

# PREPARATION AND CHARACTERIZATION OF POLYMER ELECTROLYTE

*Thesis submitted for the Award of degree of*

*Master of Science*

*by*

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*Under the Academic Autonomy*

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# **DECLARATION**

I hereby declare that the work carried out in this thesis is entirely original. It was carried out at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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## **CERTIFICATE**

This is to certify that the thesis entitled “**Preparation and Characterization of Polymer Electrolytes**” being submitted by **Suchetana Sadhukhan** in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by her under our supervision. To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date

(Dr. Dillip Kumar Pradhan)

(Dr. Sidhartha Jena)

## **ACKNOWLEDGEMENT**

I humbly prostrate myself before the Almighty for his grace and abundant blessings which enabled me to complete this work successfully.

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Suchetana Sadhukhan

***DEDICATED TO MY  
PARENTS***

## **ABSTRACT**

Two groups of polymer electrolyte samples were prepared by solution cast technique with different Oxygen: Sodium ratio ( $O/Na = 0, 4, 8, 20, 40, 60, 80, \text{ and } 100$ ). Polyethylene Oxide, ( $CH_2 -CH_2-O$ ) and Polyurethane, ( $RNHCOOR'$ ) were taken as polymer host matrix and sodium perchlorate ( $NaClO_4$ ) as salt. X-ray diffraction analysis (XRD) shows the complexation of polymer with salt and existence of both crystalline and amorphous phases. The crystallite size and inter-planar spacing of the polymer electrolytes were calculated for XRD data. The Vibrational characterization was carried out by FTIR spectroscopy. The microstructure/surface morphology of the polymer electrolytes was analyzed by Scanning Electron Microscope. The SEM images confirmed the existence of the crystalline spherulite phases separated by amorphous boundary. Frequency dependence of dielectric property and ac electrical conductivity of polymer electrolytes were studied within the frequency range of 100 mHz to 1MHz using complex impedance analysis technique.

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# Chapter 1

## **1. INTRODUCTION**

The branch of science and technology dealing with the study of materials and application aspect of ionically conducting solid is known as “Solid-State Ionics”. The major part of this is devoted to: **(i)** physics and chemistry of defects in solids; **(ii)** reactions in and on solids, e.g. intercalation, corrosion, oxidation, sintering; **(iii)** ion transport measurements, mechanisms and theory. So it becomes major thrust area of research worldwide. Liquid electrolyte and solid electrolyte are the parts of solid state Ionics [1].

An electrolyte is any substance containing free ions that make the substance electrically conducting. It is mainly used in battery for storing charges. The most typical electrolyte is an ionic solution.

### **1.1 LIQUID ELECTROLYTES**

Electrolyte solutions are normally formed when a salt is placed into a solvent like water and the individual components dissociate due to the thermodynamic interactions between solvent and solute molecules, in a process called solvation.

For example



When NaCl dissolves in water it dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$  which form the liquid electrolyte.

All the electrochemical devices have three main components;

- Anode.
- Cathode.
- Electrolyte.

Despite of the popularity of the use of liquid electrolytes there are several significant disadvantages of the liquid electrolytes. Owing to the flow of the liquids the foremost problem with the devices using liquid electrolytes is leakage. Adding to the troubles is the reaction



between the electrodes and the electrolyte which gradually corrodes the electrodes. This ultimately decreases the lifespan of the device. The boiling point of the solvent used limits the temperature range of operation of the device. Besides the devices using the liquid electrolytes are bulky and can hardly be transported or carried frequently inside the solution. All these inconveniences posed by the liquid electrolytes paved the way for solid electrolytes. With the solid electrolytes eliminating the above mentioned problems the devices using them are successfully replacing the conventional electrochemical devices [2].

## **1.2 SOLID ELECTROLYTES/ FAST ION CONDUCTOR/ SUPERIONIC SOLID**

Solid electrolytes find its uses in all solid state super capacitors, batteries and fuel cells, and in various kinds of chemical sensors.

### **Required Properties of the Solid Electrolytes**

1. Ionic conductivity should be very high in range of  $10^{-1}$ - $10^{-4}$   $\text{Scm}^{-1}$  at room temperature with negligible electronic conduction ( $<10^{-6}$   $\text{Scm}^{-1}$ ).
2. Principal charge carrier should be ion only (i.e. ionic transference should be close to unity ( $t_{\text{ion}} \sim 1$ )).
3. Activation energy should be very low. [3]

### **1.3 Classification of solid electrolytes**

Depending upon the microstructure and physical properties, the ionic conductor can be classified into four categories.

- Framework crystalline/ polycrystalline materials
- Composite or dispersed phase electrolytes
- Amorphous glassy electrolytes
- Polymer electrolytes

Ionically conducting polymer electrolyte materials display many advantages over other electrolytes like

- I. It can be used for fabrication of ultra-thin alkali-metal cells of different geometrical shapes for their excellent processability and flexibility so that high energy and power density could be achieved.
- II. It is much safer due to the absence of flammable organic solvent and lower reactivity of macromolecules towards the alkali metal inhibits the corrosion of the electrodes consequently increasing the lifespan of the device.
- III. It also prevents the growth of dendrite crystals upon cycling.

**So we choose polymer electrolyte as my sample.**

#### **1.4 POLYMER ELECTROLYTE**

We can define a material as a Polymer electrolyte only if the system is solvent (liquid) free, where the ionically conducting phase is formed by dissolving salts in a high molecular weight polar polymer matrix. This is polymer electrolyte in original sense.

Polymeric materials also have better mechanical properties for the construction of all practical solid-state electrochemical cells. Due to their high molecular weight, they exhibit macroscopic properties that have attributes of true solid. At the same time in the atomic level local relaxation provides liquid like degrees of freedom which are not significantly different from those of the conventional liquid. In addition to this, since the polymers are not brittle; they are able to form good interfacial contacts with electrode materials.

#### **Physics of Polymer Electrolyte**

The polymer electrolytes are complexes of alkali metal salts (MX), with polymers as the host matrix.

Important features of polymer-salt complex are listed below:

- I. Polymer that forms salt complexes should have polar group (Lewis bases) on the polymer chain, to solvate the salt effectively.
- II. The salts having low lattice energy are most likely to form polymer salt complexes. These salts usually contain univalent alkali ions with larger anions (e.g.  $\text{CF}_3\text{SO}_3^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{HPO}_4^-$  etc).

- III. Polymers with low cohesive energy density and high flexibility (as indicated by low glass transition temperature) have the greatest tendency to interact with salts.

Due to the above excellent properties of the polymers, the idea of using polymer electrolyte has been conceived by the scientific community as compared to other solid electrolytes. In the present study we have chosen Polyethylene Oxide (PEO) and Polyurethane (PU) as polymer host [4].

### **1.5 STRUCTURE AND MORPHOLOGY OF POLYETHYLENE OXIDE**

Polyethylene oxide is a host for electrolyte formation. PEO is a semi crystalline material with about 70-85% crystallinity and amorphous elastomeric phase at room temperature. Due to partial crystallinity in the structure the problem arises both at microscopical and macroscopical level. Microscopically, it is due to arrangement of atoms and macroscopically it is due to arrangement of crystalline and amorphous phases in the polymer and polymer-salt complex. The form of the polycrystalline phase is often dendritic or spherulitic crystalline structure with well separated amorphous boundary. The gross morphological structure of PEO-salt complexes may play an important role in determining the ion transport properties of the material [4]. PEO is a linear polymer and the regularity of the unit is  $-(\text{CH}_2-\text{CH}_2-\text{O})-$ , which has a crystallinity of  $\sim 70-80\%$  of the polymer. The melting point,  $T_m$  of the crystalline phase is  $65^\circ\text{C}$  and the glass transition temperature,  $T_g$  of the amorphous phase is  $-60^\circ\text{C}$ .

