Thermoplastic Polyurethane – Polyaniline (TPU-PANI) Composite Membranes for Electrochemical & Electrodiaylsis Applications

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Synthesis and Characterization

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2017-MS-CH-46

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A thesis submitted in fulfilment of the requirements for the degree of Master of Science in Chemical and Engineering. The University of Engineering & Technology, Lahore.

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A THESIS SUBMITTED IN THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF ENGINEERING AND TECHNOLOGY LAHORE, IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMICAL ENGINEERING

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Dedication

I dedicate this thesis to my parents.

Abstract

Intrinsically conducting polymers (ICPs) based composite ion exchange membranes have gained the attention of researchers and industry because of their unique properties which include high electrochemical, optical and electrical conductivity properties. Their ease of processing, low production cost and thermal and mechanical stability make them a valuable choice for various applications.

In the present study, PSS/DVB incorporated polymer matrix (Thermoplastic polyurethane, TPU) membrane has been modified with polyaniline (PANI) as a conducting component of membrane, using in-house built two-compartment permeation cell technique. The deposition of PNAI in bulk on ion exchange membranes using two-compartment permeation cell is performed for the first time in this study. The intercalation of PANI in membrane matrix was controlled by varying time of polymerization (2, 4 and 8 hours). Pristine (TPU-PSS/DVB) and PANI modified heterogeneous cation exchange membranes (TPU-PANI) were characterized for their surface morphology, physical, structural and electrochemical properties by using scanning electron microscopy (SEM), measurement of water uptake and ion exchange capacity, electrical conductivity and transport number measurements, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) and electrodialysis.

Membrane surface morphology was studied by using scanning electron microscopy (SEM) whereas the gravimetric method was used to evaluate PANI intercalation levels in the composite membranes. Increase in the values of intercalation levels with increased polymerization times show the deposition of PANI in the bulk of the membrane as high as 24% (w/w). Increased PANI coating on membrane matrix resulted in lower water uptake and lower ion exchange capacity values with increased aniline polymerization time. Excessive PANI layering resulted in loss of hydrophilic ion exchange particles because of hydrogen bonding between PANI and sulfonic acid functionality of the resin ($-SO3^-$). Reduction in ion exchange capacity values occurred due to the replacement of H^+ ions with secondary amine group in PANI. Increased values of electronic conductivities with prolonged polymerization times showed the presence of PANI in emeraldine salt form as it is the only conducting form of PANI. TGA curves showed the

overall decrease in the thermal stability of PANI modified membranes. Electrochemical study in a two-compartment permeation cell showed a decreasing trend of transport numbers with increased polymerization time for monovalent ion and increasing trend of transport numbers for divalent ions. The transport number of Ca^{+2} found significant lower as compared to Na^+ ions. This trend can be attributed to the smaller radius of sodium ions as compared to calcium ions. Hence, membranes are more permselective for Na^+ at 2 hour polymerization time. Trends of % salt rejection of composite membranes using electrodialysis were also in accordance with trends of transport number. Membrane with high transport number showed the maximum increasing trend of % salt rejection that decreased with increased deposition time.

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Chapter One

Introduction

1.1. Membrane Based Separation Processes

A process that converts the mixture of substances into its distinct products, and sometimes fully distributes the mixture into its pure constituent elements, is called the separation process. Separation processes are performed based upon their physical and chemical properties difference like mass, size, charge, shape chemical affinity, density freezing and boiling points. Separation processes include liquid-liquid extraction, gas serration, leaching, distillation etc. For the purification of raw material and products, these processes play essential role for process industry. But there are boundaries to these processes as well. Depending upon their nature, phase change, transference of species across different phases, high energy demanding and phase equilibrium are the limitation associated with these processes.

Membrane separation processes have grown from simple laboratory scale development to an industrial level application [1]. Membrane based processes are implementing on a large scale applications e.g. in reverse osmosis to converts sea water in portable form, in electrodiaylsis to clean effluents producing by industry, in ultrafiltration to fractionate macromolecular solutions in the food and drug industry, and in dialysis to lean blood stream from urea and other toxins in artificial kidney etc [2].Membrane based separation processes are emerging in the field of separation industry and give many advantages such as non-equilibrium transference across the phases, efficient energy utilization, low temperature operation, easy scale up, recovery etc [3].

A large number of separation process which are integral part of process industry, come under the cover of membrane separation processes. In these processes, the important performance parameters of membranes such as selectivity, porosity and charge are the essentials to separate a solution mixture into its components. During the permeation process, retention/rejection size of the particles is the factor that can be made base for the classification of membrane based

processes of separation [4]. In membrane based separation processes, the feed can be separated into two streams. The one is permeate that passes through the membrane and the other one that is not passed through membrane is retentate. Classification criteria for membrane separation processes, depends upon size of the particles needs to be separated and magnitude of given driving force [4].

