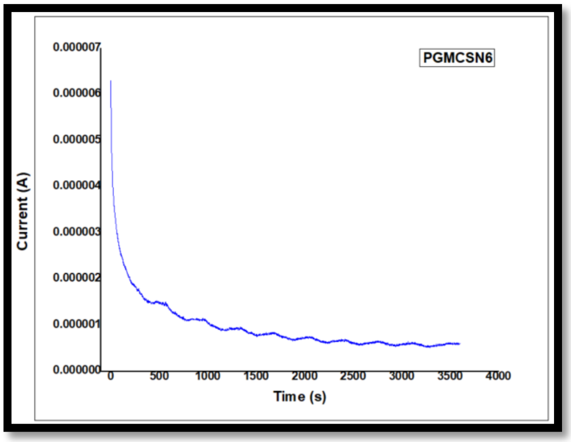


Fig 35 c. Transport number curve of PGMCEC6

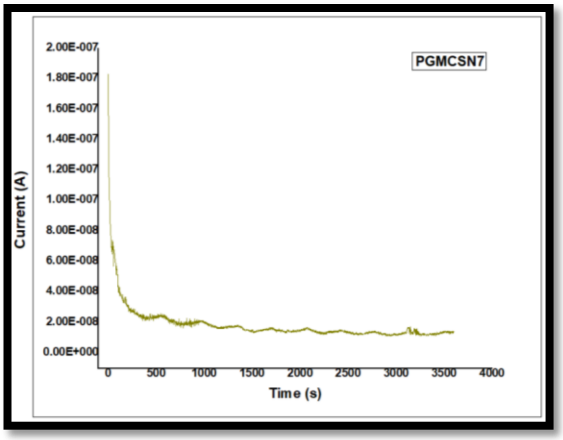


Fig 35 d. Transport number curve of PGMCEC7

Fig 35.Transport number curve for Pectin-GG-$MgCl_2.6H_2O$-EC blend polymer electrolytes