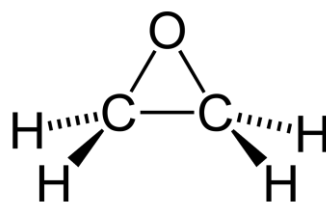


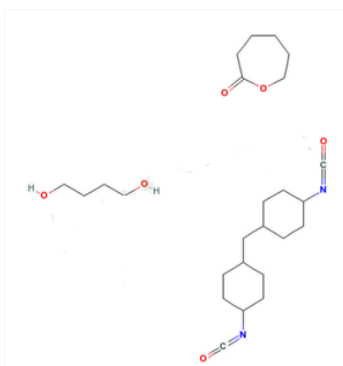
Fig 1.2: Structure of Polyethylene

### **1.6 STRUCTURE AND MORPHOLOGY OF POLYURETHANE**

Polyurethane polymers are formed by step-growth polymerization of monomers containing at least two isocyanates functional group in presence of a catalyst. The unique property is that, it offers the elasticity of rubber combined with the toughness and durability of metal which adds to

its advantage. Another benefit of urethane is its availability in a very broad hardness range (eraser-soft to bowling-ball-hard) so it can replace rubber, plastic and metal in abrasion resistance and physical properties.

Polyurethane has excellent insulating properties and is used successfully in many molded wire and cable harness assemblies [5].



**Fig 1.3: Structure of Polyurethane**

### **1.7 LITERATURE SURVEY:**

The pioneering work on polymer electrolyte was started by Wright and co-workers who were the first to report the ionic conduction in PEO-alkali metal salt complexes [6, 7]. Later Armand et. al. [8] explored the various device applications of these materials. Then it becomes an area of research interest around the globe to find out a suitable polymer electrolyte for device applications. Till now, low ionic conductivity at ambient temperature of polymer electrolytes act as a barrier to their utility for device applications, when compared with the existing conventional liquid/hybrid electrolytes. Polymer electrolytes consisting of PEO and  $\text{LiCF}_3\text{SO}_3$  were synthesized by solution cast technique as a function of different EO/Li ratio. Dielectric spectroscopic studies were performed to understand the ion transport mechanism in polymer electrolyte. The dielectric loss spectra showed the presence of one relaxation for all composition, which is associated with the motion of the Li-ion coordinated polymer segments [9]. Polymer electrolyte membranes consisting of a novel hyper branched polyether, PHEMO (poly(3-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy)methyl-3'-methyloxetane})), PVDF-HFP (poly(vinylidene fluoride-hexafluoropropylene)) and LiTFSI have been prepared by solution casting technique. The effects of different amounts of PVDF-HFP and lithium salts on the conductivity of the

polymer electrolytes were studied. The ionic conductivity of the prepared polymer electrolytes were found to be  $1.64 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  at 30 °C and  $1.75 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at 80 °C [10]. A sodium ion-conducting polymer electrolyte based on polyvinyl pyrrolidone (PVP) complexed with  $\text{NaClO}_4$  was prepared using the solution-cast technique. Investigations were conducted using X-ray diffractometry (XRD), Fourier transformation infrared (FT-IR) spectroscopy. The ionic conductivity and transference number measurements were performed to characterize the polymer electrolyte for battery applications [11]. Plasticized composite polymer electrolyte based on polymer salt complex of  $\text{PEO-NaClO}_4$ ,  $\text{SnO}_2$  as ceramic filler and polyethylene glycol (PEG200) as plasticizer were prepared and analyzed. The effects of plasticizer concentration on structural, microstructural, thermal, and electrical properties have been studied. The suppression of crystallinity was observed from DSC and XRD analysis. Also an improvement in electrical conductivity without any sharp deterioration in the thermal, electrochemical and mechanical stability of the PCPE thin films has been observed [12]. Blend-based polymer electrolytes of PEO and fully amorphous cross-linked poly (ethylene oxide-co-propylene oxide) were prepared and their thermal behavior, surface morphology, electrical, and mechanical properties were systematically investigated. Experimental results showed the crystallization tendency of PEO in the blend-based polymer electrolytes. It also showed excellent mechanical strength [13].

## **1.8 OBJECTIVES**

The following are the objectives of this research work

- I. Synthesis of polymer electrolytes by solution cast technique.
- II. Structural characterization of polymer electrolytes by XRD.
- III. Vibrational Characterization by FTIR technique.
- IV. Microstructural characterization using SEM
- V. Studies of frequency dependence of dielectric and ac electrical conductivity for better understanding of relaxation phenomena in polymer electrolyte.

### **Materials Under Present Investigation**

**Group1-**  $(\text{PEO})_x\text{-NaClO}_4$  ( $x = \text{O/Na}0,4,8,20,40,60,80,100$ )

**Group 2-**  $\text{PU}_x\text{-NaClO}_4$  ( $x = \text{O/Na} = 0, 4, 8, 20, 40, 60, 80,100$ )

## **1.9 ORGANIZATION OF THE THESIS** – This thesis has been discussed in four chapters.

**Chapter 1:** This chapter gives a brief idea about solid state ionics, liquid electrolyte, solid polymer electrolyte and structure of PEO and PU. The main focus is given on overview of the conceptual, theoretical and materials aspects of the polymer electrolytes. This chapter also summarized an overview of the past work done on polymer electrolytes. Main objective of the work and materials under investigations has been discussed in this chapter.

**Chapter 2:** The different possible methods of preparation of polymer electrolyte, and characterization techniques have been discussed. The procedure adopted by us for preparation of polymer electrolyte also has been discussed. The flow charts of sample preparation are provided to have a better understanding.

**Chapter 3:** This chapter deals with detailed studies of the structural, micro structural and vibrational characterization carried out by XRD, SEM and IR spectroscopy. It also gives detailed studies of the electrical property of polymer electrolyte with the help of impedance spectroscopy analysis at different frequency. Resistance has been evaluated from the complex impedance plot.

**Chapter 4:** Presents the conclusion drawn from the present work.

# Chapter2

## 2. SAMPLE SYNTHESIS

### 2.1 DIFFERENT METHODS OF PREPARATION

There are different methods of preparation of polymer electrolytes. Below we are discussing some of the methods of preparation.

**Solution Casting Method:** This method is the simplest one. The essential criteria for solvent selection is that it should be water-free, having boiling point not more than 65 °C, and at the same time should be a common solvent for both salt and polymer. The main advantage of this method is that drying can be performed at temperatures of around 65°C. This is necessary since most the polymers used in these studies have a melting point of maximum value around 65°C. Following steps are involved in this method:

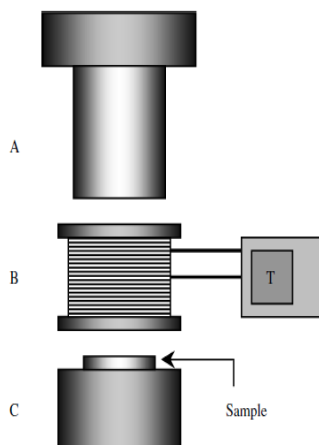
- (a) Dispersion of ceramic fillers in the salt solution.
- (b) Addition of a specified amount of polymer to the mixture.
- (c) Mixing by means of stirrer or ultrasonic equipment.
- (d) Casting the mixture homogeneously on a substrate.
- (e) Finally drying in vacuum or in an inert atmosphere.

#### **Spin Coating:**

The spin-coating method is very similar to the casting method. Instead of casting the film on a substrate, in this method, the mixture is dropped on a substrate and placed in a spin coater that can be rotated at an adjustable rotation speed. The film thickness can be controlled either by adjusting the viscosity (concentration) of the mixture or the speed of the rotation. However, this method is only available if the viscosity of the mixture is not too high. For a gel mixture, the spin coater rotation is not enough to spread the mixture droplet to form thin film.