Based upon driving forces i.e. pressure, vapour pressure, concentration and electrical potential the membrane based separation processes are classified as follows :
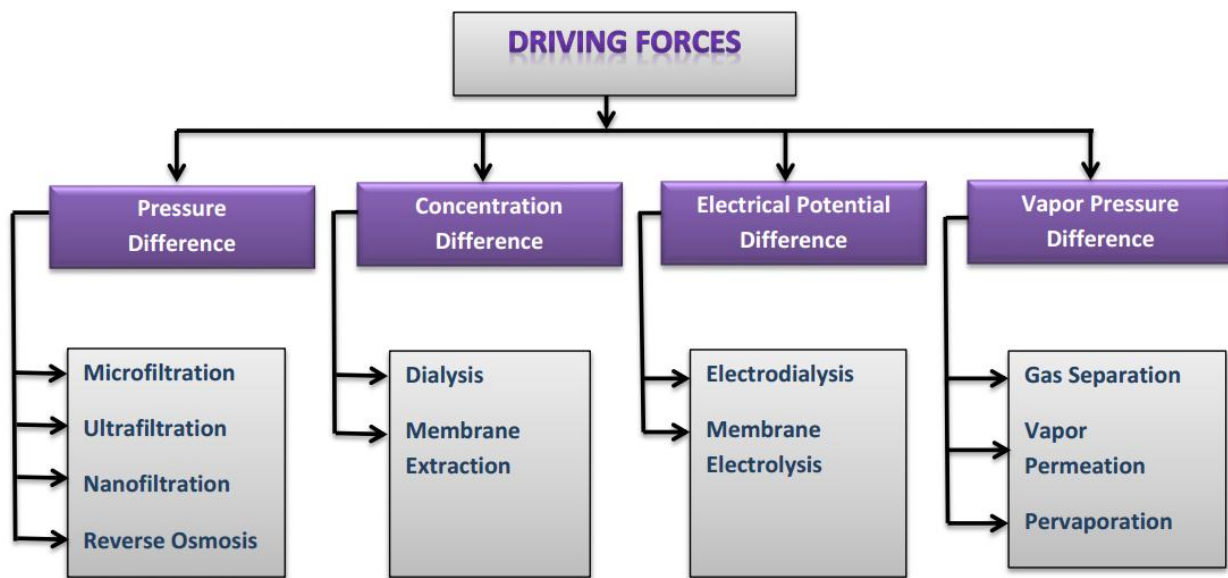
Figure1.1: *Classification of membrane processes based on driving forces.* [5]

Micron and submicron level particles can be easily separated using pressure driven microfiltration membranes. These membranes used as pre-filters for the suspended particles i.e. suspended solids, microorganisms and emulsion droplets and they are retained by a sieving action [6]. Reverse osmosis, on the lower side, is such a pressure driven process that is utilized to make water salt free, while the pervaporation process is used to separate solvent (short-chain) molecules. Governing mechanism in MF, UF and NF membranes is based upon size exclusion that is based upon sieving effects, while mechanism in RO and PV is solution diffusion that is based upon solvating tendency and rate of diffusion in bulk membrane.

Whereas for the processes, where interaction between permeating species and fixed charges is

required to achieve separation charges membranes are used. In these membranes, polarity of the ions which are embedded in the membrane structure is an important factor to allow permeation for counter-ions and exclusion of co-ions. The separation processes i.e. dialysis, electrolysis and electrodiaylsis are based upon ion exchange strategy. For salt and alkali production electrolysis process is employed where deposition takes place through electrochemical reaction. In dialysis the driving force is difference in concentration. Whereas for electrodiaylsis based separation process electric current is applied across ion exchange membrane.

Permeation flux and selectivity are the two important performance parameters in membrane separation processes. In any process where membranes are employed for separation, theses performance parameters are of major concern. As these parameters are inversely proportional to each other, it is always required to achieve trade-off between them to make any process economical [6]. In order to achieve desirable properties, different materials have been utilized and different processes have been adopted for the synthesis of membranes. Polymeric or the organic materials are widely used for this purpose. Inorganic materials have also been utilized; however polymeric materials have gained more interest because of their easy processing and tunable properties suitable for a particular application [6].

1.2.   Membrane Technology: Challenges and Prospects

Membrane technology for the application of water treatment owes much to the German nation for the pioneering work, back to mid-19th century [1]. As a unique purification and separation technology, membrane based processes have been widely used and play important role in number of domains including treatment of industrial waste water, dyes industry, recovery of salt from sea water and desalination of brackish water [2]. Along with serving as a novel separation and purification technology to these domains, membrane technology also helps towards cleaner production, environmental protection and energy recycling. Membrane technologies are vital in the development of sustainable commercial processes [2]. As compared to other typical separation processes such as distillation and drying, membrane separation processes are least energy intensive because membrane processes do not require phase changes and do not require additives and can also be performed at low temperatures [4].

At present the membrane technology is broadly applied for the treatment of wastewater. Though, the advanced level research and innovations in the membrane separation processes have made this technology the most emerging and desirable one based upon diversity of applications in every industrial zone. But still there are few challenges to selects the membrane technology in terms of operational complexities and maintenance cost, because it requires a high level of vigilance to keep the membrane surface clean for smooth operation. Hence these challenges are yet to be comprehensively addressed [7].

Separations in non-porous or dense membranes is usually determined based on solution diffusion model which involves two step mechanism i.e. initially the absorption of molecules into the membrane followed by diffusive transport under chemical potential gradient. The efficiency of the membrane for separating a binary mixture in generally defined in terms of selectivity i.e. normalized fluxes ratios ($\alpha_{A/B}$) with respect to the driving forces across the membrane. To obtain the membranes with enhanced selectivity, a well-established approach is to modify structural and chemical. This approach affects the physical mechanisms associated with solubilities and diffusivities of the membrane mixture [7]. Fast development in membrane technology is because of the growing awareness on the potential of this technology. Several gains of membrane technology like high separation capacity, energy efficiency, reduction in a number of unit processes, high selectivity and low cost make this technology suitable in numerous applications [8]. These advantages of membrane based processes have bound industries to evaluate their production procedures and capitalize in membrane technology to improve the performance of manufacturing processes and to save production cost [8].

1.3. Scope of Intrinsically Conducting Polymers (ICPs) in Membrane Technology

Intrinsically conducting polymers (ICPs) that are used in membrane separation technology have become an important area of R&D (research and development) for worldwide researchers. Since last few decades, this unique class of polymers has been developing from a unique science to a new emerging technology [8]. ICPs are gaining attraction in membrane separation processes mainly due to their high range of electrical and electrochemical properties, simple processing and the choice of both chemical and electrochemical synthesis [9]. ICPs are a fascinating class of polymers which exhibit many interesting features such as high electrical conductivity,

electrochemical activity and switchability in the properties upon doping and undoping [10]. Several ICPs i.e. polypyrrole & polyaniline, have been utilized to regulate the transport of liquid and gasses by altering the polymer's oxidation state [10]. Their versatility of synthesis makes them potentially suitable material for the synthesis of membranes. They can be easily synthesized as pristine films, in the form of layers or as a thin film on substrates (polymeric materials) [11]. Selective mass transport characteristic is another important feature of ICPs based upon their chemical tenability [11].

