

**SYNTHESIS AND STUDY OF PERVAPORATION  
MEMBRANES DOPED WITH VARIOUS FILLERS AND  
THEIR APPLICATION IN SEPARATION OF ETHANOL-  
WATER MIXTURE**

A PROJECT

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REQUIREMENTS FOR THE AWARD OF THE DEGREE

OF

**MASTER OF TECHNOLOGY**

IN

**POLYMER TECHNOLOGY**

**Submitted by**

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## DECLARATION

I **Arun Chaudhary**, (2k17/PTE/01) of M.Tech. in Polymer Technology, hereby declare that the project dissertation titled “**SYNTHESIS AND STUDY OF PERVAPORATION MEMBRANES DOPED WITH VARIOUS FILLERS AND THEIR APPLICATION IN SEPARATION OF ETHANOL WATER MIXTURE**” which is submitted by me to the department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is original and not copied from any other source without proper citation. This work has not been previously formed the basis for the award of any degree, Diploma Associateship, Fellowship or other similar title or recognition.

Arun Chaudhary

Place: Delhi

Dated:

## **ACKNOWLEDGEMENT**

Apart from my efforts, the success of this project depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who have been instrumental in the successful completion of this project.

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In the end I would like to thank all my classmates for their support.

## **CERTIFICATE**

I hereby certify that the project Dissertation titled **“SYNTHESIS AND STUDY OF PERVAPORATION MEMBRANES DOPED WITH VARIOUS FILLERS AND THEIR APPLICATION IN SEPARATION OF ETHANOL-WATER MIXTURE”** which is submitted by Arun Chaudhary (2K17/PTE/01) in partial fulfilment for the award of degree of Master of Technology in Polymer Technology to Delhi Technological University, Delhi, is a record of the project work carried out by him under my supervision. To the best of my knowledge this work has not been submitted in part or full for any degree or diploma of this university or elsewhere

Signature of Supervisor

NAME OF SUPERVISOR:

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Prof. ARCHNA RANI

## ABSTRACT

For the manufacturing of ethanol from biomass or in the brewery sector, separation of ethanol-water mixtures is of great significance. Ultrafiltration processes as well as pervaporation procedures can be used to process fermentation and separation continuously. In this assessment, pervaporation accomplishes the removal of ethanol from the feed blend as it has a number of benefits over other procedures. Pervaporation membranes are successful in removing elements in dilute form. Efficiency of membrane can be depicted in terms of flux, sorption coefficient, separation factor and permeance. These variables are associated with the membrane thickness, temperature, and feed concentration. Initially membranes of different compositions are made using different fillers for the pervaporation process. Method of solution casting in situ polymerization is used. various crosslinking fillers are added to enhance the performance of the composite membrane. For pervaporation, the prepared membranes are tested. Higher flux is observed at low membrane thickness and increased water feed concentration and selectivity decreases at increased temperatures due to increased free volume, less viscosity and higher feed side pressure. Results are shown for membranes that are preferentially permeable to ethanol and others that are preferentially water-permeable

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# **CHAPTER 1**

# **OVERVIEW OF**

# **THE RESEARCH**

## 1.1 INTRODUCTION

Membrane separation is a constantly evolving technology in recent years. Its main role as a selective barrier is to distinguish two bulk phases and control the transfer of mass between them. This allows the interest species to be enriched and separated from the sample matrix. commonly used methods for membrane separation are dialysis, gas separation, osmosis, electro dialysis, desalination, ultrafiltration, dehumidification, and pervaporation

Among these, pervaporation (a membrane-based separation technology) offers competitive advantages over conventional techniques of separation such as distillation, It is widely used for separation of azeotropic mixtures, thermally volatile compounds and organic-organic mixtures, and removal of diluted organic compounds from sewage. This technique requires the feed liquid solution to reach one side of a semi-permeable membrane, whereas a vacuum or is applied to the membrane's permeate side to create a chemical potential difference for separation.

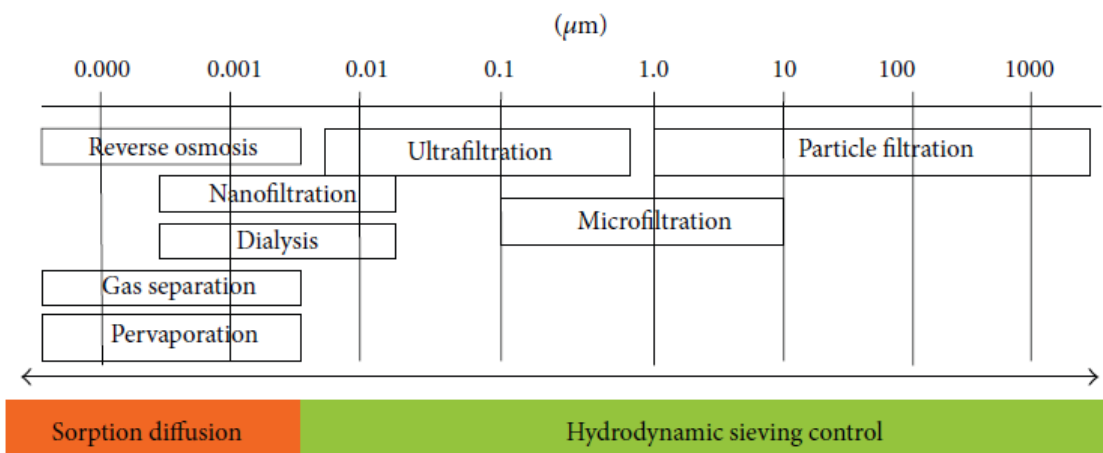


Fig:1 membrane classification with respect to size

Hydrophilic and hydrophobic membranes were commonly used in pervaporation to dehydrate organic solvents and distinct volatile organic compounds respectively from water bodies.

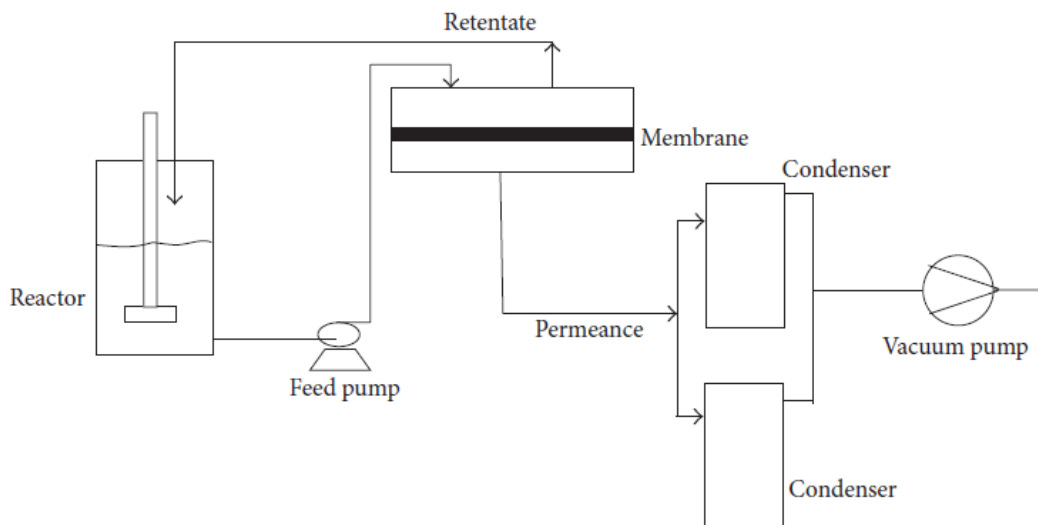


Fig 2: Schematic diagram of pervaporation set up

Pervaporation for the separation of hydrocarbon mixtures using non-porous polyethylene films were studied. Valuable contributions were made by some authors to modify the polymeric membranes through cross-linking. By this way the membrane becomes more stable at high temperature at which the permeation flux becomes high for industrial use.

High permeability, excellent selectivity and solid stability are key considerations in selecting appropriate membranes for pervaporation. Hydrophilic polymers have elevated permeability and excellent selectivity for organic solvent dehydration, but aqueous solution lacks stability.

## **1.2 POLYMER COMPOSITES**

Polymer composites are materials that have extremely industrial applications. Over the previous few decades, polymer matrix composites (PMCs) have been of interest to industry and academia, especially in the automotive, aerospace, electronic devices, medical products, civil engineering, chemical and other consumer applications industries. This is due to their superior features such as high strength-to-weight ratio, outstanding electrical insulation, load transfer capacity and easy and inexpensive handling.

A lot of job has been performed to develop PE composites using different additives. Improving the power of interfacial bonding is one of the main difficulties faced by researchers particularly for the addition of natural fibre. Polyethylene can be categorized into several distinct classifications

Type of PE	Density ( $\text{g cm}^{-3}$ )	Melt flow index (g/10 min)
HDPE	0.941–0.965	0.2–3.0
MDPE	0.926–0.940	1–2.0
LDPE	0.915–0.925	0.3–2.6
LLDPE	0.915–0.925	0.1–10.0
VLDPE	0.870–0.914	0.026–0.1