## **Hot Press:**

Hot press technique equipment is illustrated in Figure 2.1 .The equipment consists of: (A) weighing cylinder, (B) heating chamber, (C) basement, and (T) temperature controller. Proper amounts of polymer, salt, and filler are mixed in a mortar for about several minutes. The powder mixture is then sandwiched between two sheets of Mylar or other materials, and positioned inside the heating chamber that is controlled at temperatures above the melting point of the polymer. If PEO is used as polymer matrix, temperature of 80°C is suitable. The sample is then pressed overnight with a pressure that can be controlled by weighing cylinder. After heating and pressing, the sample is then slowly cooled to room temperature. The sample is then separated from the Mylar sheet and placed in a glove box.



**Fig 2.1: Illustration of hot press equipment: (A) weighing cylinder,(B) heater, (C) base, and (T) temperature controller.**

We have selected the solution casting method as it is the simplest among all the methods. Another advantage of this method is that it can be used to produce polymer film of thickness ranging from micrometer up to several millimeters. PEO and PU based polymer electrolytes was prepared by solution cast technique.

## **2.2 PROCEDURE**

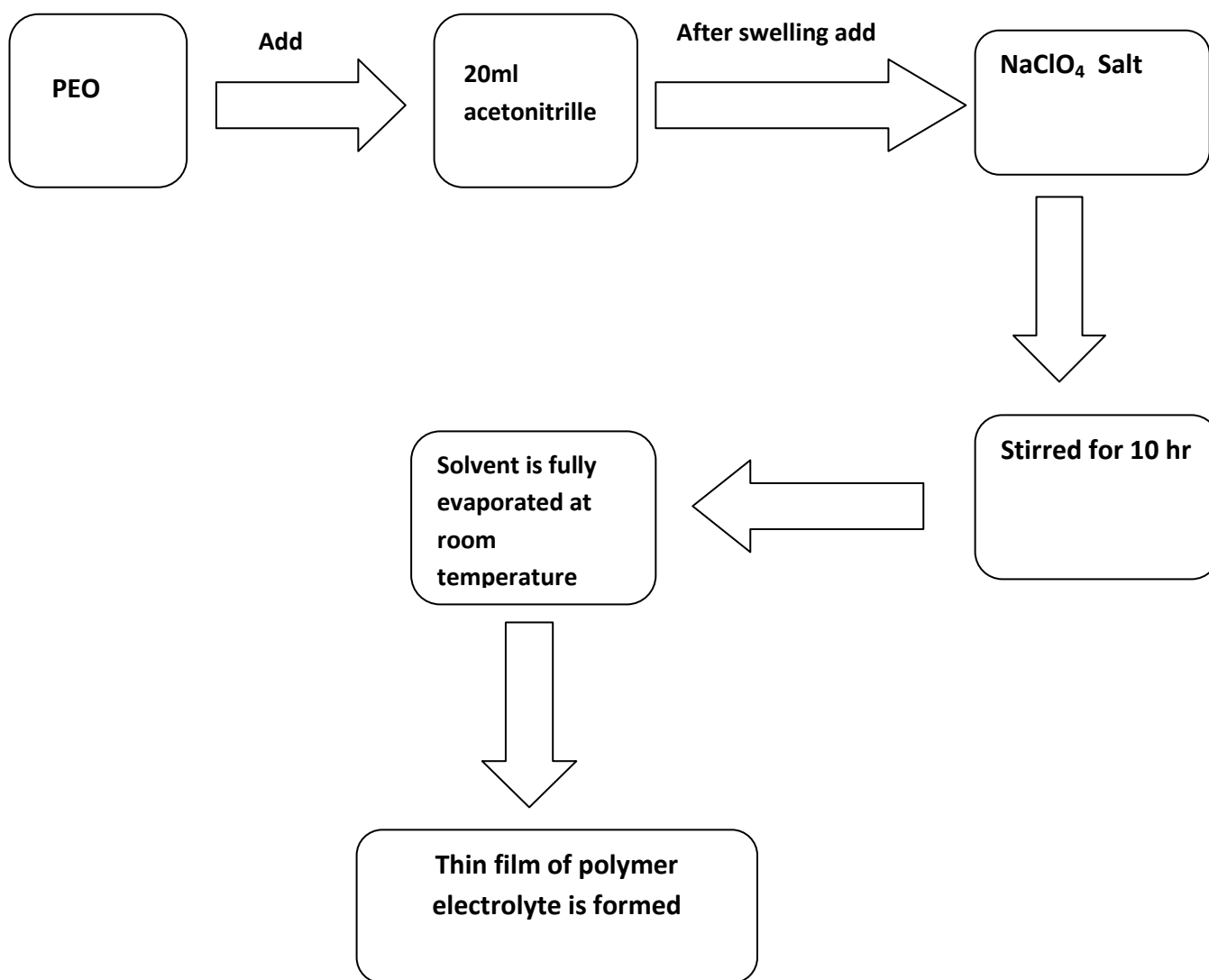
### **Preparation of polymer electrolyte based on PEO :**

- I. Appropriate ratio of polymer host, PEO was taken and dissolved it in 20 ml acetonitrile and left overnight for swelling.



- II. After swelling of polymer in the acetonitrile, appropriate amount of salt was dissolved in the solution.
- III. Then the solution was stirred for 10 hours.
- IV. The solution was casted in a petridishes and allowed to evaporate slowly at room temperature followed by vacuum drying.
- V. Thin films of polymer electrolyte composite are obtained.