Performance of membrane is linked with its ability to regulate and prevent permeation of counter and co ions [12]. Separation by selective permeation is rapidly growing process of membrane technology. Therefore, there is need to develop such polymers that carry the properties of higher permeabilities as well as enhanced selectivities [13]. ICPs are new class of polymers and strong interest exist in design and development of ICPs based membranes due to their extensive range of separation application [14]. Pristine ICP or membranes modified with ICPs are utilized in different separation processes such as pervaporation, gas permeation and electrodiaylsis [15]. Figure 1.3 is summarizing the scope of ICPs to membrane technology

Figure 1.2: Scope of ICPs in Membrane Technology.[2]

ICPs exhibit different oxidation states and phenomena of absorption and desorption of doping anions causes each of the oxidation states to exhibit different morphology. Generally, in lower oxidation state ICP exhibits compact film structure while higher oxidation state results in loose structure. Separation processes based on the size-exclusion such as gas separation and nanofiltraion, have been utilized this variation in the morphology of ICPS. In case of pervaporation separation depends on the solution-diffusion based interaction between permeating

species and membrane structure. The use of ICPs enhances the solvent-polymer interaction owing to the electrochemical activity of ICPs that result in the increase of selectivity [16]. Apart from membrane based applications, barrier properties of ICPs have extensively been utilized in non-membrane applications such as corrosion resistant coating, ICPs modified electrodes and electrochemical and biological sensors [16]. Different techniques are employed to synthesize pristine ICP or ICP based composite membranes including the processes that are employed in the development of conventional membranes. These synthesis methods include in situ and electrochemical polymerization, grafting, and polymer blending.

Though ion-exchange membranes have made their application space in every industrial sector but still there are few limitations because of a high areal resistance, fouling, low permselectivity and high fuel crossover [16]. Hence to achieve IEMs with better characteristics and enhanced performance selection of material, additives blending having specific properties and surface modification are the several ways that can be adopted to improve the properties of IEMs [16]. Among these approaches that are used for enhancing the performance of membrane, surface modification is the one that has been proved to be the most authentic and heavily used method to obtain membranes with better desired properties. This is a well-established fact that a membrane that is designed properly can enhance the performance of membrane based processes [16][17]. Ion exchange membranes modified with intrinsically conducting polymers have been established to have enhanced performance in terms of permeability and selectivity [14]. High electrical conductivity, electrochemical activity and switchability between oxidation and doping states are the characteristics that make ICPs worth using in ion exchange membrane separation processes. These membranes covers vast areas of application including treatment of drinking and waste water, preparation of ultrapure water, gas separation, sensors and biosensors, fuel cells etc. [14].

Among common ICPs and their derivatives such as polypyrrole (PPy), polythiophene, polyacetylene (PAc), (figure 2.3) PANI has been utilized the most. The reasons include its environmental stability [10], electrical conductivity, interesting redox properties [14], crystallinity [11], and processability [14]. Based on the above mentioned unique properties, PANI was selected as active conducing component of the composite membranes in the present thesis.

1.4. Objectives of the Present Research

The experimental strategies are designed in the present study with the aim to achieve the following objectives:

- To study the controlled and desired level PANI deposition in the bulk of the composite membranes matrix at different polymerization times using chemical oxidative polymerization technique by utilizing the two-compartment permeation cell technique for the first time.

- Enhancement of the selectivity and conductivity of heterogeneous cation exchange membranes by utilizing the electrochemical characteristics of conducting polymers (PANI in this study) to be incorporated in membrane matrix.

- Analysis of the allied effects of PANI deposition on physical and structural properties of the composite membranes.

1.5. Scope of the Present Research

The scope of this work involves the experimentation and discussion on the following aspects :

- Synthesis of heterogeneous cation exchange membrane using solution casting technique.

- PANI deposition on the base membrane for different times using two compartment permeation cell

- Structural and thermal characterizations using scanning electron microscopy (SEM), Fourier-Transform Infrared (FTIR) Spectroscopy (FTIR) and thermogravimetric analysis (TGA).

- Membrane performance measurement using water uptake, ion exchange capacity, membrane potential, transport number, electronic conductivity and electrodiaylsis.

Chapter Two

Literature Review

2.1. Electrodiaylsis- An Advanced Application of the Electromembrane Processes

Electrodiaylsis is a separation process which utilized electric potential as a driving force and established between both faces of semipermeable membranes [18]. Ions are moved according to electric field applied. Generally, cations head towards cathode and anions move towards anode. Ion exchange membrane (IEM) acts as selective barrier to ions. Cation exchange membranes permit cations and prevent anions. Opposite to this, anion exchange membranes permit anions while act as barrier for cations [19].
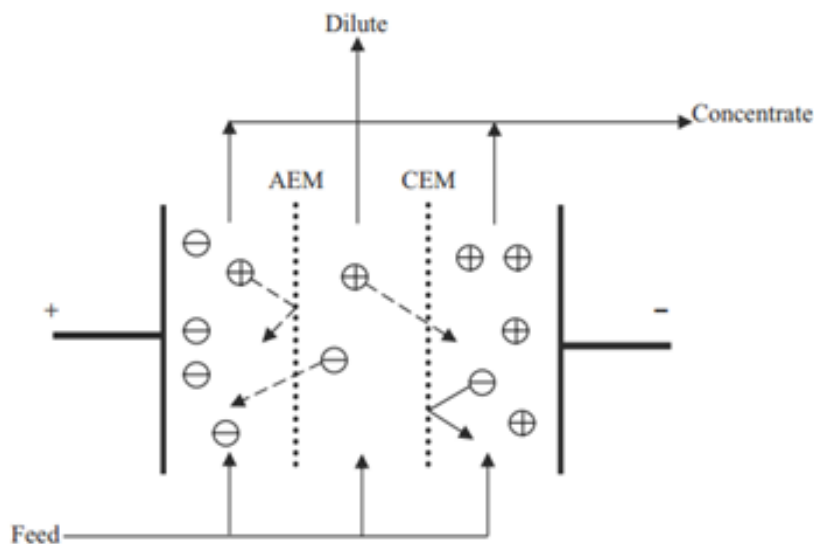
Figure 2.1: Schematic view of an electrodiaylsis cell.[20]