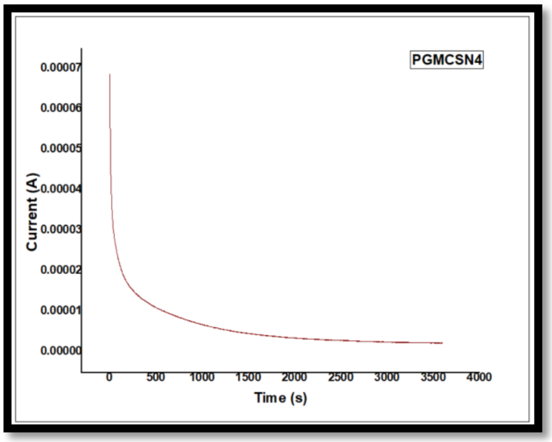


Fig 36 a. Transport number curve of PGMCSN4

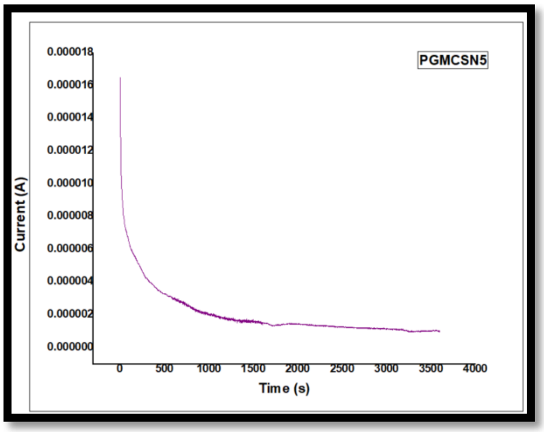


Fig 36 d. Transport number curve of PGMCSN5

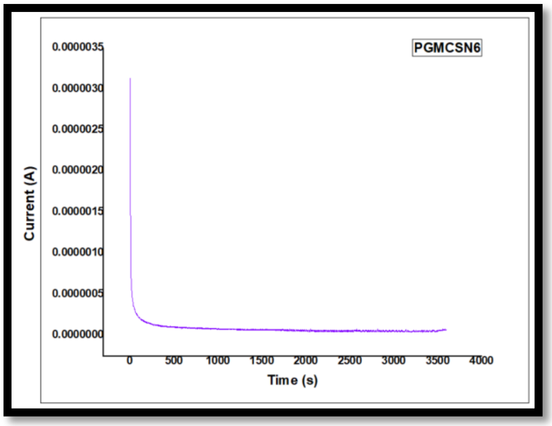


Fig 36 c. Transport number curve of PGMCSN6

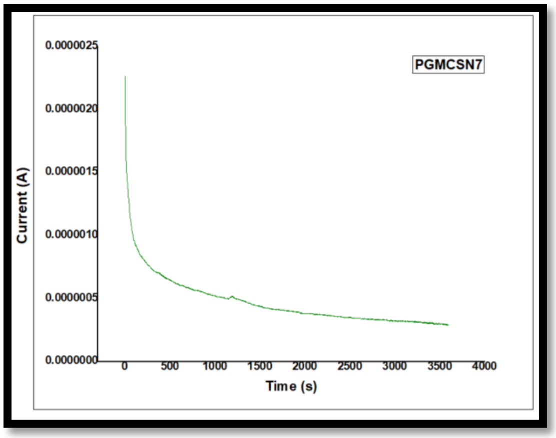


Fig 36 d. Transport number curve of PGMCSN7

Fig 36.Transport number curve for Pectin-GG-$MgCl_2.6H_2O$-SN blend polymer electrolytes

Table 13. Transport number for Pectin/Guar gum/$MgCl_2.6H_2O$/EC blend polymer electrolytes

Code	**Composition**	**Transport number(t_{ion})**
PGMCEC7	45:25:25:5	0.78
PGMCEC6	40:20:35:5	0.65
PGMCEC5	35:15:45:5	0.94
PGMCEC4	30:10:55:5	0.83

Table 14. Transport number for Pectin/Guar gum/$MgCl_2.6H_2O$/SN blend polymer electrolytes

Code	**Composition**	**Transport number(t_{ion})**
PGMCSN7	45:25:25:5	0.87
PGMCSN6	40:20:35:5	0.98
PGMCSN5	35:15:45:5	0.94
PGMCSN4	30:10:55:5	0.96

From the table 13, it is obvious that the transference number (t_{ion}) for the maximum conductivity polymer electrolyte PGMCEC5 (35:15:45:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/EC) was found to be 0.94. This is because of the reason that the ionic conductivity is directly proportional to the transport number.

From the table 14, it is evident that the transference number was found to be maximum (0.98) for the polymer electrolyte PGMCSN6 (40:20:35:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/SN). Generally, ionic conductivity depends on the concentration of carrier ions as well as mobility of ions. But the conductivity was found to be higher for PGMCSN4 (2.63×10^{-3} S/cm) when compared to PGMCSN6 (3.15×10^{-6} S/cm) polymer electrolyte. Therefore, the interaction between the cation Mg^{2+} and the anion of the plasticizer might be higher in the case of PGMCSN6 **[102]**. This may be the reason for the maximum transport number of PGMCSN6 even though the ionic conductivity of PGMCSN6 is lesser than PGMCSN4.

SUMMARY AND CONCLUSION

Chapter V

Summary and Conclusion

SUMMARY

The main features of the present study on the preparation of solid biopolymer electrolytes are summarized below:

- A series of transparent thin films (Pectin/Guar Gum/Magnesium chloride/Ethylene carbonate, Pectin/Guar Gum/Magnesium chloride/Succinonitrile, Pectin/Guar Gum/Magnesium sulphate/Ethylene carbonate and Pectin/Guar Gum/Magnesium sulphate/Succinonitrile) of solid biopolymer electrolytes have been prepared by solution casting technique.
- Out of four electrolytes prepared, the two electrolytes Pectin/Guar Gum/Magnesium sulphate/Ethylene carbonate and Pectin/Guar Gum/Magnesium sulphate/Succinonitrile were not good enough for the characterization, because of the opaque and rigid nature of the films of pectin/guar gum prepared with the magnesium sulphate salts. Hence, further characterizations for these two polymer electrolytes were not carried out.
- The results from FTIR study show that complexation has occurred in the prepared polymer electrolyte systems of Pectin/Guar gum/$MgCl_2.6H_2O$/EC and Pectin/Guar gum/$MgCl_2.6H_2O$/SN.
- The amorphous nature of Pectin/Guar gum/$MgCl_2.6H_2O$/EC and Pectin/Guar gum/$MgCl_2.6H_2O$/SN has been confirmed by X-ray study and observed that 40:20:35:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/EC also 40:20:35:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/SN possesses maximum amorphous nature.
- The morphology study of polymer electrolyte thin films was carried out by 3D laser profilometry analysis and the results revealed that in Pectin/Guar gum/$MgCl_2.6H_2O$/EC, PGMCEC7 (45:25:25:5 M. wt%) and PGMCEC5 (35:15:45:5 M. wt%) were comparatively smoother than the other two compositions PGMCEC6 (40:20:35:5 M. wt %) and PGMCEC4 (30:10:55:5 M. wt%).

  In Pectin/Guar gum/$MgCl_2.6H_2O$/SN, the two compositions PGMCSN7 (45:25:25:5 M. wt%) and PGMCSN5 (35:15:45:5 M. wt%) were smoother than PGMCSN6 (40:20:35:5 M. wt %) and PGMCSN4 (30:10:55:5 M. wt%).

- The thermal stability of the thin films was carried out by TG/DTA and the results revealed that all the polymer films are thermally stable up to 500°C.
- From the impedance study, it has been found that the film PGMCEC5 (35:15:45:5 M. wt %) exhibits highest conductivity of 3.51×10^{-3} S/cm. The maximum ionic conductivity was found to be 2.63×10^{-3} S/cm for PGMCSN4 (30:10:55:5 M. wt %).
- The maximum transport number of 0.94 was obtained for the film PGMCEC5 (35:15:45:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/EC) and 0.98 for PGMCSN6 (40:20:35:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/SN).

CONCLUSION

In this study, new novel biodegradable electrolytes based on Pectin/Guar Gum/$MgCl_2.6H_2O$/EC and Pectin/Guar Gum/$MgCl_2.6H_2O$/SN were prepared by the method of solution casting technique and were characterized by various techniques such as Fourier Transform-Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), 3-D Laser Profilometry and Thermogravimetric analysis (TG/DTA). The ionic conductivity was measured using AC impedance studies and transport number was calculated using chronoamperometry. The highest conductivity of 3.51×10^{-3} S/cm was achieved for 35:15:45:5 M wt % of Pectin/Guar Gum/$MgCl_2.6H_2O$/EC polymer electrolyte and 2.63×10^{-3} S/cm was achieved for 30:10:55:5 M wt % of Pectin/Guar Gum/$MgCl_2.6H_2O$/SN polymer electrolyte. The maximum transport number of 0.94 was obtained for the film PGMCEC5 (35:15:45:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/EC) and 0.98 for PGMCSN6 (40:20:35:5 M wt% of Pectin/Guar gum/$MgCl_2.6H_2O$/SN). Transference number data showed that the conductivity mainly arises due to ions rather than electrons. Thus, due to the highest conductivity of prepared biopolymer electrolytes, its utilization can be implied for energy storage devices like batteries.

RECOMMENDATION

Based on the present work **'Biopolymer Electrolyte for Magnesium-Ion Batteries – Preparation and Evaluation'** solid polymer electrolyte preparation comprises of host polymer Pectin/Guar Gum and $MgCl_2.6H_2O/MgSO_4.7H_2O$ as ionic dopant, the following are the recommendations for the future work.

- In the preparation of Pectin/Guar Gum/$MgCl_2.6H_2O$/SN polymer electrolytes, the PGMCSN4 exhibits higher conductivity (2.63×10^{-3} S/cm) compared to the electrolytes containing less concentration of salt. So, the electrolytes can be prepared by increasing the salt concentration and see whether it increases or decreases.