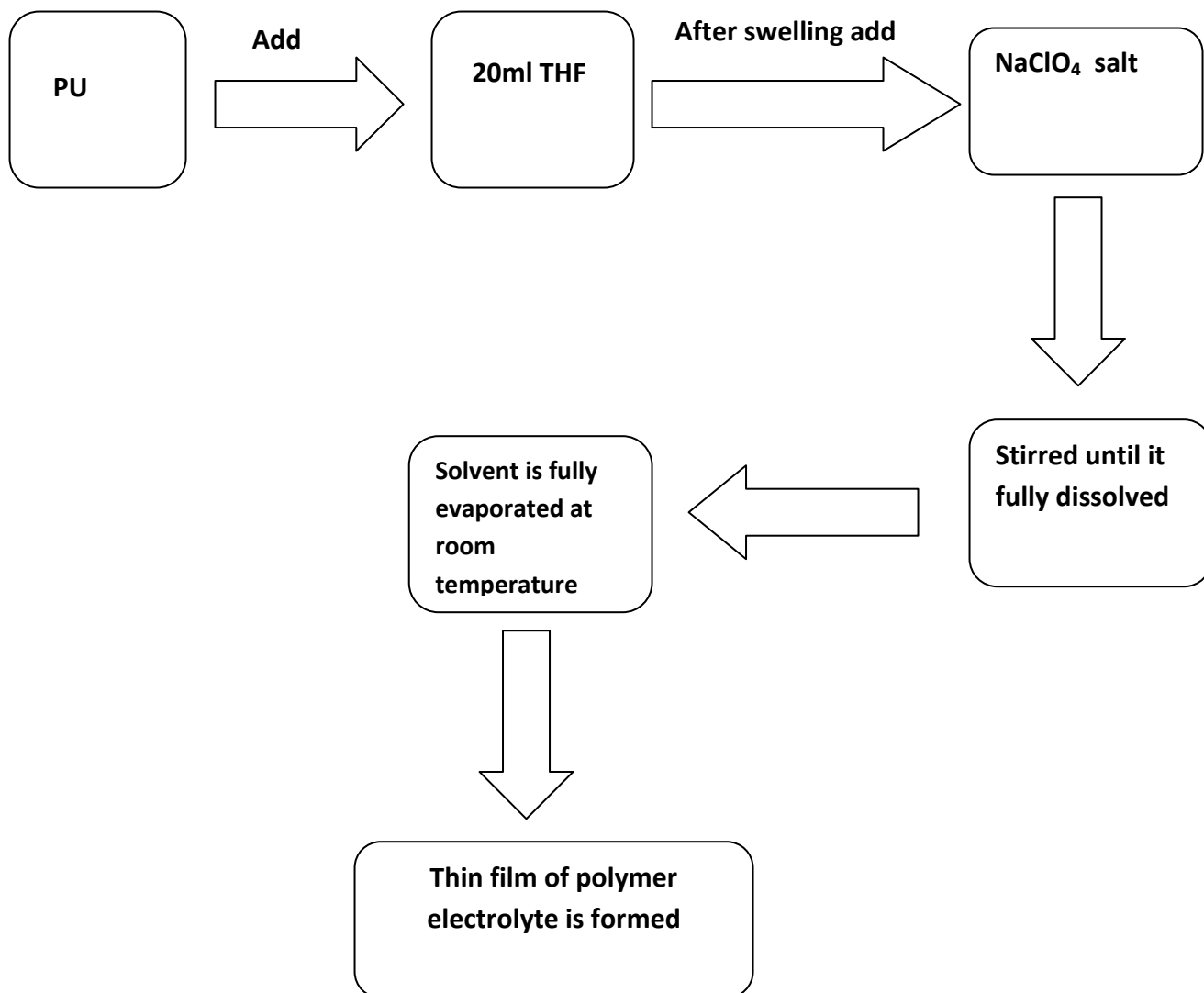
**Flow Chart:**



### **Preparation of polymer electrolyte based on PU :**

The procedure is same as PEO only Acetonitrile was replaced by Tetrahydrofuran (THF) because PU will not dissolve in the Acetonitrile. The flow chart is given below.

#### **Flow Chart:**



### **2.3 CHARACTERIZATION:**

One can investigate the composition and structure (including defects that are significant for a particular preparation), and study the properties like structure, surface morphology, thermal, electrical, mechanical, optical etc., for use of the material by different experimental techniques.

### **X Ray Diffraction:**

The X-ray diffraction technique is used to determine the atomic arrangements (i. e., crystal structure) of the material because the inter-planar spacing (d-spacing) of the diffracting planes is of the order of X-ray wavelength. For a crystal of given d-spacing and wavelength  $\lambda$ , the various orders, n of reflection occurs only at the precise values of angle,  $\theta$  which satisfies the Bragg condition

$$2d \sin\theta = n\lambda$$

The accurate determination of inter-planar spacing, lattice parameters etc. provides an important basis for understanding the various physical properties of materials.

For structural characterization of the polymer, the XRD pattern of all the compounds have been recorded at room temperature (25°C) using X-ray powder diffractometer (**Philips X-ray diffractometer**) with Cu  $k_{\alpha}$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) in a wide  $2\theta$  (Bragg angle) range ( $10^{\circ} \leq 2\theta \leq 60^{\circ}$ ) at a scanning rate of 3°/min.

**Scanning Electron Microscope:** The surface morphology/micro structural studies of the material sample can be studied by using a computer-controlled Scanning Electron Microscope (**JEOL T-330**). The polymer films were platinum coated prior to being scanned under high-resolution field emission gun SEM.

**Fourier Transform Infrared Spectroscopy:** Infrared spectroscopy can be used to identify the chemical composition, chain structure and physical properties (i.e., chain orientation, crystallinity, and chain conformation or chain dynamics) of the polymer electrolyte sample. A common laboratory instrument that uses this technique is a FTIR spectrometer scanning from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . The vibrational characterization of PEO and PU with different O/Na ratio was done by FTIR (**Thermo Nicolet, NEXUS –870**).

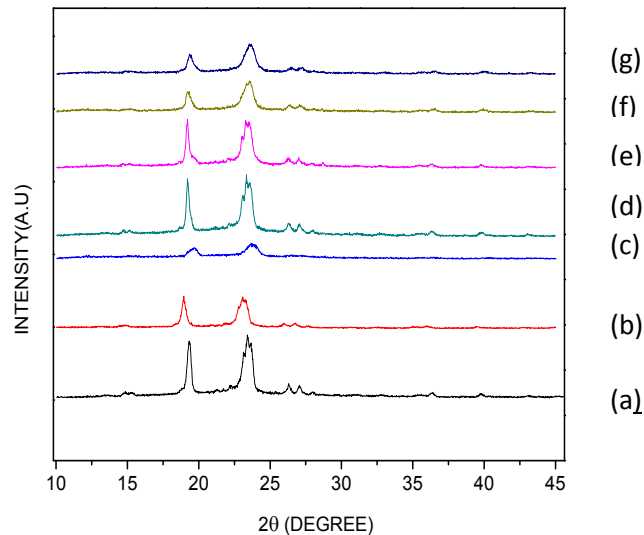
**Impedance Analysis:** Complex impedance analysis is a powerful technique to characterize the electrical properties of the electrolytes. The complex impedance measurement were carried out using a computer-controlled impedance analyzer (**PSM 1735 Impedance Analysis Package, Newton 4th Ltd.**) in the frequency range of 100 mHz to 1MHz at a a.c. signal of 100 mV at

room temperature. The polymer electrolyte film is sandwiched between two stainless steel block electrodes used as cell for the electrical measurement. The complex impedance spectrum data was used to evaluate the bulk d.c. conductivity and other related electrical properties. The main advantage is that this instrument employs the direct-current-voltage measurement technique, rather than the auto balancing bridge method. Therefore, it yields accurate measurements over a much wider impedance and frequency range.

# Chapter 3

## 3. RESULTS AND DISCUSSION

### 3.1 XRD Analysis



**FIG 3.1 (A)- PEO , (B)-PEO (O/Na=4), (C) PEO(O/Na=20), (D)-PEO(O/Na=40), (E)- PEO(O/Na=60), (F)=PEO(O/Na=80),(G) PEO(O/Na=100)**

The XRD patterns of PEO with different O/Na ratio were depicted in the Fig 3.1. Several characteristic peaks of host polymer were coming, out of which two main peaks were appearing at  $\sim 19^\circ$  and  $23^\circ$ . The polymer-salt complexes have similar XRD pattern to that of the host PEO indicating the complexation of polymer with salt. No extra peaks are observed in the XRD patterns of complexes indicating that salt is not precipitated. The XRD patterns indicate that the solid polymeric films are composed of a combination of crystalline and amorphous phases.

#### Determination of crystallite size-

Average crystallite sizes can be estimated from the full width half – maximum (FWHM) of the strongest diffraction peak using Scherer’s formula given by.

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the crystallite size,  $\lambda$  is the wave length of Cu  $k_{\alpha}$  ( $\lambda = 1.5405 \text{ \AA}$ ),  $\beta$  is the FWHM and  $\Theta$  is the diffraction angle of the strongest characteristic peak.

Crystallite sizes of PEO at different concentration of PEO are shown in the Table3.1. The inter-planar spacing was found using the Bragg's formula.

$$2d \sin\theta = n\lambda$$

where d is the inter-planar spacing. The values of inter-planar spacing and crystallite size of PEO for different O/Na (0, 4, 8, 20, 40, 60, 80, and100) ratio are given in the Table 3.1 below.