In 1890, Maigrot and Sabates proposed the concept of electrodiaylsis for the first time [20]. They did not use the term electrodiaylsis but established an initial concept by demineralizing sugar

syrup. They used carbon electrodes, permanganate paper as a membrane and dynamo for current supply [19]. In 1900, term electrodiaylsis found for the first time in a patent in which Schollmeyer adopted the same procedure to purify sugar syrup as Maigrot and Sabates but used zinc or iron anodes [21]. The literature reflects that the electrodiaylsis was not theorized completely until 1911. It is the year when Donnan presented his principle of exclusion. This principle claims that, it is possible to synthesize a membrane that is selective to anions with fixed positive charges and a membrane that is selective to cations with fixed negative charges [21]. Few years later, this exclusion principle was confirmed by Teorell experimentally. The advancement in electrochemical principles based upon ion exchange membranes opened the way to the development of an multiple compartments electrodialyzer [22]. However, multi-compartment electrodiaylsis concept was established in 1950, when W. Juda and W. A. McRay synthesized an ion exchange membrane using an ion exchange resin [21]. In 1954, Ionics (US) used these ion exchange membranes for first electrodiaylsis plant for Aramco (Saudi Arabia) [21]. After that electrodiaylsis technology has developed rapidly because of improvement in the properties of ion exchange membranes and better choice of materials [23].

Till the date a large volume of literature has been reported based upon electrodiaylsis derived processes, alternatives and end applications. It has provided a booster to the development of electromembrane technologies. Figure 2.2 is showing the timelines in which the important developments associated with electrodialysis and its related processes is reported.
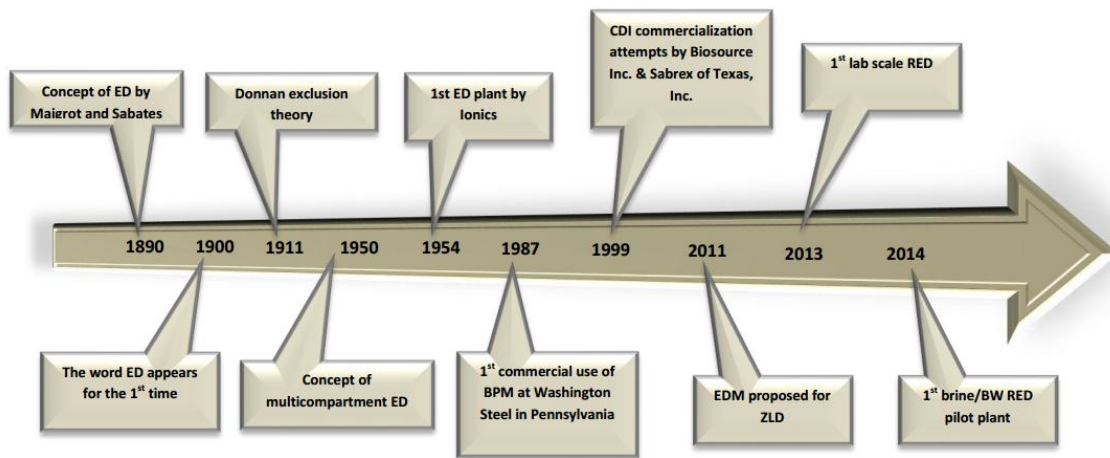
Figure 2.2: Timeline showing the significant developments in ED.[19]

Electrodiaylsis is an isothermal process with major applications in treatment of waste water, brackish water desalination and production of salt [3]. Electrodiaylsis can be operated in both batch and continuous mode. Batch mode is adopted usually for small scale operations [24] while continuous mode is more common on industrial level [3]. During electrodiaylsis process feed water is separated into product water (acceptably low conductivity and total dissolved (TDS) content) and concentrated or brine water (high TDS content) [23]. Application of electrodiaylsis in water treatment or water reuse has been focused in many studies. EDR based membrane desalination system to make municipal wastewater salt free was studies by Goodman et al. [25]. The objective of this study was to provide a recycled water source for agriculture. Hsu et al. [26] considered two lines of different processes (sand filter/ultrafiltration/reverse osmosis and sand filter/electrodiaylsis reversal) at the wastewater treatment plant of municipal water in Taiwan. He evaluated in terms of stability of the processes and quality of treated water. The results of this studies showed that electrodiaylsis is the cost effective separation technique. Phosphorous removal from municipal water using electrodiaylsis has also been reported [27]. Electrodiaylsis has been applied for the samples of municipal sludge, obtained from conventional wastewater treatment process [20].

In recent years, an extensive volume of research has been reported leading to the development of new membrane materials with high selectivity, high chemical and physical resistance and improved electric performance. Advancement in these areas has played a key role for the revival of electrodiaylsis operation and has also enhanced its possibilities of application at commercial level [18].

2.2. Ion Exchange Membranes: Properties & Applications

Different kind of membranes including microfiltration, ultrafiltration, nanofiltratin, reverses osmosis, pervaporation and electrodiaylsis membranes have been synthesized and commercialized [28]. Among all these membranes, one of the most developed and studied separation membranes is ion exchange membrane [29]. The advancements in the synthesis of ion selective membranes is the key factor in the expansion of the applications of electromembrane processes in which ion exchange membranes represent the key component [18]. Table 2.1 is showing the applications of IEMs for electromembane processes [30].