Fig 3: Table showing different types of polyethylene

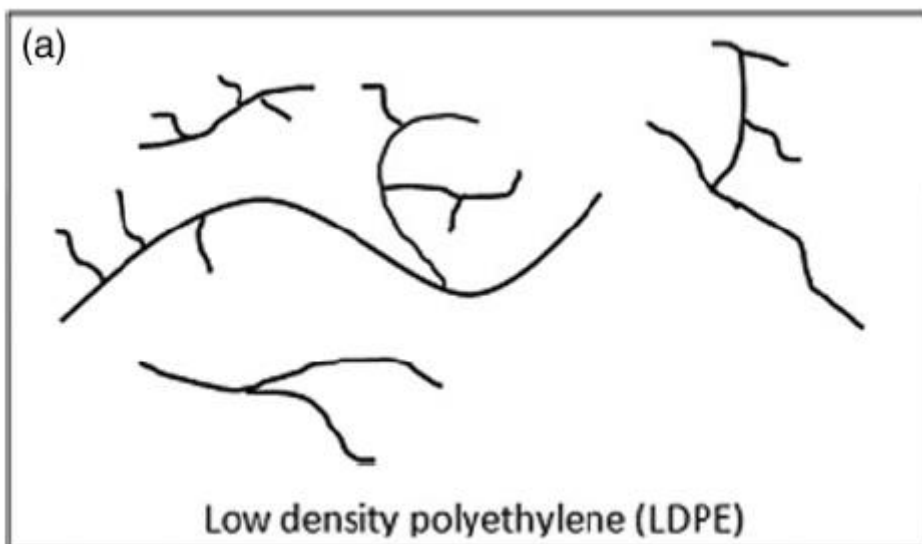


Fig 4: LDPE Structure

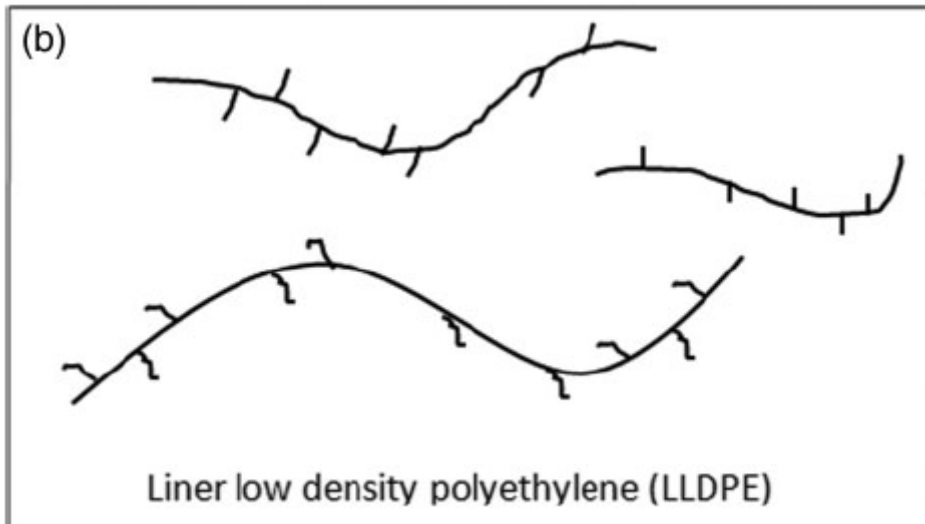


Fig 5: LLDPE Structure

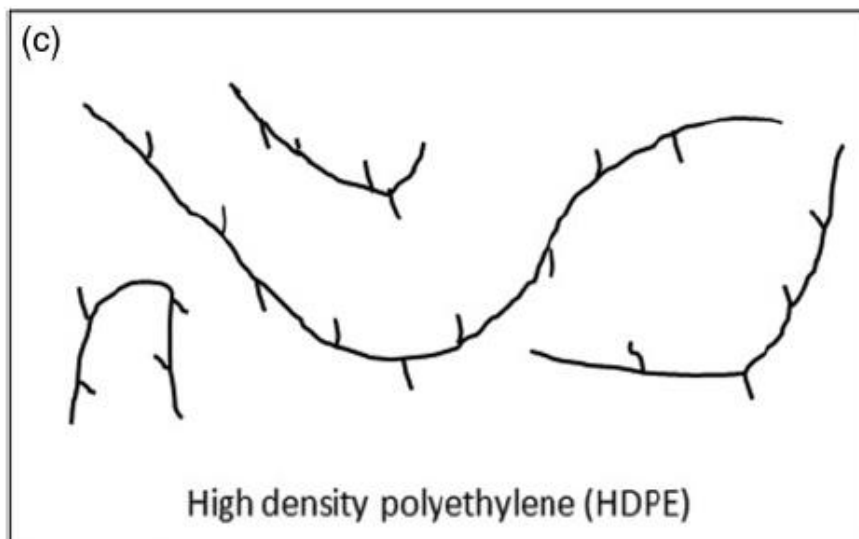


Fig 6: HDPE Structure

### 1.3 METHOD OF PROCESSING

#### Flowchart of the entire process

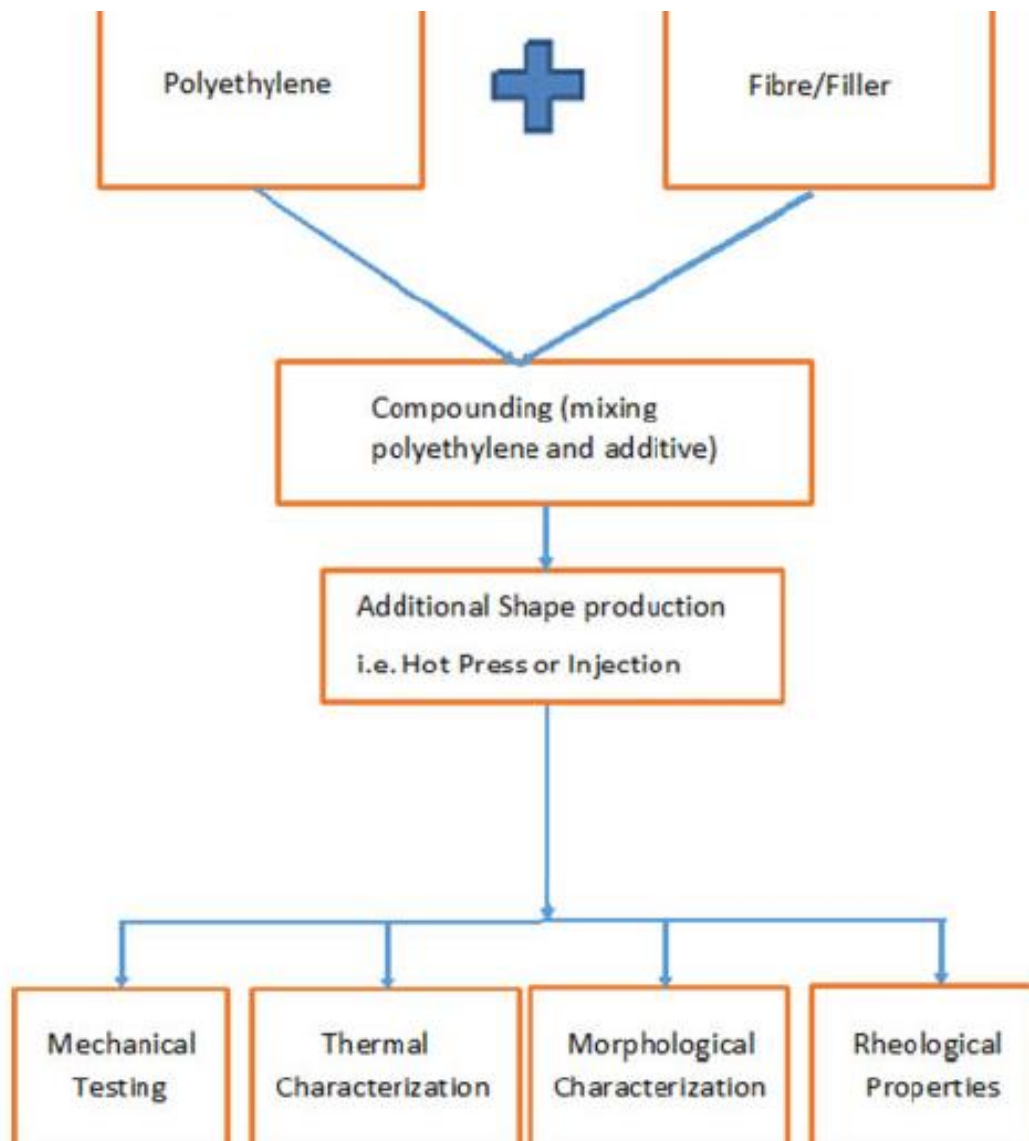


Fig 7: Overview of the whole process

Once the polyethylene composite has been made and tested it is further studied for its application. Polyethylene composite of different composition and different filler additives are made and studied [23]. The applications of this polymer composite are wide like pervaporation, desalination, and dye adsorption. Based on the properties obtained it is put to use. Different membranes show different characteristics and hence vary in their application and efficiency of application.

## **1.4 PROBLEM STATEMENT**

Besides economic reasons, there are several critical factors, some of which are related to one another that must be taken into consideration in order for the pervaporation process to succeed [24]. The correlation among these factors is shown below.

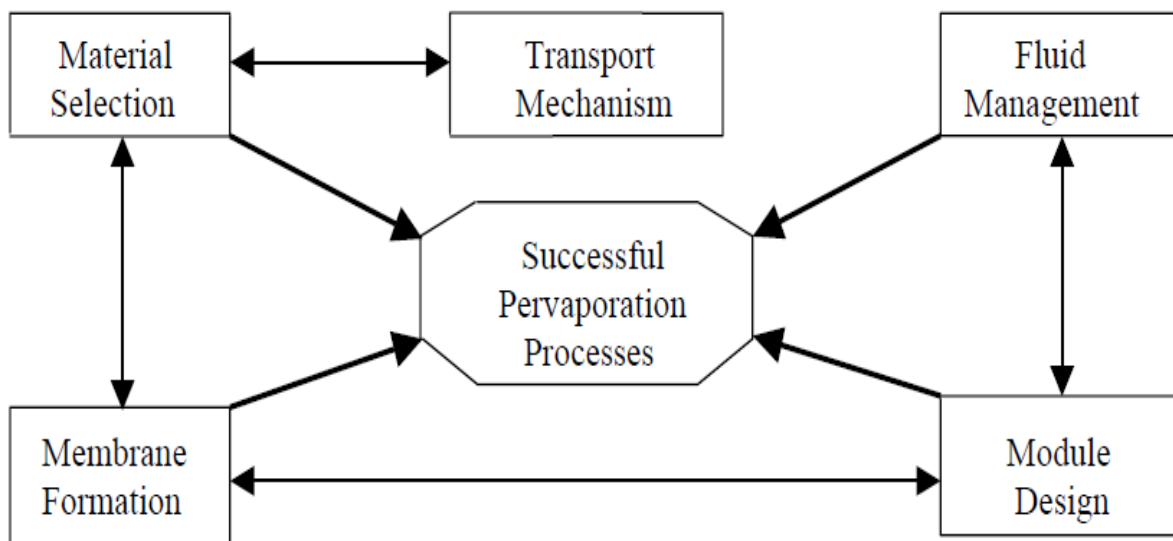


Fig 8: The critical factors controlling the successful pervaporation process

A successful pervaporation process can be measured in terms of permeation flux (productivity), selectivity, reliability and stability. All the factors above mentioned should be addressed in order for the process to be used economically.