**Table 3.1: Calculation of crystallite size and inter-planar spacing**

PEO Concentration	2 $\theta$ (in degree)	Inter-planar Spacing ( $\text{\AA}$ )	Crystallite Size (nm)
PEO	19.330	4.587	25.34
	23.443	3.791	10.86
PEO <sub>4</sub> -NaClO <sub>4</sub>	19.330	4.587	23.845
	23.474	3.786	8.140
PEO <sub>8</sub> -NaClO <sub>4</sub>	19.522	4.530	25.115
	23.569	3.771	14.085
PEO <sub>20</sub> -NaClO <sub>4</sub>	19.605	4.250	9.479
	23.691	3.723	8.940
PEO <sub>40</sub> -NaClO <sub>4</sub>	19.237	4.601	33.382
	23.411	3.717	11.104
PEO <sub>60</sub> -NaClO <sub>4</sub>	19.205	4.660	36.396
	23.427	3.793	10.799
PEO <sub>80</sub> -NaClO <sub>4</sub>	19.279	4.602	21.025
	23.468	3.787	12.335
PEO <sub>100</sub> -NaClO <sub>4</sub>	19.404	4.599	20.016
	23.579	3.787	10.132

### XRD Pattern Of Polyurethane:

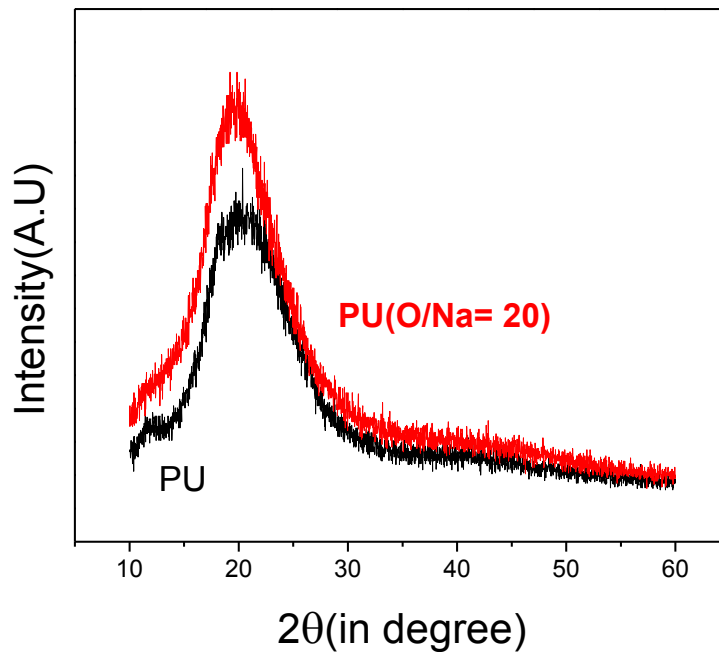


Fig 3.2:- PU and PU (O/Na=20)

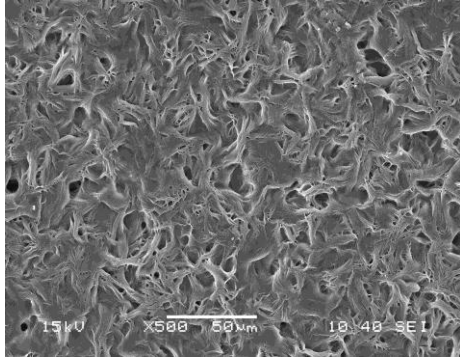
The XRD patterns of PU and after adding  $\text{NaClO}_4$  salt with  $\text{PU}_{20}\text{-NaClO}_4$  are shown in the Fig 3.2. A single main peak is observed in both the cases. In PU the peak appear at  $19.978^\circ$  and in PU (O/Na=20) the peak slightly shifted and appear at  $20.24^\circ$ . The values of inter-planer spacing and crystallite size of PU (O/Na=0, 20) is given in the table 3.2,

**Table 3.2: Calculation of Inter-planar Spacing:**

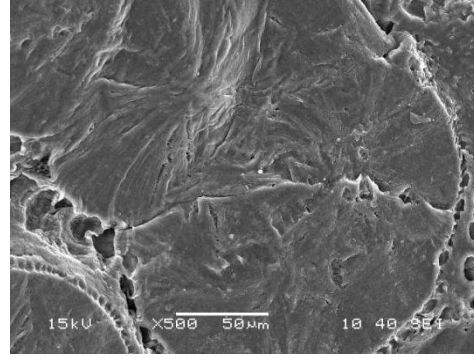
PU Concentration	2θ in degree	Inter-planar Spacing ( $\text{Å}^\theta$ )
PU	19.978	4.343
PU20	20.243	4.440

## 3.2 SCANNING ELECTRON MICROSCOPE ANALYSIS

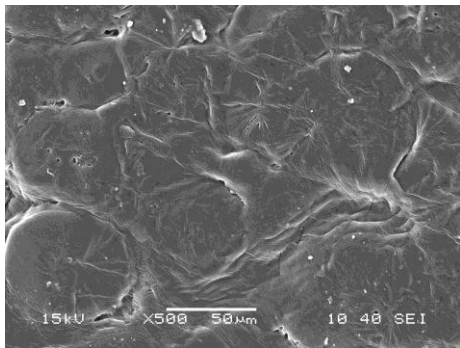
### PEO



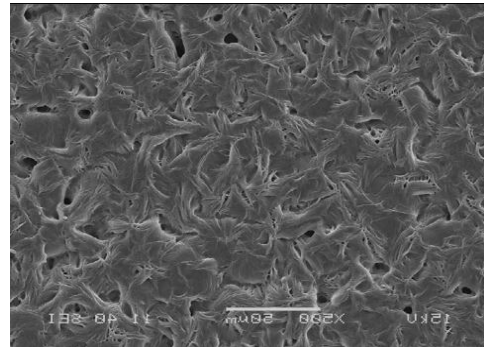
(Fig 3.2 -PEO)



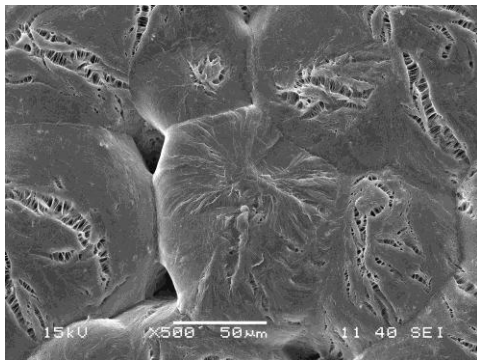
(Fig3.3PEO (O/Na=4) )



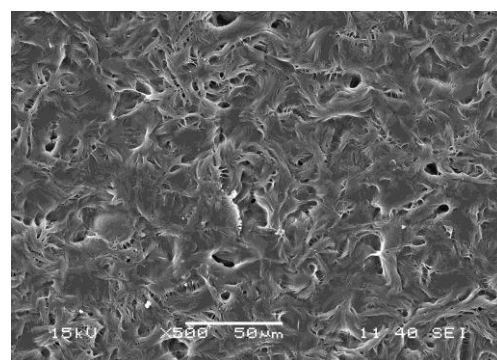
(Fig 3.4-PEO (O/Na=20))



(Fig 3.5-PEO (O/Na=40))



(Fig 3.6-PEO (O/Na=80))



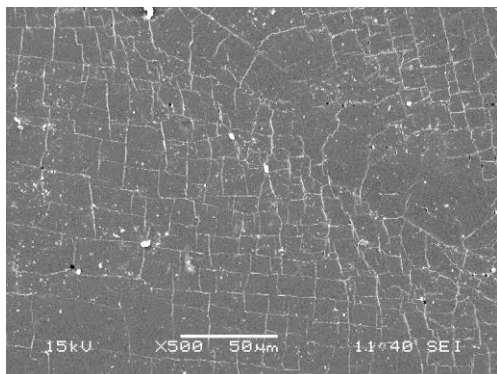
(Fig 3.7-PEO (O/Na=100))

Scanning electron micrographs of PEO with different O/Na ratio (O/Na=0, 4, 8, 20, 40, 60,100) was shown respectively in the above Fig 3.2, 3.3, 3.4, 3.5, 3.6, 3.7., The presence of distinct spherulites having characteristic lamellar microstructure is clear from the micrographs of the

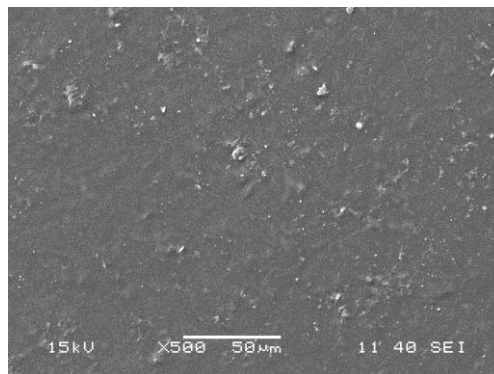


polymer-salt complexes. The region between spherulite boundaries comprises of amorphous phase. The micrographs tell that the polymer electrolytes are crystalline in nature with amorphous boundary. There is no systematic change in the surface morphology with different polymer to salt ratio.