Table 2.1: *The applications of IEMs for electromembrane processes*

Methods	Ion exchange membranes	Applications
Electrodialysis	Cation, anion and bipolar exchange membrane	Concentration or desalination of electrolyte, separation of ionic material, production of acid and base by water splitting etc.
Electrolysis	Cation and anion exchange membranes	Separation of electrolytes
Diffusion dialysis	Anion exchange membranes	Recovery of acid from waste acid solution
Donnan dialysis	Cation exchange membranes	Recovery of trace amount of ions
Piezodialysis	Mosaic and amphoteric exchange membranes	Concentration, desalination and separation of electrolytes
Reverse osmosis	Anisotropic cation and anion exchange membranes	Concentration, desalination and separation of electrolytes
Facilitated transport	Cation and anion exchange membranes	Separation between ions with same charge
Cell and battery	Cation and anion exchange membranes	Electrolyte of fuel cell, reverse electrodialysis, separator of redox flow cell etc.

IEM for electrodiaylsis are classified as anion and cation exchange membranes based upon the negative and positive charges, respectively [3]. A cation exchange membrane (CEM) carries a negative charge and allows the counter-ions (positive ions) to pass through it, while acts as a barrier for co ions (negative ions). On the other hand, an anion exchange membrane (AEM) carries a positive charge and allows the counter-ions (negative ions) to pass through it, while acts as a barrier for co ions (positive ions). Usually quaternary ammonium groups impart fixed positive charge to AEMs [23].

Development of IEM based processes was initiated in 1890 by Ostwald. Ostwald studies the semipermeable membrane properties for the first time and analysed that a membrane can be impermeable for any electrolyte [2]. To describe this phenomenon, the membrane potential was postulated between a membrane and solution in it surrounding, as a result of difference in concentration. The existence of such boundary was confirmed by Donnan in 1911 and called as Donnan exclusion potential [31]. However, in 1925 the studies about ion exchange membranes principles were carried out by Michaelis and Fujita [32]. In 1940, synthetic ion exchange membranes were developed because of the growing interest in industrial applications [33]. Meyer and Strauss proposed process of electrodiaylsis with alternatively arranged cation and anion exchange membranes to form parallel compartment of solution using two electrodes [29]. At that time it was not feasible to move toward commercialization of this process because ion

exchange membranes with high stability and selectivity were not available. With the advancements of ion exchange membrane in terms of stability, selectivity and permeability in 1950 ion exchange membrane based electrodiaylsis processes became an important process for desalination of brackish water and concentration of electrolyte. Since that time, ion exchange membrane and electrodiaylsis have greatly been improved and substantially utilized in many fields [29].

The production of salt from seat water was first realized by Asahi Co. in 1960s, with ion permselective membranes (monovalent). In 1970s, sulfonated polytetrafluoroethylene based cation exchange membrane was first time developed by DuPont (Nafion). In similar years, Chlanda et al. [29] developed a composition of cation and anion exchange layer into a bipolar membrane which proved novel for the applications of electrodiaylsis [34]. With the improvement in the properties of IEMs in terms of electrical resistance, better selectivity, improved stability, application of IEMs have been grown from brackish water desalination to the industry of drug, food and chemical process industry including treatment of waste water [35]. Other than polymeric materials used in the synthesis of ion exchange membranes, inorganic materials such as bentonite, zeolites or phosphate salts can also be utilized to develop ion exchange membranes [29]. But IEM based on inorganic material are incompetent due to their high synthesis cost, and relatively poor electrochemical properties [36].

Based on their morphology, structure and synthesis procedures commercial IEMs can be classified into two major classes i.e. homogeneous and heterogeneous [2]. Three main manufacturing methods for homogeneous ion exchange membranes are monomer polymerization, imparting charged species on polymer based film and other method is to impart charged species into a polymer that is followed by melting of polymer and film casting [29]. Membranes based on styrene-divinyl benzene are notable examples of homogeneous membranes. These are used in electrodiaylsis applications widely where production of table salt by concentrating seawater [37]. Based upon second method of homogeneous ion exchange membrane development polypropylene and polyethylene are used as a polymeric materials [38]. Third method of manufacturing is concerned with soluble polymers [39]. These are important as they give choice for synthesizing cheap membranes for electrodiaylsis [40].

Microscopic size ion exchange particles are incorporated in a binding polymer for the development of heterogeneous ion exchange membrane [29]. Heterogeneous in exchange membranes are thicker membranes with good mechanical properties but poor electrochemical properties. They can be synthesized by using low cast polymer binders [40]. The development of heterogeneous ion exchange membrane is accomplished by adding powered ion exchange resins into polymer binder by three different procedures [19]. These procedures are calendaring, dry moulding and resin particle dispersion in the solution containing polymer binder followed by film casting and evaporation of solvent [29].

One major parameter that affects the mechanical properties of heterogeneous ion exchange membranes the most is the distribution of particle size. It is reported that by decreasing the particle size, the flexibility of membrane increases. On the other hand increase in the particle size results in brittle membrane [41]. Kariduraganavar et al. [42] and Adhikari et al. [29] studies that the different mesh size resin particles affect electrochemical and mechanical properties of the membrane. It is studies that a brittle membrane is formed by increasing the ion exchange resin powder loading while at the same time a flexible membrane is formed by incorporating the finer parties of resin [29]. Table 2.2 is showing the main producers of ion exchange membranes worldwide[23].