Considering that the recovery of alcohol from aqueous solutions by pervaporation is very promising, this dissertation thesis draws attention to such recovery process as its general topic. Most studies of pervaporation have focused on improving the pervaporation performance process through condition modifications. This work is aimed at improving the membrane material.



## **1.5 RESEARCH OBJECTIVE**

The objectives of this study are described below,

- To prepare membrane of polyethylene polypropylene composite
- To investigate the effect of different fillers on the membrane at different composition.
- To investigate pervaporation by using ethanol- water model mixture and see the effect of feed concentration on separation process.

Here in this study new crosslinked polyethylene polypropylene membrane was prepared by solution casting method in the presence of solvent Trichloro Benzene. These membranes showed good selectivity and flux towards organics.

For pervaporation experiment we use ethanol water mixture and use different composition from 15-60% and see the effect of feed composition on flux and selectivity. Membranes prepared with optimal amount of fillers give better hydrophobic character and separation performance.

# **CHAPTER 2**

# **BACKGROUND**

# **AND**

# **LITERATURE**

# **REVIEW**

## **2.1 INTRODUCTION**

Pervaporation is an energy-efficient mixture of membrane permeation and evaporation in its easiest form. For a multitude of procedures, it is regarded an appealing alternative to other techniques of separation.

## **2.2 PERVAPORATION**

Pervaporation includes the separation of two or more components by different diffusion rates through a thin polymeric membrane and an evaporative phase change .

Characteristics of the pervaporation process include:

1. Low energy consumption
2. No entrainer required, no contamination
3. Permeate must be volatile at operating conditions
4. Functions independent of vapor/liquid equilibrium

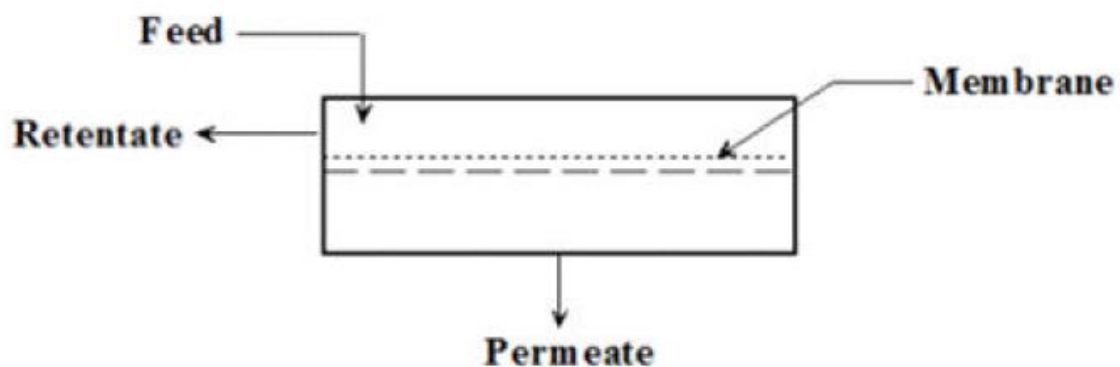


Fig 9: Schematic overview of pervaporation

Separation of the alcohol-water mixture by pervaporation through membranes has received increasing attention in industry. The method may provide an economical

alternative to distillation for alcohol–water separations and avoids the limitation of osmotic pressure imposed on reverse osmosis process by maintaining the permeate below its saturated vapor pressure.

Membranes used for pervaporation of the alcohol–water mixture are classified into two categories, water-selective membranes and alcohol-selective membranes.

Polyethylene membrane is one of the widely used membrane in this process.

To enhance the properties of this membrane various additives are used.

Alcohol water separation by polyethylene membrane has been studied before intensively. Most studies focus on determining the pervaporation performance of various alcohol water based systems based on membrane material and process conditions . The modification of membrane materials and membrane preparations include polymer synthesis (blending, copolymerization, etc.) and crosslinking to control the hydrophobicity and the degree of swelling. Feed composition and operating temperature were found to be the most important process variables; some investigations also studied the effect of other process conditions such as membrane thickness and permeate pressure. Some mixtures being separated by different membranes have been listed below in the table.

Also a table showing the different polyethylene composites and their additives added is shown:

Sr.No.	Membrane	System	References
1	PVDF, DMAc	Ethanol, water	36
2	Nylon 6, methanol	Ethanol, water	37
3	Chitosan, silk fibroin	Alcohol, water	38
4	Polyacrylic acid, PVC	Alcohol, toluene	39
5	Polyurethane	Benzene, cyclohexane	40
6	Polyethylene	Propan-1-ol, Propan-2-ol	41
7	HDPE, polypropylene	Hexane, acetone	42

8	Polyethylene	Propan-2-0l, water	43
9	Cellulose acetate, PEG	Alcohol, toluene	44
10	Polyethylene terephthalate, polypropylene	Alcohol, water	45
11	PDMS, polycarbonate	Methyl anthranilate, water	46
12	PVC, cellulose acetate	Alcohol, water	47

#### Summary of literature studies on composite membranes and fillers

Sr. No.	Membrane composite	Filler	References
1	Polyethylene	Tio2	48
2	Polyethylene	Tio2, Sio2	49
3	Polyethylene	Aluminium based	50
4	Polyethylene terephthalate	Magnesium hydroxide	51
5	Polyethylene, Montmorillonite	Plasticizer, Tio2	52
6	Polyethylene	Zno	53
7	Polyethylene terephthalate	FeSo4.7H2O	54

8	Polyethylene, lignin	Zeigler Natta catalyst	55
9	Polyethylene, MoS2	Zeigler Natta catalyst	56
10	Polyethylene	kaolin	57
11	Polyethylene	Graphene oxide	58
12	Polyethylene	Silver nanofibre	59
13	LDPE	Multi walled CNT	60
14	HDPE	Starch	61

Table 2: List of polymers and their additives

## **2.3 PERFORMANCE OF PERVAPORATION**

Generally speaking, the performance of pervaporation separation is characterized by two parameters, i.e., permeation flux and selectivity. The permeation flux represents the rate of permeation that can be achieved by the membrane and is expressed in term of amount of permeate collected ( $W$ ) per effective area ( $A$ ) of the membrane through which the permeant passes per unit operating time ( $t$ ) [62],

$$J = W/A * t$$

The selectivity describes the degree of separation attained in pervaporation. It can be measured by either the separation factor ( $\alpha$ ) or enrichment factor ( $\beta$ ):

$$\alpha = c'(1-c)$$

$$\beta = c'/c$$

where  $c'$  and  $c$  are the concentrations (in mass fraction) of the desired permeant in the permeate and feed, respectively. Obviously, if the target component concentration is very low in feed and permeate (i.e.,  $c \ll 1$ ,  $c' \ll 1$ ), then the separation factor will approach the enrichment factor numerically.

## **2.4 PROCESS VARIABLES IN PERVAPORATION:**

The separation performance of pervaporation is determined by the physicochemical nature of the membrane material and the species to be separated, the structure and the morphology of the membrane, and the process conditions. Pervaporation is a rate process that occurs under a driving force of chemical potential gradient. The chemical potential can be formulated as a function of temperature ( $T$ ), activity, and pressure ( $P$ ) in terms of the following equation [63]

$$d\mu_i = \mu_{i0} + RT \ln(\gamma_i y_i) + v_i dp$$

where  $\mu_i$  is the chemical potential of component  $i$ ,  $\mu_i^0$  is the chemical potential of pure  $i$  at a reference pressure, whereas  $\gamma_i$ ,  $y_i$  and  $v_i$  are the activity coefficient, mole fraction and molar volume of component  $i$ , respectively. The process variables, including feed concentration, temperature, and pressures at feed and permeate sides, can directly affect the chemical potential, and thus pervaporation performance will change when the process conditions vary.

## **2.5 SELECTION OF MEMBRANE MATERIAL**

Generally speaking, the membranes used in pervaporation can be classified into two types, hydrophilic and organophilic. Hydrophilic membranes absorb water preferentially, whereas organophilic membranes absorb organic compounds preferentially.

Fourier transform graph can also be used to understand the relation between the feed and the product obtained after the pervaporation process after the feed has been passed by different membranes. Based on the graph obtained the different products can be examined as how effective each membrane is in terms of separation efficiency and the flux obtained [71].