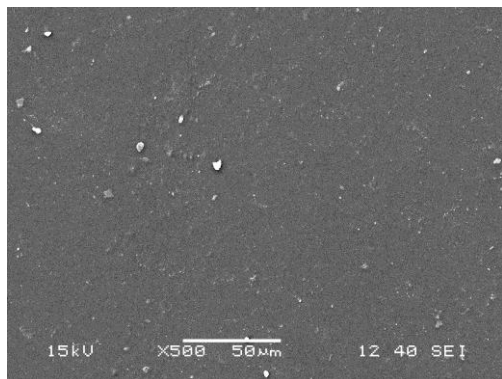
## PU



**(Fig 3.8 PU)**



**(Fig 3.9:- (PU-O/Na-20))**



**Fig 3.10:- (PU (O/Na-80))**

Scanning electron micrographs of PU with different O/Na ratio (O/Na=0, 20, 80) was observed in the above Fig 3.8, 3.9, 3.10 respectively. From the figures it has been observed the surface morphology become smoother as compared to PU when salt is being added in the PU.

### 3.3 INFRARED SPECTROSCOPY STUDY:

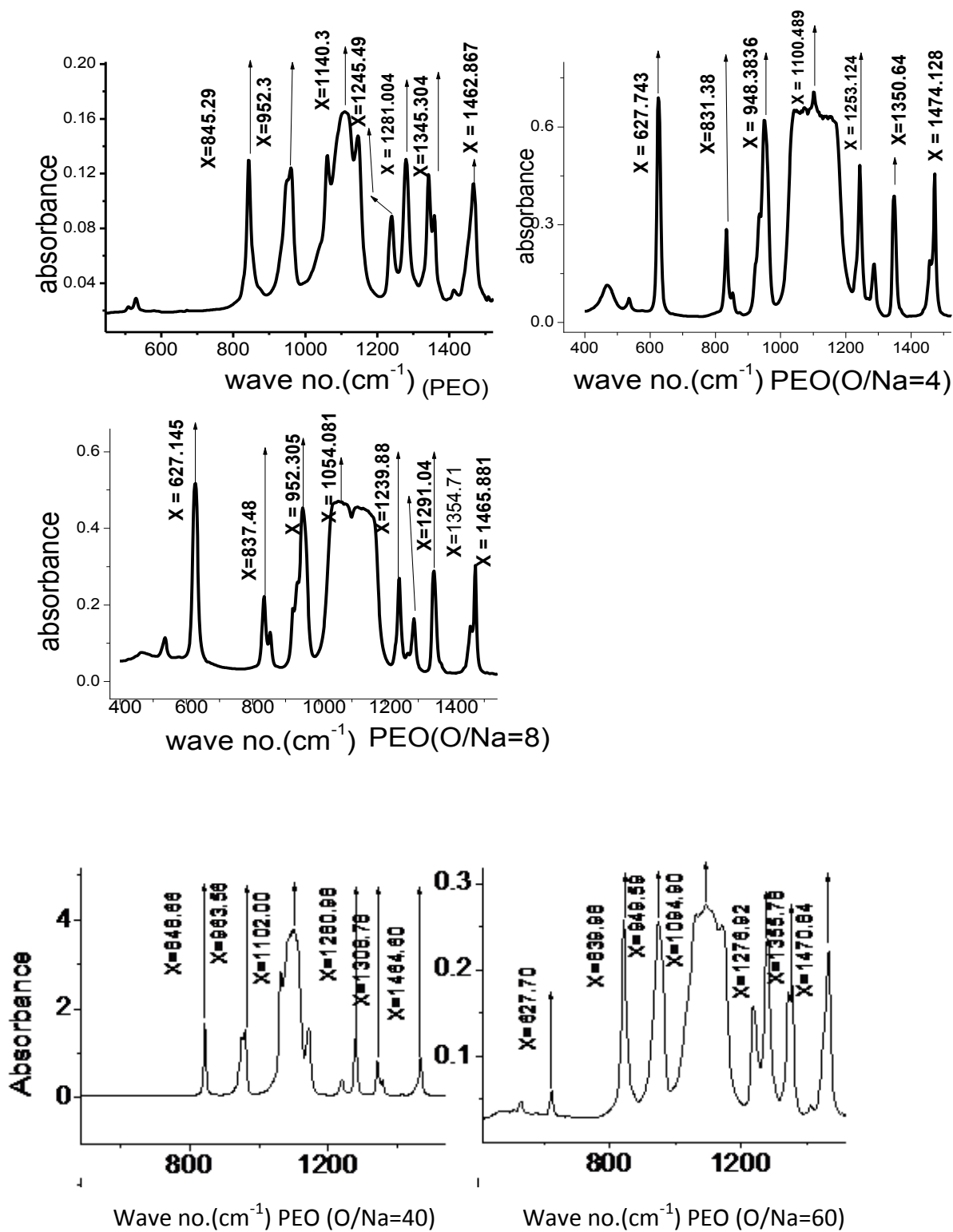


Fig 3.11:-PEO, PEO (O/Na=4), PEO (O/Na=8) for range 400 to 1500 cm<sup>-1</sup>

In Figure 3.11 we have shown the IR spectra of PEO and PEO<sub>x</sub>-NaClO<sub>4</sub> for x= 0, 4, 8, 40, 60 in the wave number range, 400-1500 cm<sup>-1</sup>. All the peaks are assigned in the fig and also shown in the Table.3.3. PEO exhibits characteristic bands in the regions 800-1000 cm<sup>-1</sup> corresponds to rocking modes, i.e., r(CH<sub>2</sub>), broad band 1000-1200 cm<sup>-1</sup> corresponds to stretching mode, i.e. v(C-O-C), 1200-1300 cm<sup>-1</sup> corresponds to twisting mode, i.e. t(CH<sub>2</sub>) and band around 1350cm<sup>-1</sup> and 1456cm<sup>-1</sup> corresponds to wagging mode, i.e. w(CH<sub>2</sub>) and bending mode, i.e. δ(CH<sub>2</sub>) respectively. But in case of polymer salt complex apart from this bands another band appears around 630cm<sup>-1</sup> corresponds to stretching mode of perchlorate band, i.e. v (ClO<sub>4</sub><sup>-</sup>). After addition of salt in polymer, the v(C-O-C) mode becomes broader as compared to the band of pure PEO, indicting the complexation of polymer with salt. There are significant changes in the peak positions, peak intensity and FWHM of the peaks of the polymer electrolyte when salts are being added to the polymer.

Different types of bonding and different types of modes are observed in the IR plots which are given in the table below.