Table 2.2: The main producers of ion exchange membranes

Methods	Ion exchange membranes	Applications
Asahi Chemical Industry Co.	Japan	Aciplex
Asahi Glass Col. Ltd.	Japan	Selemion
DuPont Co.	USA	Nafion
FuMA-Tech GmbH	Germany	Fumasep
GE Water and Process	USA	AR, CR,
LanXess Sybron Chemicals	Germany	Ionac
MEGA a.s.	Czech Republic	Ralex
PCA GmbH	Germany	PC
Tianwei Membrane Co. Ltd.	China	TWAED
Tokuyama Co-Astom	Japan	Neosepta

2.3. Limitations of the Current Ion Exchange Membrane Technology

Ion exchange membranes are used in electromembrane processes as an ion-selective barrier. In the field of water and wastewater dealings and product purification and concentration, IEM-based methods have initiate many applications. With the growth of IEM technology, the focus is also at obtaining the membrane with simpler process and lesser cost of fabrication. Few limitations that are hampering the application of commercial IEMs are low selectivity, low electrical conductivity, high areal resistance and fouling. Hence, there is a need to adopt such approaches for the synthesis of IEMs that could impart best performance characteristics to membrane in terms of permeability, selectivity, conductivity etc [42].

Surface modification of membrane is one of the best methods to develop membrane with enhanced desired properties. Surface morphology of the membranes plays a key role in improving the performance parameters (high selectivity, transport number, permeability and electrical conductivity) of the membranes and it can be enhanced through surface modification. Intrinsically conducting polymers (ICPs) have widely been used as a surface modifying agents because of their unique properties such as corrosion resistance, high conductivity and high selectivity. [43]

In the past few years, research directed to the synthesis of ion-exchange membranes based on polymer composite either by various polymer blending or by adding inorganic/ion exchange material into the blend has taken considerable attention in both academic and industrial level [44]. IEMs based on conventional polymers offer improved characteristics as compared to their single-polymer material counterparts. Composite ion-exchange membranes are widely used in separation applications including electrolysis, fuel cells, electrochemical separations, solid polymer electrolysis etc [45].

2.4. Intrinsically Conducting Polymers as Surface Modifying Agents

Since the discovery of first ICP i.e. polyacetylene in 1976, ICPs are the centre of interest for the researchers and technologist because of their unique electrical and optical properties [45]. Conducting polymers contain conjugated π bond in their backbone which is responsible for delocalization phenomena. This delocalization produces conductivity by the formation of

polarons and bipolarons throughout the polymer chain [46]. The process of doping can be used to further increase the conductivity of the polymer [47]. The key features of conducting polymers such as conductivity, stability and ease of processing make them novel as compared to other conducting material such as carbon nanotubes (CNTs) and graphene oxide (GO) [48].

A large volume of research related to physical and chemical properties of intrinsically conducting polymers (ICPs) has been reported since the discovery of ICPs [49]. Intrinsically conducting polymers (ICPs), are technologically important materials because of their unique properties. These properties include change in the volume upon redox reaction, charge storage ability, change in colour with oxidation state and variation in porosities [50]. With these properties ICPS are used in applications such as polymeric batteries, membranes, actuator devices, ion exchange materials, smart windows, corrosion protection, anti-static materials, coatings etc. The end properties of ICPs are greatly based upon the condition adopted during their synthesis [50].

Along with the unique properties of ICPs there are also few problems associated with them which include poor solubility and yield and poor mechanical properties. These drawbacks of ICPs have restricted their applications in different fields like optical, solar and coatings devices [51]. To overcome these limitations, a number of methods have been suggested by researchers for their synthesis which involve the incorporation of ICPs in conventional polymers to develop their composite, copolymer blend and nanocomposite [45]. Development of composite material using conventional polymers is the most suitable approach to solve the above mentioned problems. In this approach base support of conventional polymer provides the desired mechanical strength and over layer of conducting polymer plays the role of active component of composite [43]. Hence these studies show that there exists a huge scope for the enhancement in the properties as well as end applications of ICPs.

There are many conventional polymers that have been used to serve the purpose such as epoxy, polyacrylates, polyurethane, alkyd etc. Among these insulating polymers thermoplastic polyurethane (TPU) is of versatile nature. It comprises of hard and soft segments [45]. It was synthesized by Otto Bayer for the first time in 1937. Unique properties of TPU include elongation, good elasticity, tensile strength, high impact, good weathering resistance, excellent

gloss, high abrasion resistance, colour retention and corrosion resistance properties [52]. These unique properties make TPU a good choice to utilize in the fields of furniture, elastomers, fibres, paints, coatings and adhesives [45]. But on the other hand TPU fails to hold these properties and under harsh condition of temperature and pressure and flops to give required thermal, mechanical and corrosion resistance performance [53]. Hence there is a need to make blend of TPU with such materials that can impart strong structural properties and make it resistible to even hard conditions. It is reported that the composite of PUs and CPs give enhanced mechanical, electrical and optical properties [51]. These modified composite materials overcome the above cited drawbacks. Hence, there is a good space of research on different PU/CP based composite materials.

Among number of ICPs such as polypyrrole (PPy), polythiophene, polyacetylene (PAc), as shown in figure 2.3, special interest has been focused on Polyaniline (PANI) because of its unique properties. These properties include high electrical conductivity, low production cost, good environmental stability and electrochemical, and optical properties [43].
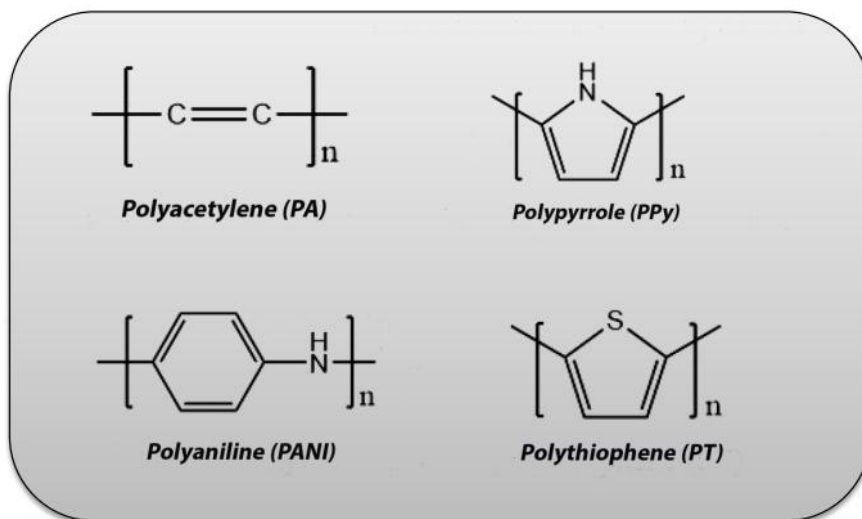
Figure 2.3: Molecular structures of common ICPs.