- The present work could be extended by using Pectin/Guar gum/$MgCl_2.6H_2O$ and Pectin/ Guar gum/$MgSO_4.7H_2O$ as an electrolyte with different plasticizers and a cell could be fabricated.

- The other way to carry out future research on the same aspect is to work with other magnesium salts as the ionic dopant and employ the same Pectin/Guar gum as the host polymer in order to increase the ionic conductivity.

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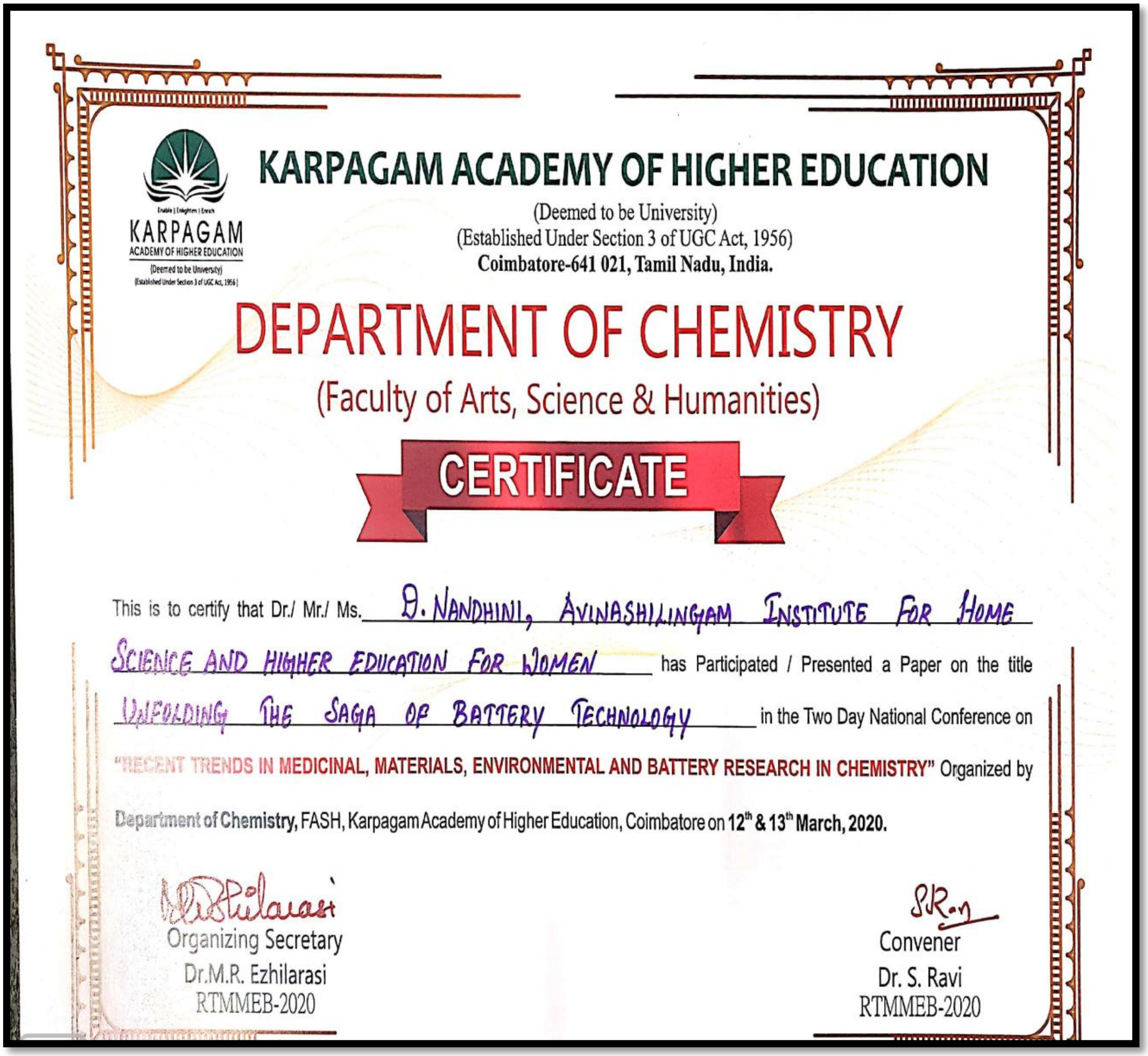

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KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
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Coimbatore-641 021, Tamil Nadu, India.