**Table 3.3: Types of bonding and different of modes from IR spectroscopy for PEO**

Assignment	Appearance In materials	O/Na = 0	O/Na = 4	O/Na = 8	O/Na = 40	O/Na = 60
v(ClO <sub>4</sub> <sup>-</sup> )	Salt	—	627.743	627.145	—	627.743
r(CH <sub>2</sub> ) <sub>a</sub>	PEO	845.29	831.38	837.48	848.66	839.98
r(CH <sub>2</sub> ) <sub>s</sub>	PEO	952.3	948.383	952.305	963.56	949.59
v(COC)	Hybrid	1140.3	1100.489	1054.081	1102	1094.90
t(CH <sub>2</sub> ) <sub>a</sub>	PEO	1245.49	1253.124	1239.88	—	—
t(CH <sub>2</sub> ) <sub>s</sub>	PEO	1281.004	1291.813	1291.04	1280.98	1276.92
w(CH <sub>2</sub> ) <sub>s</sub>	PEO	1345.304	1343.751	1354.71	1308.78	1355.78

### 3.4 STUDY OF ELECTRICAL PROPERTIES:

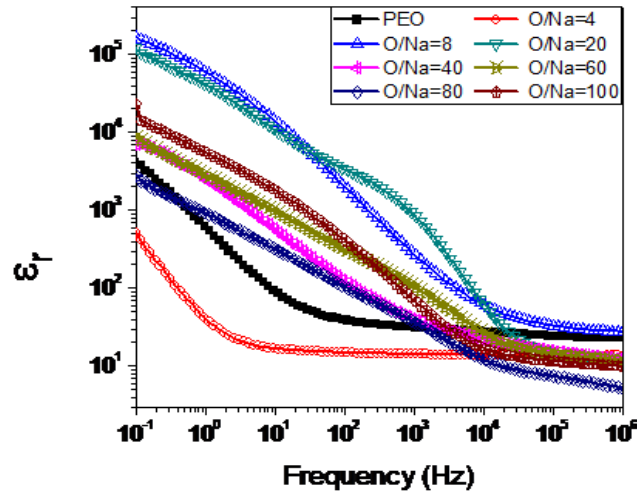


Figure 3.12:  $\epsilon_r$  vs Frequency

Complex impedance spectroscopy is a powerful technique to study relaxation phenomena in the materials and also to calculate the d.c. electrical conductivity of the materials. Fig 3.12 shows the variation of dielectric constant with frequency for different polymer is to salt ratio of PEO based polymer electrolytes. For all the cases the relative dielectric constant decreases sharply in the lower frequency region and showing a frequency independent value at higher frequency region irrespective of polymer to salt ratio. The decrease of  $\epsilon_r$  with increase in frequency may be attributed to the electrical relaxation processes.

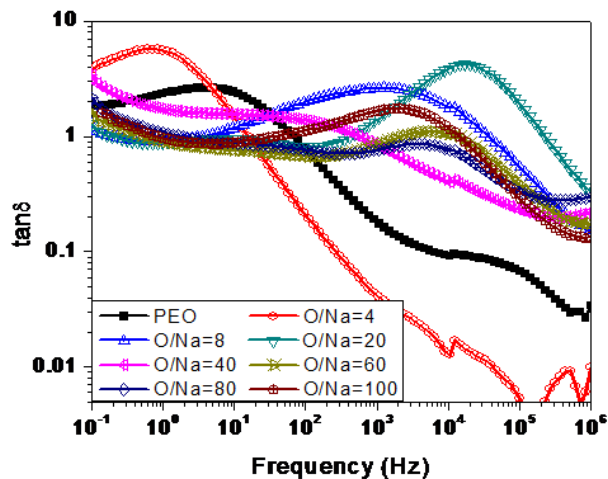


Fig 3.13:  $\tan \delta$  vs. Frequency

Fig. 3.13 shows the variation of tangent loss with frequency at different polymer is to salt ratio for polymer electrolyte. The tangent loss spectra of all these samples are characterized by peaks, appearing at characteristic frequencies. The  $\tan \delta$  peaks are shifted towards higher frequency side on increasing frequency. The appearance of peaks for each concentration in the loss spectrum (tangent loss) suggests the presence of relaxing dipoles in the polymer electrolyte.

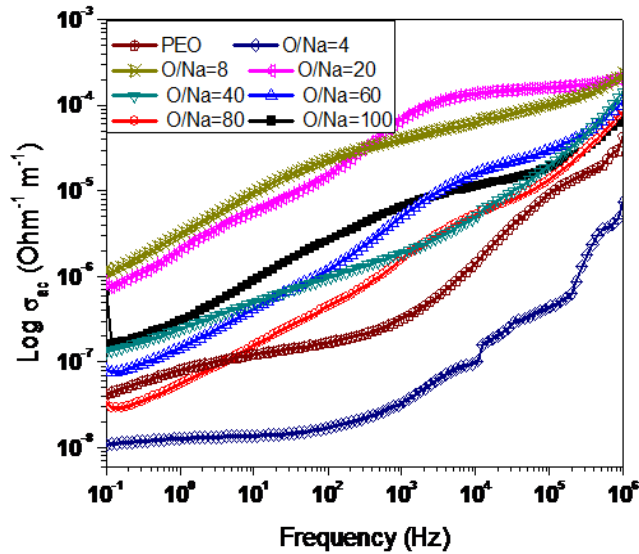


Figure 3.14: Log  $\sigma_{ac}$  vs Frequency

The frequency dependence of AC conductivity for different concentration is shown in Fig. 3.14. The AC conductivity ( $\sigma_{ac}$ ) of the material was calculated using measured dielectric data using a relation,

$$\sigma_{ac} = \omega \epsilon_r \epsilon_0 \tan \delta \text{----- (iii)}$$

where  $\omega = 2\pi f$  is the angular frequency,  $\epsilon_0$  the vacuum permittivity. The a.c conductivity pattern indicates a progressive rise in a.c conductivity on increasing frequency .

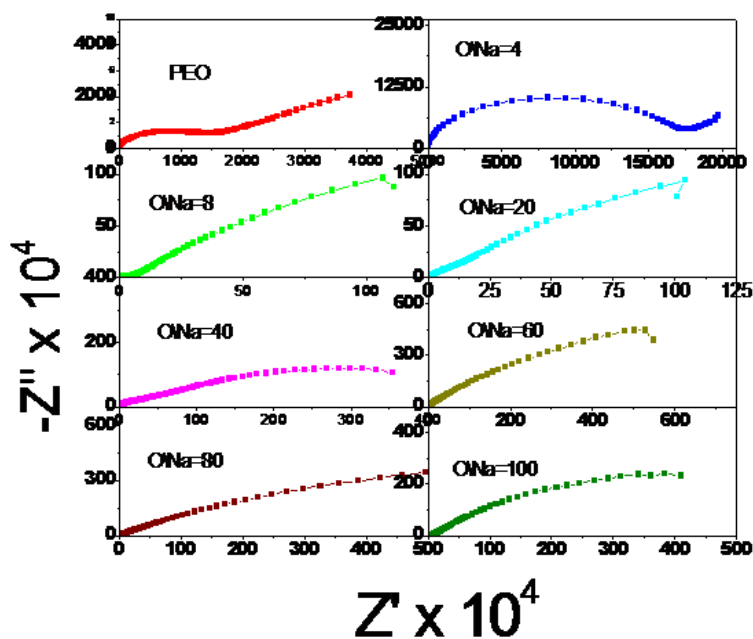
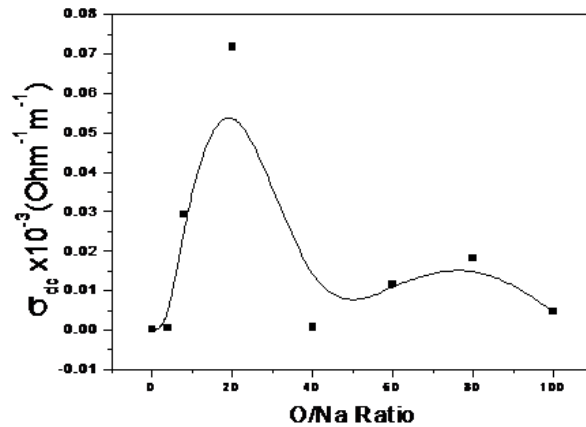


Fig 3.15:-Graph for real vs. imaginary impedance

Figure 3.15 shows the complex impedance spectrum of  $\text{PEO}_x\text{-NaClO}_4$  with different values of  $x$  (0, 4, 8, 20, 40, 60, 80, and 100). The typical complex impedance spectra (i.e., Nyquist plot) of the samples comprises of a broadened semicircle in the high frequency region followed by a tail (spike) in the lower frequency region for low polymer to salt ratio. But for higher polymer-salt ratio, only one incomplete semicircle has been observed. The high frequency semicircle is due to the bulk properties, whereas the low frequency spike arises due to the material-electrode interface of the material. The intercept of the semicircle with the real axis ( $Z'$ ) gives rise to the bulk (ionic) resistance ( $R_b$ ) of the materials.