2.5. Polyaniline (PANI) as a Promising Conducting Polymer for Membranes

PANI among other organic conducting polymers has won a privileged role in the field of research and end applications. PANI is a conducting polymer, and it has received a considerable attention of researchers due to its high conductivity and potential application in electronics. PANI based composite materials have also been the part of studies because of their role in gas sensors, biosensors, electrodes and membranes [43].

PANI exists in three oxidation states namely, leucoemeraldine-base (completely reduced), emeraldine-base (partial oxidized) and pernigraniline-base oxidation state (completely oxidized). Upon doping/undoping PANI can be transformed from one state to another (figure 2.4). In all these oxidation states PANI exist as an insulating material except emeraldine-salt form. The formula for ideal PANI materials in its base form comprise of benzenoid units ($-C_6H_4-NH-$) and quinoid unit ($-N=C_6H_4=N-$) [54].

Figure 2.4: PANI transformation from one state to another upon doping/undoping.

There are different techniques that are utilized to deposit PANI layer on base membrane. These techniques include casting or spin coating, layer-by-layer technique (LbL), Langmuir–Blodgett (LB) technique, electrochemical deposition and in situ polymerization [55][56]. Among all the methods for the s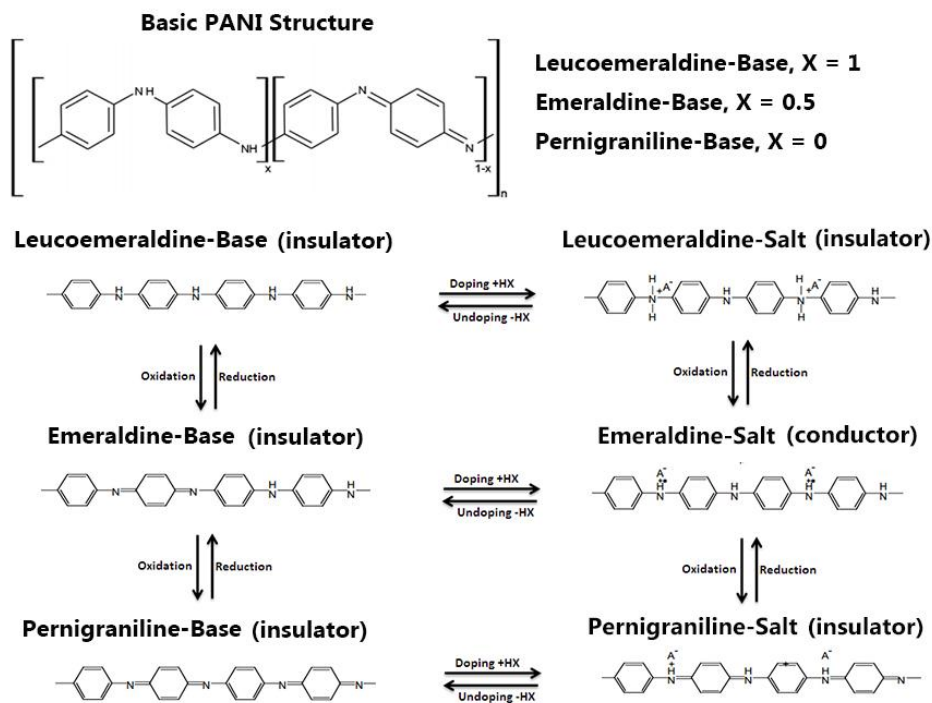ynthesis of PANI composite membranes, the one which has attained attention is chemical oxidative polymerization of aniline because of low cost and simplicity of procedure. It gives the provision to adopt different contacting patterns of substrate and species which is to polymerize. This diversity gives different site and extent for PANI deposition and consequently gives different permeability and different permselectivity properties of membrane. PANI intercalation in membrane depends upon the technique adopted for polymerization [56].

Numerous groups have done chemical polyaniline polymerization to modify ion exchange membranes to improve its properties. Usman et al. established ion exchange membranes based on PANI and thermoplastic polyurethane blends. The PANI nanoparticles were made using solution-phase chemical oxidation of aniline monomer [57]. In a study, deposition of PANI on Nafion has been examined with different ammonium persulfate (APS) concentrations. With higher APS concentration PANI was deposited on surface, while with lower APS concentration PANI was deposited in bulk [58]. In another investigation study, with various aniline chemical polymerization PANI- polyethylene terephthalate (PET) membranes synthesized. Utilizing different condition of polymerization gives unique morphologies of membranes. Using chemical polymerization of aniline method on porous polyethylene membranes PANI-polyolefin composite membranes have been synthesized. In another learning brominated poly(2,6-dimethyl-1,4-phenylene oxide (BPPO)) was used by changing MDPP content to synthesize anion exchange membrane. After synthesis these anion exchange membranes were employed to ED and compared with commercial anion exchange membranes [59].

Malik et al. synthesized unique heterogeneous IEM by depositing PANI on resin particles. Resin was poly styrene sulfonated divinyl benzene. The extent of PANI deposition was varied with changing time. The characterization results showed that PANI deposition had an effect on properties like morphology, water swelling, and thermal stability etc [60]. As compared to conventional polymers, PANI as a conducting polymer offers number of advantages specifically in terms of selectivity, flux and stability.