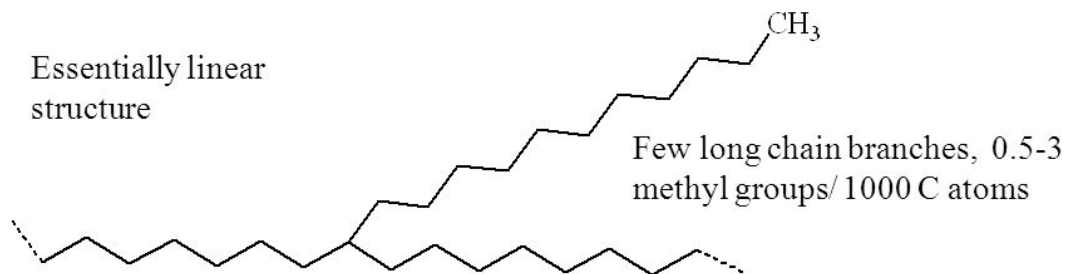
# **CHAPTER 3**

# **MATERIALS AND**

# **METHODS**



# Polyethylene (HDPE)



Molecular Weights: 50,000-250,000 for molding compounds

250,000-1,500,000 for pipe compounds

>1,500,000 super abrasion resistance—medical implants

MWD = 3-20

density = 0.94-0.96 g/cm<sup>3</sup>

T<sub>m</sub> ~ 133-138 C, X'linity ~ 80%      Generally opaque

Applications: Bottles, drums, pipe, conduit, sheet, film

Fig 10: HDPE properties

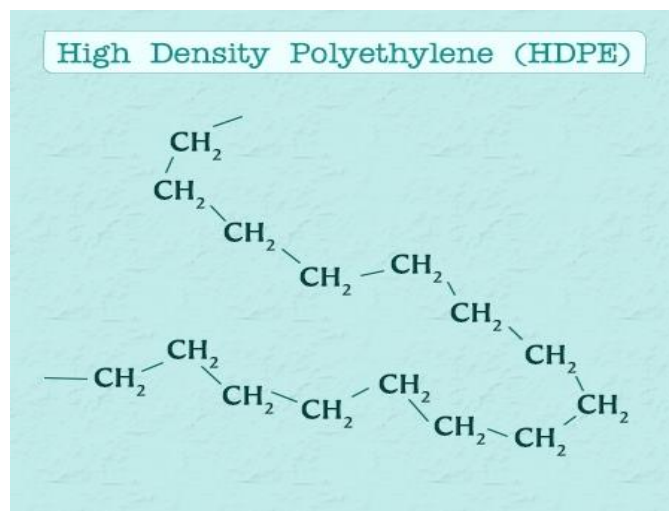


Fig 11: HDPE Structure

### **3.1 INTRODUCTION**

There have been many studies on the separation of alcohol water from its solution by pervaporation. Various membranes were suggested for the separation process. Membranes made of polyethylene, PVC, cellulose, polystyrene are widely used based on the requirements. The separation process depends on the type of membrane and the process conditions. Prior studies have shown that Polyethylene membrane had a very good separation efficiency. However a successful pervaporation process is measured from other aspects also. Here a new type of membrane is prepared using polyethylene, polypropylene mixture along with new fillers to enhance the properties such as nanoclay, diethyl phthalate. It gives excellent hydrophobicity, denseness to membrane structure and separation performance. Various cross linking agents were also added to enhance the properties. Characterization of membranes was done through X-RD, FTIR, and SEM. The experiment of pervaporation was performed and FTIR and RI analysis of the final products was carried out to check which membrane was more efficient in separation.

### **3.2 MATERIALS:**

Solvents available:

1) Water insoluble/Partially soluble solvents

- Xylene
- Tri chloro benzene(Avra, LR grade 98%)

2) Water was also used as a solvent

Solute Available:

- Polyethylene(CDH, M.W. 1700-4000)
- Polypropylene(CDH, M.W. approx. 67000)

Filler Available:

- Nano clay (SRL, Avg. particle size 80-150nm)
- Silica(Fisher Scientific, 60-120 mesh)
- Diethyl phthalate(CDH, LR 97%)
- Tio<sub>2</sub> (CDH, AR 99.9%)

Based on the above mentioned available solvents, solutes and fillers available different samples were prepared to make a polymer composite membrane of different concentration.

A common solvent was chosen based on solubility of solvents in different solvents

Common solvent for different solutes are:

- Polystyrene- Toluene, Tetra hydrofuran
- Polyethylene glycol- Tetra hydro furan
- Cellulose acetate- N-N Dimethyl acetamide
- Polyvinyl chloride- Polyethylene glycol, Tetra hydrofuran
- Polyethylene- Tri chloro benzene, xylene, toluene

Among all the different solutes and solvents available polyethylene and polypropylene blend was made. All chemicals were used without further purification.

### **3.3 MEMBRANE PREPARATION :**

Solute selected: Polyethylene(PE), Polypropylene

Solvent selected: 1,2,4 Tri-chloro benzene

Plasticizer used: Diethyl Phthalate

Filler used: Nano clay hydrophilic bentonite, Silica, Titanium dioxide

**SAMPLE 1:**

Solute: 2 gm PE + 0.5 gm PP

Solvent: 20 ml TCB

The solute and the solvent were mixed at a temperature of 150 degree Celsius and stirred in a magnetic stirrer for 5 hours for uniform dispersion. The sample was then sonicated for an hour and the sample was spread on a flat plate and allowed to cool in an open atmosphere for 24 hours. Then the sample was heated at 160 °c for 15 minutes. Then the sample was dried in open atmosphere to get the final film.

**SAMPLE 2:**

Solute: 2 gm PE + 0.5 gm PP+ 0.2 gm Plasticizer

Solvent: 20 ml TCB

In this process also the sample was stirred and dried as the above mentioned method.

**SAMPLE 3:**

Solute: 2 gm PE+ 0.5 gm PP+ 0.2 gm Plasticizer+ 0.2 gm Nanoclay

Solvent: 20 ml TCB

In this process also the sample was stirred and dried as the above methods.

**SAMPLE 4:**

Solute: 2 gm PE + 0.5 GM PP+ 0.5 gm silica

Solvent: 20 ml TCB In this process also the sample was stirred and dried as the above methods.

#### SAMPLE 5:

Solute: 2 gm PE + 0.5 gm PP + 0.25 gm TiO<sub>2</sub>

Solvent: 20 ml TCB

In this process also the sample was stirred and dried as the above mentioned method.

Solute selected: Polyethylene(PE), Polypropylene

Solvent selected: 1,2,4 Tri-chloro benzene

Plasticizer used: Diethyl Phthalate

Filler used: Nano clay hydrophilic bentonite, Silica, Titanium dioxide

#### SAMPLE 6:

Solute: 2.5 gm PE + 0.75 gm PP

Solvent: 20 ml TCB

The solute and the solvent were mixed at a temperature of 150 degree Celsius and stirred in a magnetic stirrer for 5 hours for uniform dispersion. The sample was then sonicated for an hour and the sample was spread on a flat plate and allowed to cool in an open atmosphere for 24 hours. Then the sample was heated at 160 °c for 15 minutes. Then the sample was dried in open atmosphere to get the final film.

#### SAMPLE 7:

Solute: 2.5 gm PE + 0.75 gm PP+ 0.2 gm Plasticizer

Solute: 20 ml TCB

In this process also the sample was stirred and dried as the above mentioned method.

**SAMPLE 8:**

Solute: 2.5 gm PE+ 0.75 gm PP+ 0.2 gm Plasticizer+ 0.2 gm Nanoclay

Solvent: 20 ml TCB

In this process also the sample was stirred and dried as the above two methods.

**SAMPLE 9:**

Solute: 2.5 gm PE + 0.75 GM PP+ 0.5 gm silica

Solvent: 20 ml TCB

In this process also the sample was stirred and dried as the above methods.

**SAMPLE 10:**

Solute: 2.5gm PE + 0.75 gm PP + 0.5 gm TiO<sub>2</sub>

Solvent: 20 ml TCB

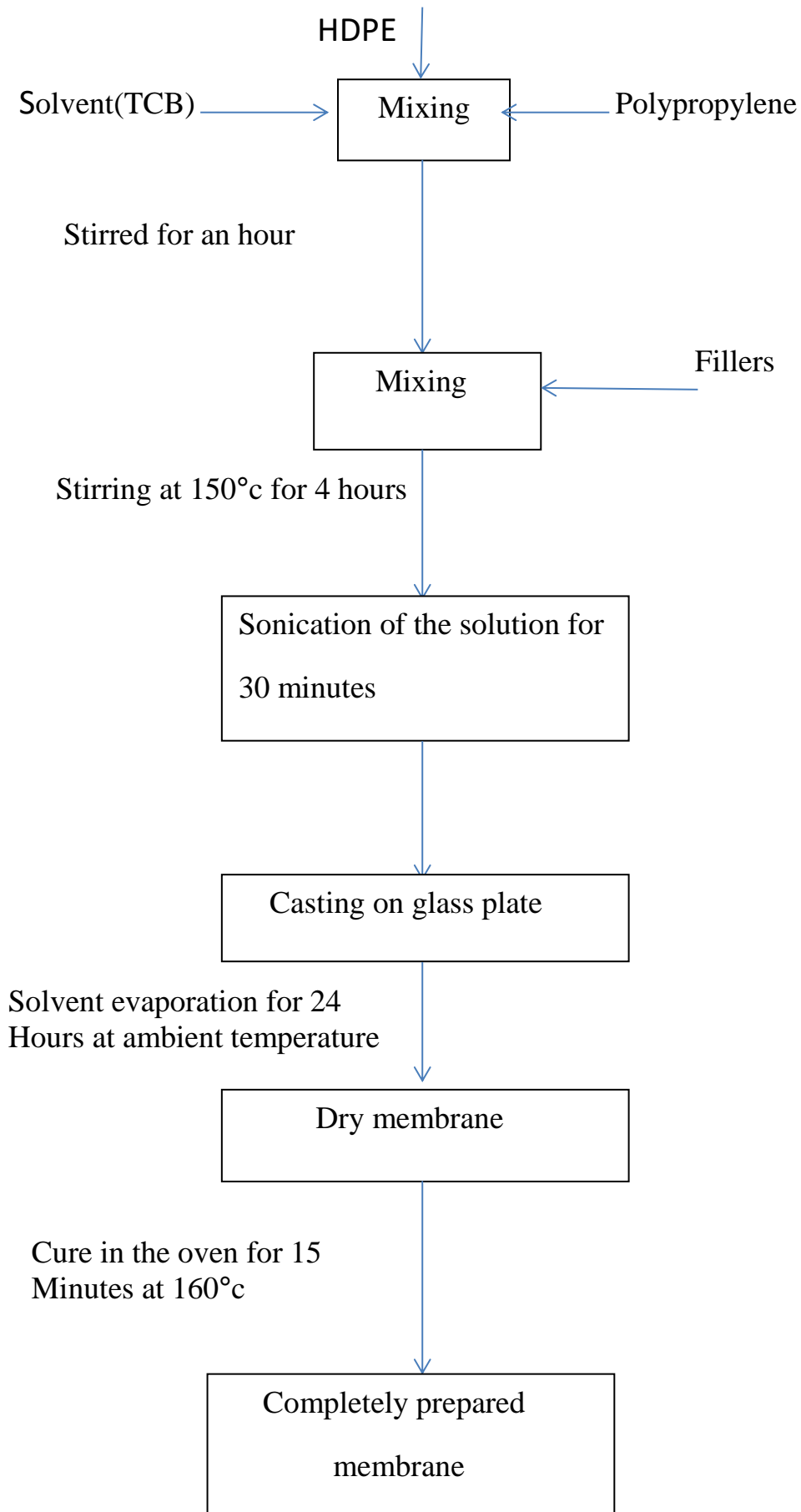
In this process also the sample was stirred and dried as the above mentioned method.