DEPARTMENT OF CHEMISTRY

(Faculty of Arts, Science & Humanities)

CERTIFICATE

This is to certify that Dr./ Mr./ Ms. D. NANDHINI, AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCATION FOR WOMEN has Participated / Presented a Paper on the title UNFOLDING THE SAGA OF BATTERY TECHNOLOGY in the Two Day National Conference on **"RECENT TRENDS IN MEDICINAL, MATERIALS, ENVIRONMENTAL AND BATTERY RESEARCH IN CHEMISTRY"** Organized by **Department of Chemistry,** FASH, Karpagam Academy of Higher Education, Coimbatore on **12th & 13th March, 2020.**

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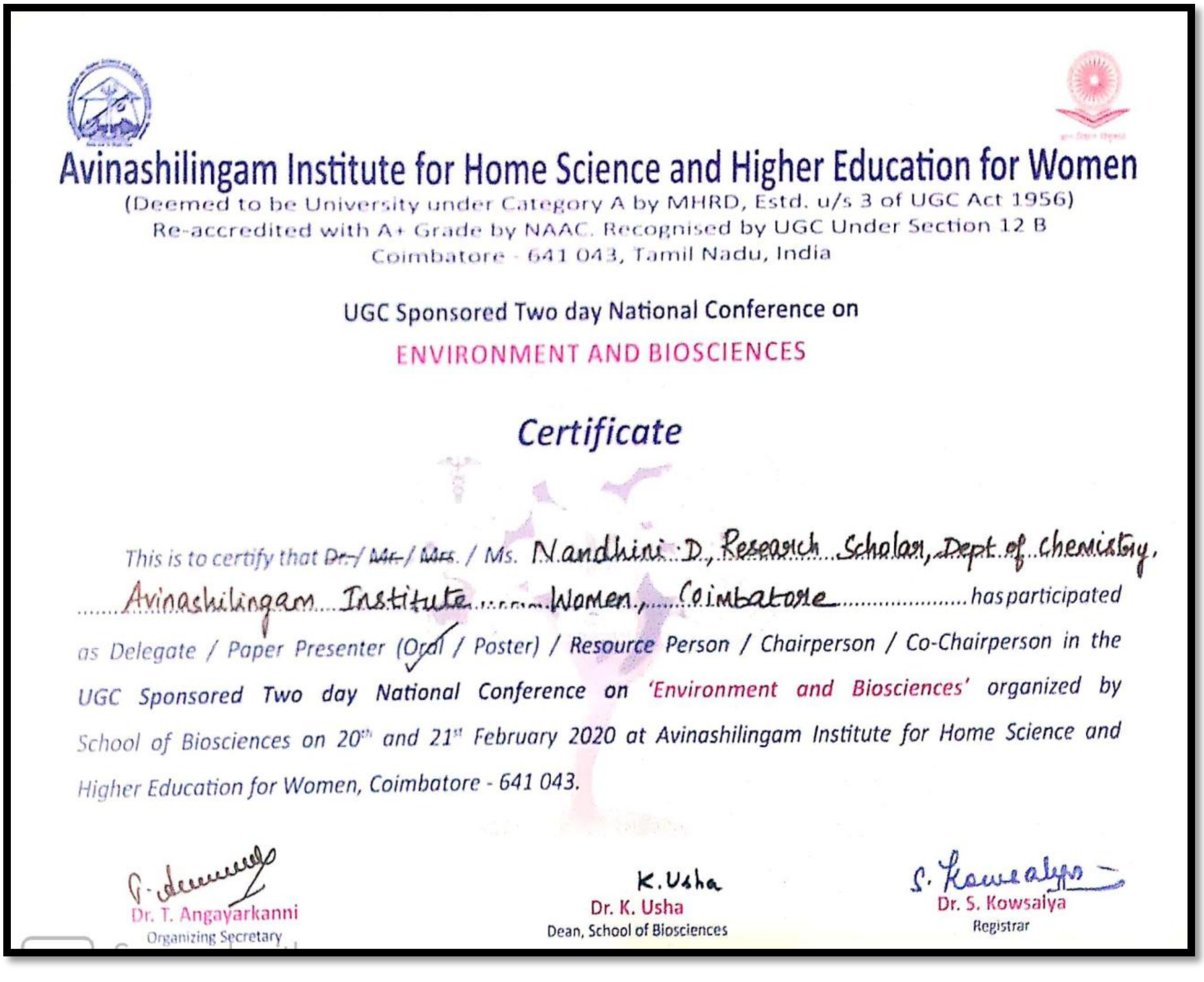