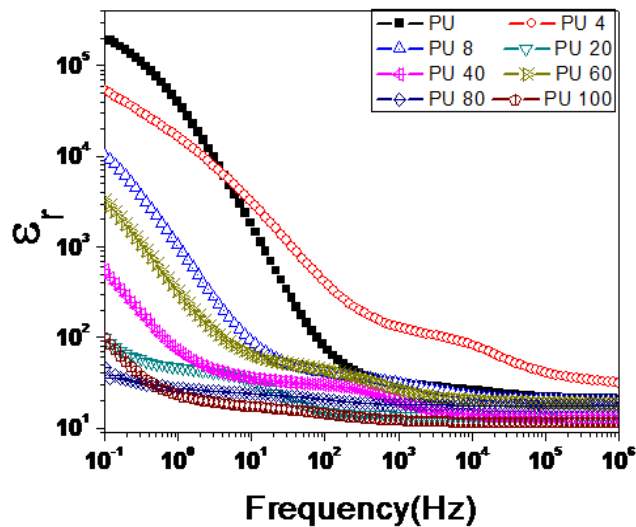
The d. c. electrical conductivity,  $\sigma_{dc}$  of the material was evaluated from the complex impedance spectrum using the relation  $\sigma = (1/R_b) * (t/a)$  where 't' is the thickness and 'a' is the area of the sample.



**Fig 3.16 : Graph for electrical Conductivity by extrapolating method**

Fig. 3.16 gives the variation of d. c. conductivity,  $\sigma_{dc}$  with different value of x for  $\text{PEO}_x\text{-NaClO}_4$  (0, 4, 8, 20, 40, 60, 80, and 100). From the graph it has been observed that the d.c electrical conductivity increases with increase in polymer is to salt ratio and attains a maximum value for x = 20 and above x = 20 the conductivity decreases.

**Dielectric study of PU**



**Figure 3.17: log  $\epsilon_r$  vs Frequency**

Fig 3.17 shows the variation of dielectric constant with frequency for  $\text{PU}_x\text{-NaClO}_4$  for different values of x (0, 4, 8, 20, 40, 60, 80, and 100). Like PEO based polymer electrolyte, PU polarization also decreases with increase in frequency. There is strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior at higher frequency region.

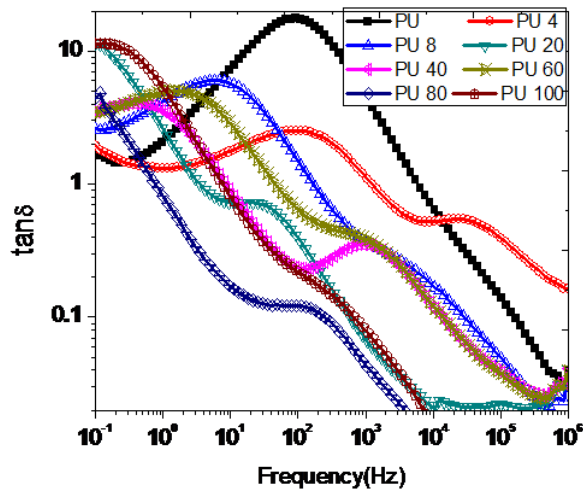


Figure 3.18:  $\tan\delta$  vs Frequency

.Fig. 3.18 shows the variation of tangent loss with frequency at different O/Na ratio for PU. The variation provides  $\tan \delta$  peak at a particular frequency for pure PU. At every concentration there are two peaks except for PU without salt. The presence of two peaks related to two different relaxation phenomena.

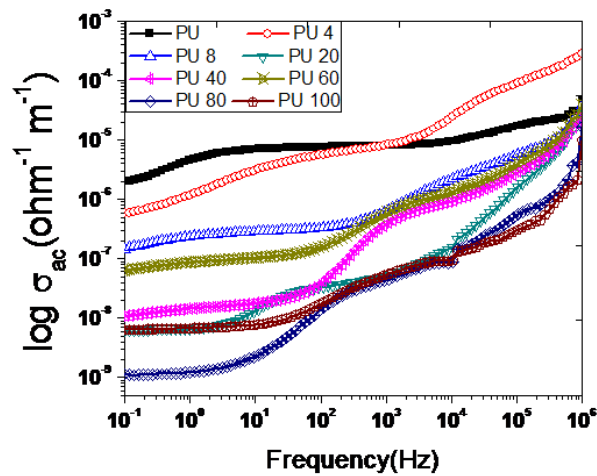


Figure 3.19:  $\text{Log } \sigma_{ac}$  vs Frequency

The frequency dependence of a.c conductivity for different concentration is shown in Fig. 3.19. The a.c conductivity,  $\sigma_{ac}$  of the material is calculated using measured dielectric data using Eq<sup>n</sup> (iii). The a.c conductivity pattern indicates a progressive rise in a.c conductivity with increase frequency.



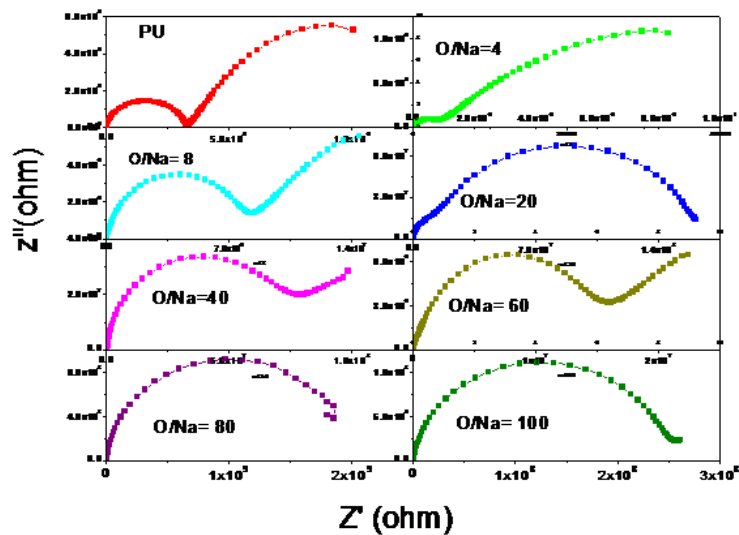


Fig 3.20:-Graph for real vs. imaginary impedance

Fig. 3.20 shows the complex impedance spectrum,  $Z'$  vs.  $Z''$  for  $PU_x-NaClO_4$  electrolyte at different concentration of O/Na. A trend of formation of two semicircular arcs is observed for low concentration of polymer is to salt ratio, whereas for higher concentration of polymer is to salt ratio only one semicircle is observed.

# Chapter 5

## CONCLUSIONS

Two group of polymer electrolytes based on Polyethylene (CH<sub>2</sub>-CH<sub>2</sub>-O) and Polyurethane (RNHCOOR') were prepared by solution cast technique with different O is to Na ratio (O/Na = 0, 4, 8, 20, 40, 60, 80, and 100), where sodium perchlorate (NaClO<sub>4</sub>) was taken as salt. The structural, micro structural/morphological, vibrational and electrical properties of the polymer electrolyte have been studied using different experimental techniques.

- I. XRD graphs show complexation of polymer with salt and crystalline structure of polymer electrolyte. The crystallite size and the inter-planar spacing of the polymer electrolytes were calculated.
- II. Again the crystallinity was confirmed by Infrared Spectroscopy (IR) analysis and position of different types of bonds and modes were identified.
- III. The microstructure/surface morphology of the polymer electrolytes was analyzed by Scanning Electron Microscope. This shows the formation of spherulites.
- IV. Frequency dependence of dielectric and ac electrical conductivity of polymer electrolytes were studied.

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