Membrane name	Base polymer(gm) (PE)+(PP)	Solvent(ml) TCB	Filler(gm)
S1	2 + 0.5	20	Nil
S2	2 +0.5	20	0.2 (Diethyl Phthalate)
S3	2 +0.5	20	0.2( Diethyl Phthalate)+ 0.2 (Nanoclay)
S4	2 +0.5	20	0.5(Silica)
S5	2 +0.5	20	0.25 (TiO <sub>2</sub> )

Membrane name	Base polymer(gm) (PE)+(PP)	Solvent(ml) TCB	Filler(gm)
S6	2.5 + 0.75	20	Nil
S7	2.5 + 0.75	20	0.2 (Diethyl Phthalate)
S8	2.5 + 0.75	20	0.2( Diethyl Phthalate)+ 0.2 (Nanoclay)
S9	2.5 + 0.75	20	0.5(Silica)
S10	2.5 + 0.75	20	0.25 (TiO <sub>2</sub> )

Table 3: Details of amounts of polymer, solvent and fillers

## FLOWCHART OF MEMBRANE PREPARATION





**Handling of the membrane:**



Fig 12: Handling of the membrane

### 3.4 EXPERIMENTAL SETUP :

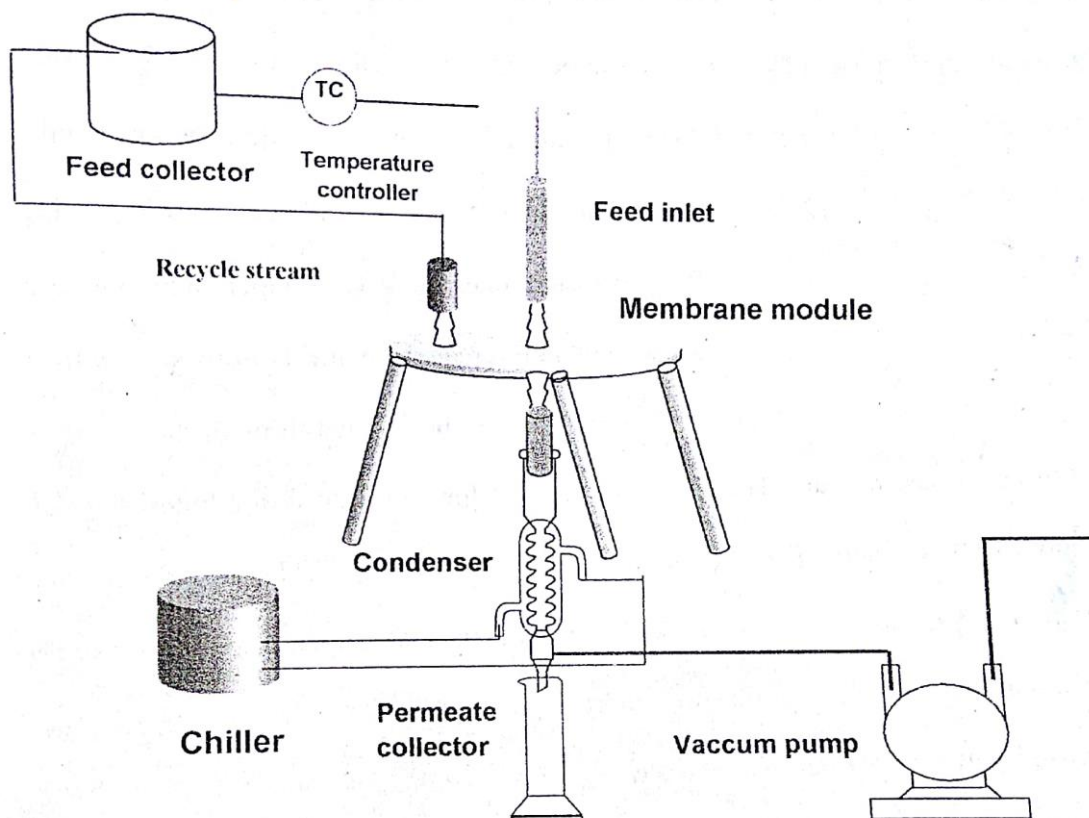


Figure 13: Pervaporation setup schematic diagram

Table 4 : Pervaporation setup components

1	Feed Collector	5	Condenser
2	Temperature controller	6	Chiller
3	Feed inlet	7	Vacuum pump
4	Membrane Module	8	Permeate collector

The above flow sheet depicts pervaporation membrane setup which was designed and fabricated for ethanol water separation. Model ethanol water mixture will be stored in the tank(feed tank)(1). The solution before being sent to the membrane module is preheated to the desired temperature , generally around 45-50°C with the help of heater(2). The membrane module(4), where the membrane is fitted with two airtight steel plates with the help of screws and bolts is shown above.

Membrane module contains three ports upper side which may or may not be used depending on our need and one port on the bottom side.

On the upper side one port is the inlet feed port(3) from where the feed enters into the module. Second port is for bypassing the retent liquid and third port for pressure exertion. Here the upper side pressure exertion is not necessary because vacuum is created in the bottom side with a vacuum pump. For high driving force pressure may be applied through the pressure port module. There is an outlet port for permeant in the bottom of the module. Vacuum pump (7) is connected to the downstream side to maintain the downstream pressure less than 5 mm Hg. A chiller (6) is used to circulate cooling water to the condenser (5) which is used to condense the permeate vapors into liquid. The condensed permeate vapors were finally collected in the permeate collector (8). The actual lab setup of the permeation schematic diagram is shown in the following figure.



Fig 14: Pervaporation setup





Fig 15: Pervaporation setup and its components

## **3.5 MEMBRANE CHARACTERIZATION:**

### 3.5.1 Membrane thickness:

The thickness of the membrane was measured by Absolute Digimatic CD-6 CSX Vernier Calliper. For measurement the membrane piece was first sandwiched between two glass slides and then the thickness of the composite was measured. Similarly the thickness of only glass plates was measured and then the total thickness of the membrane along with the glass was used to subtract it. This gives us the thickness of the membrane. Different samples of varied thickness were obtained.

### 3.5.2 X-Ray diffraction (XRD):

X-Ray diffraction spectra of Polyethylene Polypropylene membranes were obtained using Rigaku Miniflex 300/600 X-Ray diffractometer. The thin polymeric membrane sample was mounted on the sample holder and the pattern was recorded in the reflection mode with a X-Ray source radiation at 40kV. 15mA and at angle  $2\theta$  range of 5-80° at a scanning rate of 2°/min with D/teX Ultra detector.

### 3.5.3 Scanning Electron Microscopy(SEM):

Scanning electron morphology was used to know the surface morphology of all prepared Polyethylene Polypropylene membranes using a Zeiss EVO 18 scanning electron microscope.

### 3.5.4 Fourier Transform Infrared(FTIR):

FT-IR of different samples were carried out. It was used to know the functional groups and to know the changes in the hydrophobic character. FT-IR spectra were obtained using Nicolet 5700 spectrometer.

Initially the FT-IR of the sample membranes were done followed by the FT-IR of the final permeate collected after the pervaporation experiment.

### **3.6 PERVAPORATION EXPERIMENT:**

Pervaporation separation of ethanol-water mixture was carried out with the prepared membranes. An experiment was performed with the setup as shown in the figure. The membrane was cut and clamped in the membrane module. Care was taken to ensure the module was air tight. The permeate collector was kept in a chiller to ensure the vapors are condensed. Feed mixture ethanol- water was heated at 50°C. The corresponding membrane area was calculated. The permeate pressure was kept below 5mm Hg with the help of vacuum pump. Composition of ethanol was kept 15,40 and 60% respectively with water. The vapour permeate across the membrane was condensed in a condenser with the help of a chiller and finally collected in the permeate collector. The experiment was repeated with different membranes to get the best membrane by determining which membrane gives the maximum efficiency in terms of permeate collected. The mean of final results were taken. The permeate collected in the collector was brought to ambient temperature and then analysed in Refractive index analyser. A reference plot was made of the refractive index of the samples. This reference plot was used to compare the refractive index of the sample permeate collected with mass fraction values. This helps us to decide the best membrane.

# **CHAPTER 4**

# **RESULTS**

# **AND**

# **DISCUSSION**

## **4.1 INTRODUCTION:**

Membrane is the most essential component of a membrane separation process. The primary role of a membrane is to act as a selective barrier to permit the passage of species or to retain the non-permeating species. For the separation of alcohol water mixture a non-porous membrane is used. The composition of the feed is varied and membranes of different fillers and composition prepared by solution casting method is used. Results of investigations carried out after all the set of experiments were performed are presented. Results of flux and selectivity is also shown and discussed [72].

## **4.2 MEMBRANE CHARACTERIZATION RESULTS:**

### 4.2.1 Thickness of membrane:

The thickness of the membrane is measured using vernier callipers is given in the table. The thickness of the membrane varies with the amount of filler added. It also varies based on the way the final solution was spread efficiently as it depends on how efficiently the casting was done. Each membrane is made of two different concentration. The thickness varies accordingly.

Table 5: Thickness of the membrane composite

Sr. No.	Membrane	Thickness(mm)
1	SL-1	0.11
2	SL-2	0.13
3	SL-3	0.12
4	SL-4	0.16
5	SL-5	0.16
6	SL-6	0.18
7	SL-7	0.21
8	SL-8	0.40
9	SL-9	0.19
10	SL-10	0.36



#### **4.2.2 SCANNING ELECTRON MICROSCOPY(SEM) ANALYSIS:**

The SEM indicates the polymer composites surface. The electron beam interacts with the surface region in the "scanning" process and generates secondary electrons from the composite. Backscattering of the incident electrons is also available. The intensity of the secondary or backscattered electrons is measured and compared with the scanned electron beam. A contrast image refers to the composite surface as shown on the screen.. The surface morphology of different prepared membranes were shown in the figure. Polypropylene particles were well dispersed. Also for pervaporation we need a non-porous membrane. It was found that the membranes were mainly non porous. Some opaqueness was observed due to aggregates or clusters. The aggregates or cluster are possible mainly because of the presence of nanoclay. Silica particles were observed in the silica reinforced membrane. Also Titanium dioxide particles were observed in the Tio<sub>2</sub> dispersed membranes. Nanoclay was added to enhance the membrane strength. Diethyl Phthalate was added as the plasticizer to enhance the plasticity and reduce the viscosity

Figure16.1 shows the simple polyethylene polypropylene blend membrane. The membrane was mainly non porous. Now to enhance its properties fillers, cross linkers were used

Figure 16.2 shows the polyethylene polypropylene membrane with plasticizer dispersed in it. The surface was observed to be somewhat rough.