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This is to certify that ~~Dr.~~ / ~~Mr.~~ / ~~Mrs.~~ / Ms. Nandhini D, Research Scholar, Dept of Chemistry, Avinashilingam Institute ...... Women, Coimbatore *has participated as Delegate / Paper Presenter ([✓ Oral] / Poster) / Resource Person / Chairperson / Co-Chairperson in the UGC Sponsored Two day National Conference on 'Environment and Biosciences' organized by School of Biosciences on 20th and 21st February 2020 at Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore - 641 043.*

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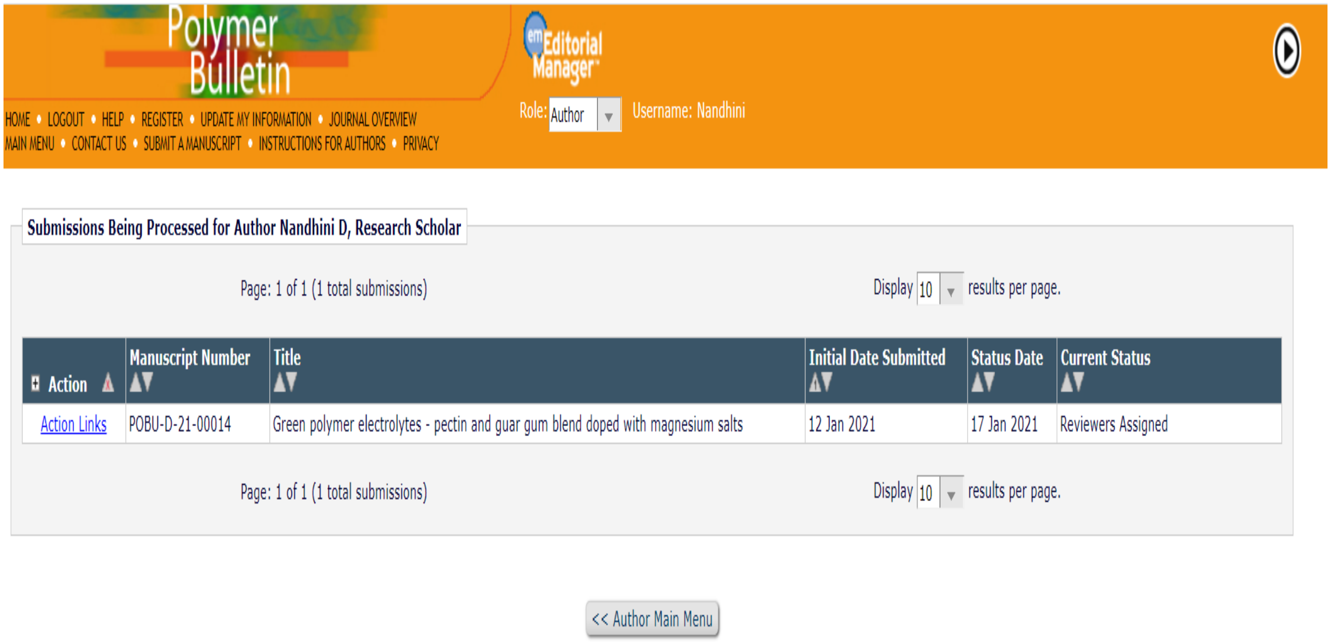

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