Figure 16.3 shows the membrane with nanoclay dispersed in it. It can be observed that the surface became more hard and rough.

Figure 16.4 shows the membrane with silica dispersed in it. It was observed that with the increase silica content the membrane became more rough.

Figure 16.5 shows the membrane with Titanium dioxide added to it. The opaqueness was reduced and the particles were agglomerated.

Figure 16.6 shows only polyethylene based membrane in tri-chloro benzene

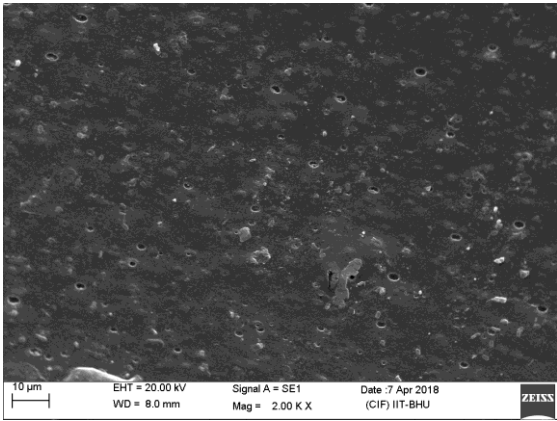


Figure 16.1

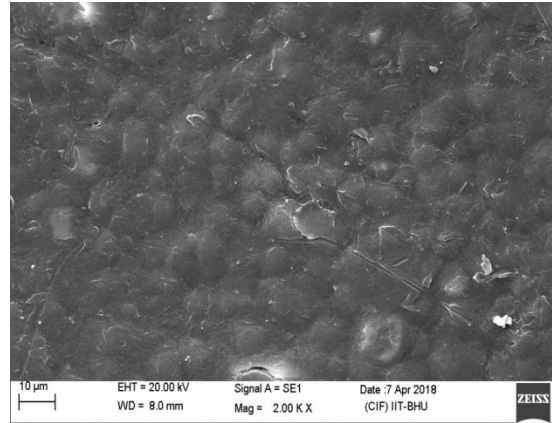


Figure 16.2

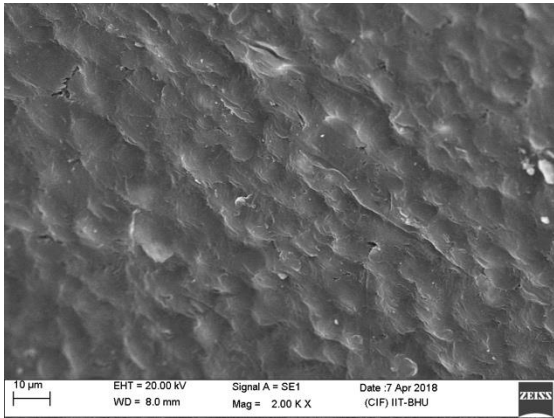


Figure 16.3

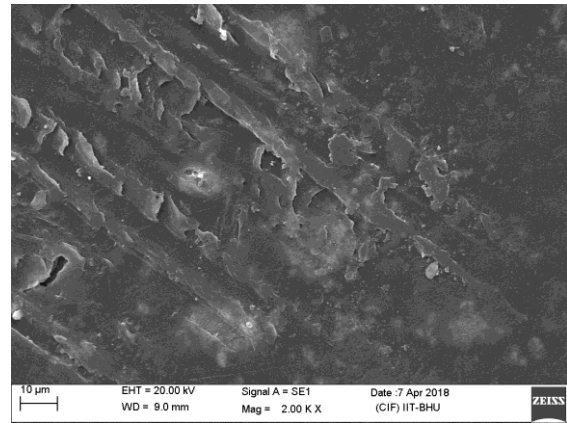


Figure 16.4

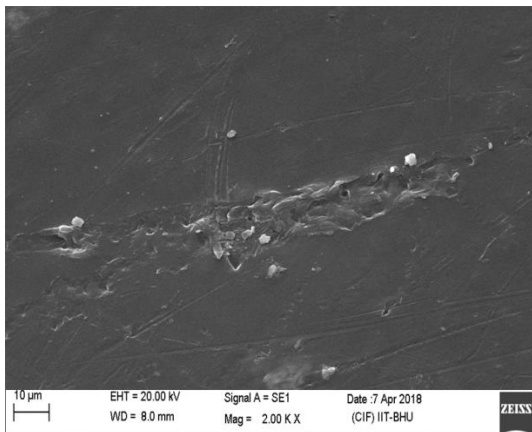


Figure 16.5

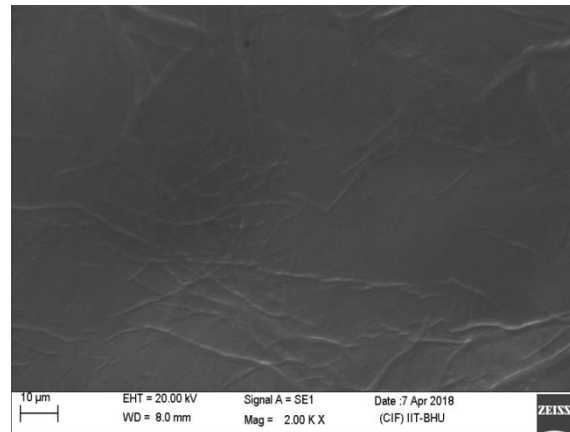


Figure 16.6

### 4.2.3 X-ray Diffraction studies(XRD) analysis:

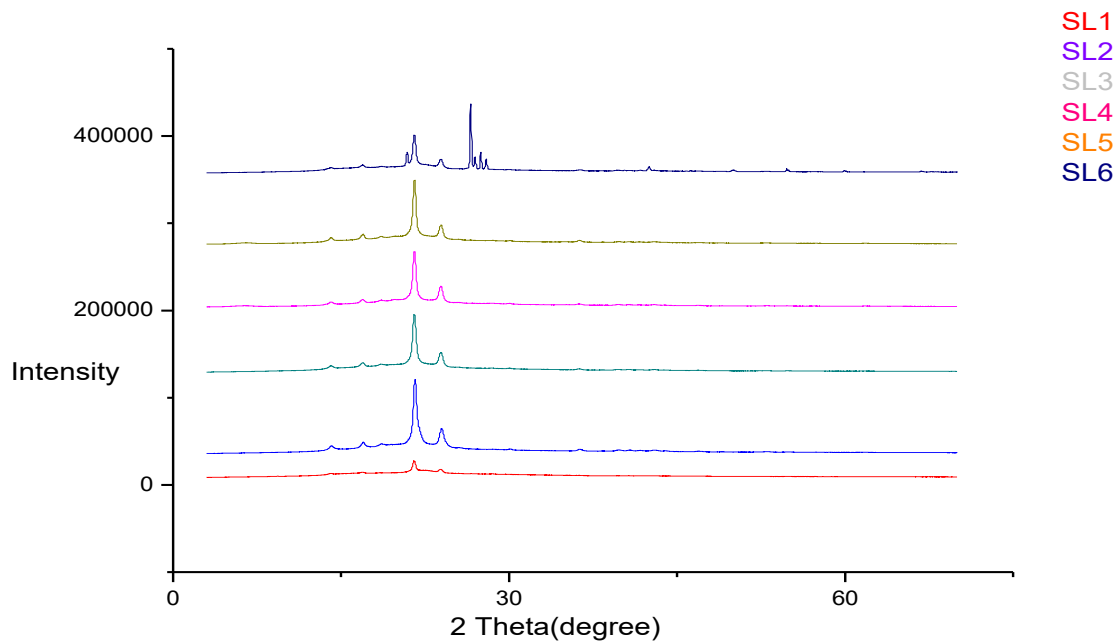


Fig 17: XRD peaks of cross-linked polymers

The method of X-ray diffraction identifies the following: preferred orientation, crystalline regions, and crystalline material grain size. If the buildings are arranged in an organized array or lattice, the interference with the structure of the X-ray's electromagnetic radiation is sharpened so that the radiation is dispersed or diffracted only under particular experimental circumstances.

X-ray diffraction techniques are helpful for semi-crystalline polymers and crystalline phase restructuring (polymorphism) of polymers. X-ray diffraction is a main method for determining the degree of crystallinity in polymers, since polymers in nature are not 100% crystalline.

The crystalline and amorphous character of the membrane was determined using X-ray diffraction measurement and shown in the figure. We can see the X-RD patterns of the membrane with different composition and different fillers.

The simple polyethylene membrane showed a small peak at a value of  $2\theta$  of  $21.9^\circ$ . After this the peaks of polyethylene polypropylene composite doped with fillers were observed.

Polyethylene polypropylene based composite showed peaks at  $2\theta$  values of  $21.5^\circ$ . A small sharp peak was also observed at  $2\theta$  value of  $23.9^\circ$ . It showed that the two solutes were well dispersed in the solvent. The new membrane formed by adding plasticizer diethyl phthalate also showed two peaks. One at  $2\theta$  values of  $21.6^\circ$  with a further small peak at  $23.9^\circ$ . When nanoclay was added to enhance the strength the peak was observed at  $2\theta$  values for  $21.7^\circ$  and  $23.8^\circ$ . These two

are the characteristic peaks of polyethylene and polypropylene composite. addition of silica showed the same peak at  $2\Theta$  values of  $21.5^\circ$ . The small curve was again obtained at  $23.9^\circ$ . Since all the values of the peak was almost similar it can be deduced that after addition of all the fillers the crystalline nature didn't change. The fillers were well dispersed in the solvent and very well soluble. The small peaks at  $23.8^\circ$  and  $23.9^\circ$  correspond to aggregation of the components added. XRD analysis was also carried out to evaluate dispersion quality and possible interactions of the  $\text{TiO}_2$  [73,74,75].

There is no much difference in the inter planar distance (d value) which represents the lattice parameter of the neat PE and the developed composites which proves that the lattice parameter is not affected by the presence of silica particles or the titanium dioxide particles. Moreover, the diffractive peaks do not shift with the addition of silica particles nor the titanium particles. Lamellar thickness (L) of PE increases with the addition of silica particles or the titanium dioxide particles which implies that silica and the titanium dioxide aid, the formation of more perfect crystals. This can be attributed to the fact that silica and Titanium particles act as heterogeneous nucleating agent inducing HDPE to form perfect and stable crystals.

Also in case of silica and titanium dioxide filler composite some small peaks were observed of very low height at  $2\Theta$  values of  $50^\circ$ ,  $54.8^\circ$  and  $59.2^\circ$  in case of silica and  $53.8^\circ$ ,  $55^\circ$ ,  $62.67^\circ$  and  $68^\circ$  for titanium dioxide [76]. It was found that with the increase in  $2\Theta$  values for these composites a decrease in d was observed.

#### **4.2.4 FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS:**

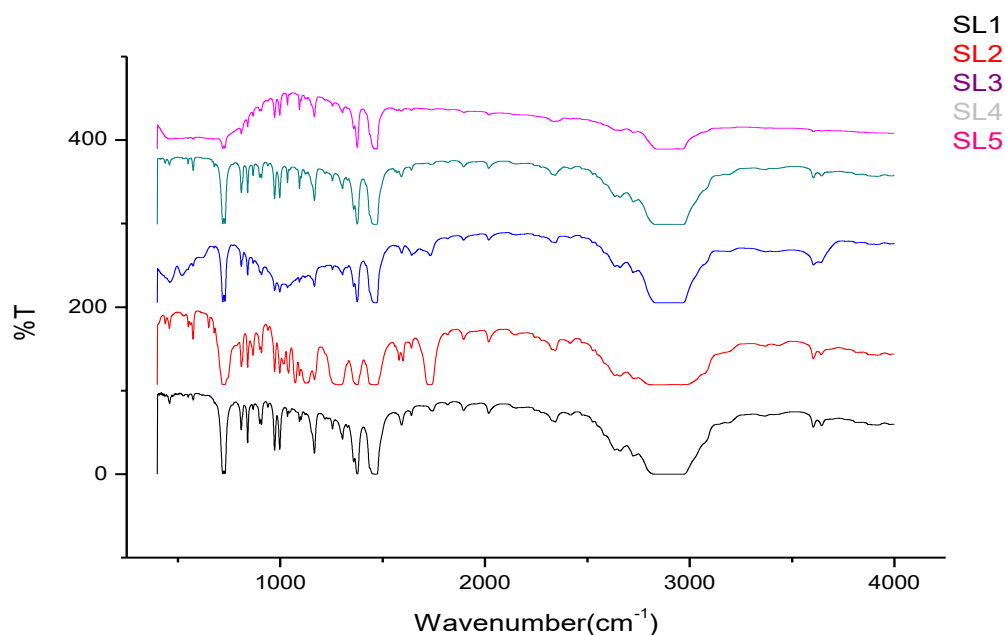


Fig 18: FTIR spectra of membrane composites

FTIR analysis of the sample membranes was done. This was done to mainly study the structure of the polymer and the functional groups attached. The analysis was done at wavenumber ranging from 0-4000 cm<sup>-1</sup>. From the graph it was observed that all the membranes showed peaks at the same range with slight variation in the intensity of the peaks. A broad peak was observed in all the graphs at the wavenumber of 2832 cm<sup>-1</sup>. This broad peak also showed variations of height and width [22].

The graph of sample 1 shows peaks at wavenumber 733.3, 1163.4, 1369.7, 1463.7 cm<sup>-1</sup>. These peaks show the presence of Alkanes and C-C stretching. The peak at 733.3 cm<sup>-1</sup> is mainly due to the presence of aromatics [. The wide peak at 2892.9 is mainly because of the presence of dimer -OH. It shows asymmetric stretching of the -OH groups TCB and water [77].

The graph of sample 2 shows small intensity peaks at wavenumber 579 cm<sup>-1</sup>. This shows the presence of alkyl halides due to TCB. The other peaks at 717, 1273.7, 1383.7, 1448.8, 1743.4 cm<sup>-1</sup> are also present. They represent the alkanes and C-C stretching. The intensity of the peak at 2868.6 cm<sup>-1</sup> is less compared to the graph 1. This is mainly because of the symmetric stretching of the -OH group of the absorbed water which decreases due to the addition of cross linker [78].

The graph of sample 3 shows small intensity peaks at wavenumber  $534\text{ cm}^{-1}$ . The other peaks at  $724$ ,  $1384.8$ ,  $1465\text{ cm}^{-1}$  are also present. The intensity of peak at  $2839.7\text{ cm}^{-1}$  increases again due to the addition of nanoclay.

The graph of sample 4 shows small intensity peaks at wavenumber  $725.6\text{ cm}^{-1}$ . The other peaks at  $805$ ,  $995$ ,  $1163\text{ cm}^{-1}$  represent the vibration due to the C-C alkanes and C=C alkenes bond. Addition of silica leads to the Si-O-H-Si vibration due to the hydrogen bond of Si-O-H group [79].

The graph of sample 5 shows peaks at  $724$ ,  $1179.3$ ,  $1369.2$  and  $1463.7\text{ cm}^{-1}$ . These were again due to the  $\text{CH}_2$  stretching. The intensity of the broad peak at  $2847\text{ cm}^{-1}$  further decreases which shows the addition of  $\text{TiO}_2$  led to a slight decrease in hydrophobic character.

The overall inference that can be drawn is that the particles were well dispersed and the addition of cross linker slightly modified the membrane property.

### 4.3 PERVAPORATION STUDIES:

To study the application of the polyethylene polypropylene composite membrane pervaporation was done. To check separation performance ethanol- water mixture was used. The mixture was passed through the different membranes at different feed concentrations and the performance was noted. Several compositions of ethanol-water mixture were used to measure the flux of ethanol across the membrane in order to study the performance of prepared membranes. The flux is shown along with the change in concentrations in the figure.

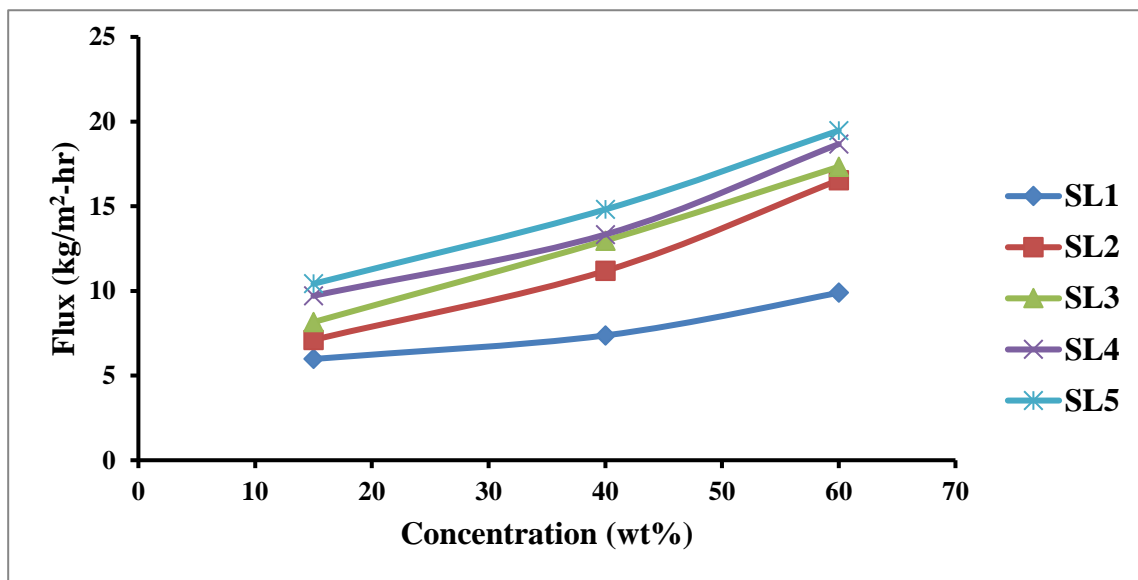


Fig 19: Effect on flux of various membranes and feed concentration

Table 6 : Flux variation with concentration change

MEMBRANE	SL1	SL2	SL3	SL4	SL5
Concentration(wt%)	Flux 1	Flux 2	Flux 3	Flux 4	Flux 5
15	5.98	7.11	8.16	9.71	10.42
40	7.37	11.18	12.97	13.34	14.81
60	9.89	16.54	17.33	18.67	19.47

The above table shows the change in flux of different membranes with respect to change in concentration. The membranes were subjected to concentration of 15%, 40% and 60% respectively.

From the figure it can be deduced that the flux of the membranes are in the order of

$$SL5 > SL4 > SL3 > SL2 > SL1$$

The membranes are made of different cross linkers and fillers. A particular membrane is passed through three different concentrations. It can be seen that on increasing the feed concentration the flux of the membranes increases. Also, it can be seen that the flux increases with the change in the filler added.

The membrane SL1 made of polyethylene-polypropylene shows the least amount of flux. On addition of the plasticizer diethyl phthalate the membranes plasticity increases and the viscosity decreases. Thus the flux is increased. This can be observed in membrane SL2 which shows enhanced property compared to SL1. The membrane SL3 has been made by addition of nanoclay. This gives excellent composite morphology and hence the flux has been further enhanced. The membrane prepared by the addition of silica is SL4. The presence of silica provided a barrier to the movement of water but the flux increased on account of the increase in the amount of ethanol collected [80]. Similarly the addition of Titanium dioxide led to an increase in flux because of the increase in ethanol collected. The density of the membrane also increased.

It was found that on using membranes of higher concentration of fillers added the flux further decreased because the fillers acted as a barrier for swift movement of the permeate at higher concentrations. The water flux also varied through these membranes. Thus the selectivity increases with the increase in concentration of feed but the degree of separation decreased at higher ratios.



### 4.3.1 Fourier Transform Analysis of the permeate(FTIR Analysis):

The flux of the membrane was determined as shown above. But the main objective is to determine the best membrane for permeation as the membrane which gives the maximum flux may not necessarily give the maximum amount of ethanol. To determine the best membrane for pervaporation of ethanol-water mixture FTIR analysis of the permeate was done. The ethanol-water mixture was passed through the membrane and based on the amount of the permeate collected FTIR of the permeate gave peaks of ethanol and alkanes.

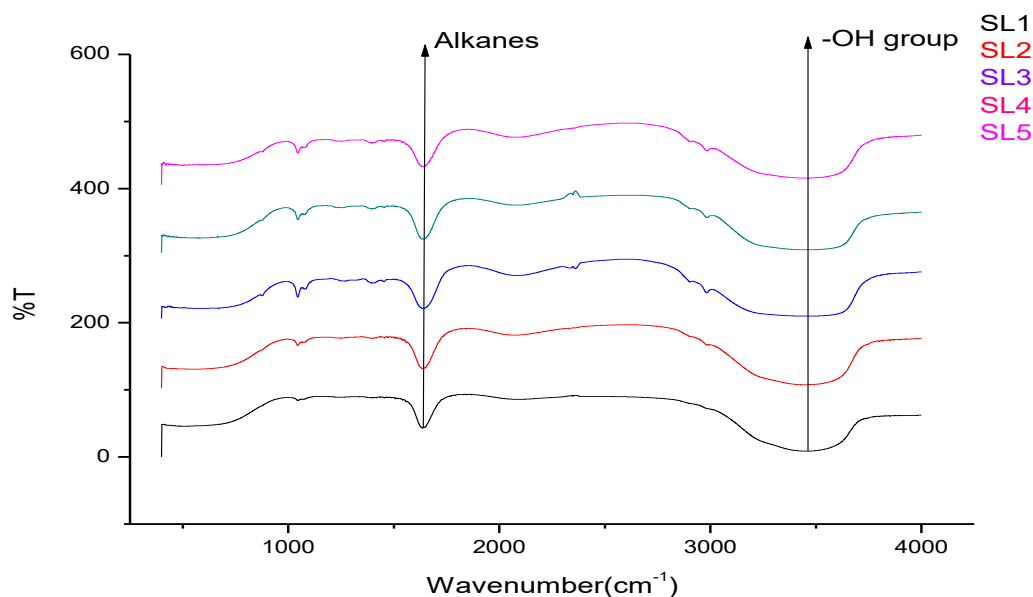


Fig 20: FTIR peaks of the permeate collected

From the figure we can see peaks at wavenumber  $1647.8\text{ cm}^{-1}$ . This shows the presence of alkanes. The peaks of  $\text{-OH}$  group can be found in the range of  $3400\text{ cm}^{-1}$  to  $3640\text{ cm}^{-1}$ . From the graphs we can deduce the curve of the membrane SL3 consist of the widest  $\text{-OH}$  group curve. A small peak is found at  $1026\text{ cm}^{-1}$ . This is followed by the presence of small peaks at  $2258$  and  $2973\text{ cm}^{-1}$ . All these peaks show the alcohol alkene stretch [22,25,81]. Slight variation can be observed in the peak of SL4 and SL5 which are less efficient compared to SL3. Thus the sequence of the permeate collected is

$$\text{SL3} > \text{SL5} > \text{SL4} > \text{SL2} > \text{SL1}$$

Thus the SL3 membrane made of polyethylene-polypropylene composite with cross linker nanoclay and plasticizer diethyl phthalate is the best membrane for the above ethanol- water pervaporation separation process.



Fig 21.1: Figure shows the permeate collected after pervaporation

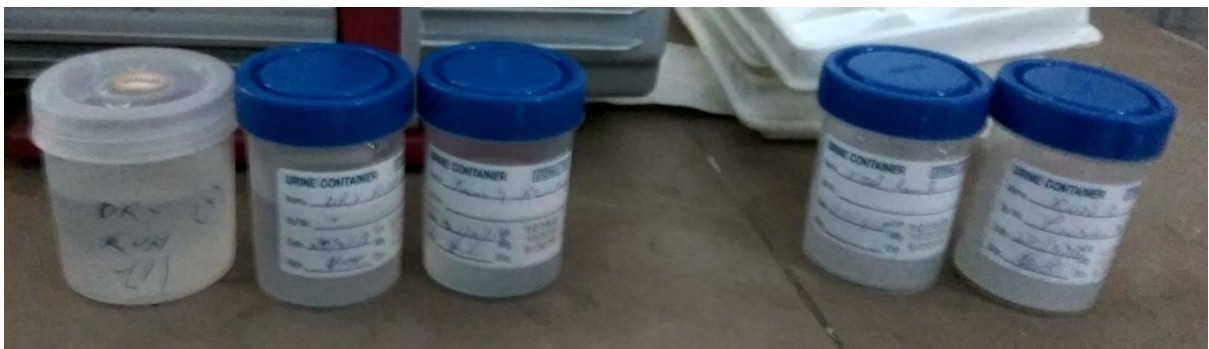


Fig 21.2: Figure shows the permeate collected and the feed sample

### **4.3.2 REFRACTIVE INDEX TEST ANALYSIS (RI TEST):**

A refractive index test was conducted to determine which membrane gave the maximum mass fraction of the permeate. For this standard samples were prepared of ethanol water mixture. The refractive index was noted. A reference graph was plotted for change in mass fraction of ethanol with RI.

Table 7: Refractive Index of standard samples

Sr No.	Sample	Mass fraction of ethanol	Refractive index
1	Pure ethanol( 10 ml)	1	1.359
2	Pure Distilled water	0	1.330
3	1 ml ethanol+ 9 ml distilled water	0.0806	1.335
4	2 ml ethanol+ 8 ml distilled water	0.1647	1.340
5	3 ml ethanol+ 7 ml distilled water	0.2527	1.343
6	4 ml ethanol+ 6 ml distilled water	0.3447	1.348
7	5 ml ethanol+ 5 ml distilled water	0.4410	1.350

8	6 ml ethanol+ 4 ml distilled water	0.5421	1.353
9	7 ml ethanol+ 3 ml distilled water	0.6482	1.357
10	8 ml ethanol+ 2 ml distilled water	0.7594	1.358
11	9 ml ethanol+ 1 ml distilled water	0.8760	1.359

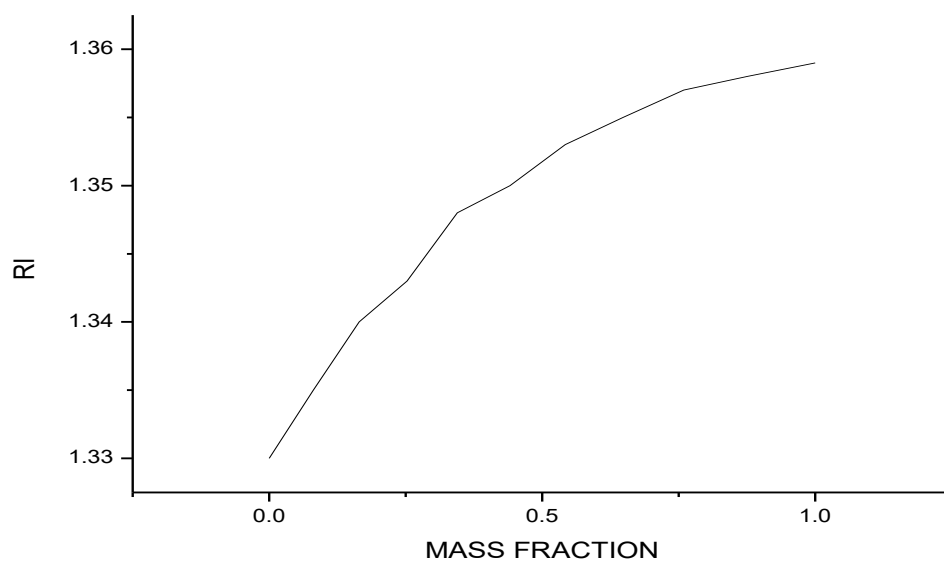


Fig 8: Reference graph showing the mass fraction variation with time

RI of the permeate is obtained. Using the reference plot the corresponding mass fraction of the permeate is obtained. The mass fraction of ethanol obtained for different permeate samples are:

Table 8: Variation of mass fraction of ethanol in permeate with RI

Membrane	RI	Mass fraction
SL1	1.336	0.0422
SL2	1.338	0.0772
SL3	1.356	0.7464
SL4	1.350	0.2183
SL5	1.353	0.5352

The results of mass fraction obtained from the refractive index test analysis confirms that the membrane in decreasing order of ethanol composition are:

$$SL3 > SL5 > SL4 > SL2 > SL1$$

Thus we can conclude that membrane SL3 is best for pervaporation process of ethanol water mixture.

# **CHAPTER 5**

# **CONCLUSION**

## **CONCLUSION:**

Hydrophobic Polyethylene Polypropylene membrane was prepared by solution casting method with varying fillers concentration. The increase in the filler/cross linker to pre-polymer ratio in the membrane increases the hydrophobicity of the membranes. The thickness of the membrane also varied due to the different composition used. The roughness of the membrane increased on addition of different fillers. Some molecular clusters or aggregates were also observed. This trend can be deduced from the SEM images. From the XRD curve it was observed the different additives did not overall change the peaks. Though the intensity of the peaks varied to small amount but the range of  $\Theta$  was almost same. This curve showed the transformation of the membrane from crystalline to amorphous. Membrane structure density increased with the addition of cross linker to polymer ratio. From the FTIR images sharp peaks in the different range show the presence of  $-CH$  stretching and also the presence of symmetric stretching band  $-OH$  for absorbed water that decreased with increase in cross linker ratio, supporting the observation of increase in hydrophobicity with increase in cross linker to polymer ratio.

To study the application of the prepared PE/PP polymer composites pervaporation was performed. Ethanol-water mixture was used as the feed and the permeate collected was examined. The ethanol flux through the membrane increased with the increase in cross linker to pre-polymer ratio but at higher concentrations it creates defects in the membrane giving increased water flux together with high ethanol flux. Feed composition showed a great impact on separation process. By increasing the amount of ethanol in the feed mixture, the flux of water and ethanol increased. The membrane prepared with  $TiO_2$  filler gave the maximum flux. Also the membrane prepared by adding plasticizer diethyl phthalate and nanoclay gave the best pervaporation result for 60% concentration. FTIR analysis of the permeate confirmed the above results. Also the RI test gave the same result.

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