Chapter Three

Experimental

The focus of this research has been the investigation of the effects of polyaniline (PANI) deposition on thermoplastic polyurethane (TPU) based ion exchange membrane (IEM) and characterization of the resultant TPU-PANI composite membrane.

TPU was used as a base material for all the membrane samples. Polystyrene sulfonated divinyl benzene (PSS/DVB) was incorporated in the base membrane material to give it an ion exchange characteristic. PANI was deposited on the base membrane using two-compartment permeation cell technique. Unmodified TPU-PSS/DVB and modified TPU-PANI membranes were characterized using various techniques are discussed in this chapter.

3.1. Synthesis of TPU-PANI Composite Membranes

3.1.1. Materials

Polyester based thermoplastic polyurethane (TPU) film grade (68T series, Bangtai Polymeric New Materials CO. LTD) and polystyrene sulfonated divinyl benzene (PSS/DVB) commercial grade cation exchange resin (Purolite® C100E) were purchased from local market. Methyl-ethyl-ketone (MEK) (Daejung, Korea), hydrochloric acid (HCl) (Daejung, Korea), aniline ($C_6H_5NH_2$) (DaeJung, Korea), ferric chloride hexahydrate ($FeCl_3.6H_2O$) (Sigma-Aldrich), sodium chloride (NaCl) (Sigma-Aldrich), calcium chloride di-hydrated ($CaCl_2.2H_2O$) (Riedel-de Haen®), sodium hydroxide (NaOH) (Sigma-Aldrich), phenolphthalein (Merck®, USA) were all reagent grade and used as received. Throughout experiments distilled water was used.

3.1.2. Pre-Treatment of Cation Exchange Resin

(PSS/DVB) cation exchange resin was pre-treated to be incorporated in the TPU-MEK solution. Resin was kept in distilled water for 24 hours and grinded using pestle and mortar to pass through a sieve size of 400 mesh. Fine resin powder was dried for 24 hours at 40°C.

3.1.3. Preparation of Resin Incorporated Base Membranes (TPU-PSS/DVB)

TPU based ion exchange membranes were synthesized by solution casting and phase inversion method. TPU was dissolved in methyl ethyl ketone (MEK) solvent by stirring using magnetic stirrer at ~35^0C for 2 hours. The ground PSS/DVB resin was added in the solution and stirring continued for another 2 hours. The composition of this solution was comprises of 50% TPU and 50% resin of total solid content. Film applicator (Sheen®, UK) was used to cast this solution of 140-150 µm thickness on a cleaned and dried glass plate at room temperature. This cast solution was air-dried for 1 hours at room temperature. After air drying, the glass plate was immersed in a water bath. The membrane was peeled-off from the surface of the glass plate. The prepared membrane was then air dried at room temperature for around 2 hours.

3.1.4. Preparation of TPU-PANI Composite Membranes

Polyaniline (PANI) deposition was carried out on an in-house built two-compartment permeation cell technique at room temperature. The cell was made of two cylindrical compartments of 150ml capacity each. Both compartments were joined together with membrane as the separating wall between them. One compartment was filled with monomer (aniline) and other one with oxidant (Ferric Chloride). Aniline (0.8 M) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (0.3 M), were prepared in 0.4 M HCl aqueous solution. Then aniline and oxidizer solutions were given different times (i.e. 2, 4 and 8 hours) to polymerize and to counter-diffuse through the membrane, simultaneously to vary intercalation levels of PANI. The schematics of this setup are shown in Figure 3.1
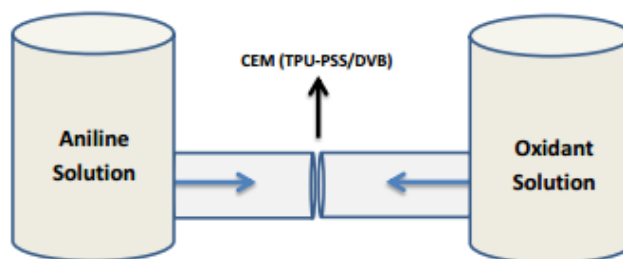

Figure 3.1 *Schematics of aniline polymerization in a two-compartment cell.*

3.2. Characterization of TPU-PANI Composite Membranes

3.2.1. Scanning Electron Microscopy (SEM)

Scanning electron micrographs of various TPU-PSS/DVB and TPU-PANI composite membranes were captured to study the surface morphology using FEI Nova 450 NanoSEM at various magnifications.

3.2.2. PANI Intercalation Levels Measurements

PANI deposition levels in the base TPU-PSS/DVB membrane were measured by using the gravimetric technique. The PANI intercalation levels were calculated by measuring weight difference between pristine and PANI modified membranes.

3.2.3. Fourier-Transform Infrared (FTIR) Spectroscopy

A number of spectroscopic techniques have been employed for the study of various materials but FTIR is more common to use because it offers high accuracy and sensitivity [61]. It is used as a chemical characterization technique to study chemical structure of the material. The advantage of simultaneous analysis of different frequency components in a single operation makes it a powerful technique [62]. The FTIR spectra of all the cation-exchange membranes were obtained using JASCO® FTIR 4100 spectrophotometer in attenuated total reflectance mode (ATR) in wavenumber ranging from 600-4000 cm^{-1}. Along with the verification of the presence of different chemical functionalities, FTIR also showed the presence of PANI layers.

3.2.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analyser (TGA) (Shimadzu Instruments, model TGA-50), was used to investigate the thermal stability of the membranes under a nitrogen atmosphere using a heating rate of $10°C$ /min from 25 to $600°C$.

3.2.5. Water Uptake Measurements

To measure water uptake, small pieces of all the membrane samples (about 1 cm^2) were immersed in distilled water for 24 hours and weighed (W_{wet}). The same pieces were then placed

in oven to dry for 24 hours and weighed (W_{dry}). Weight difference method was employed to calculate percentage water uptake. [61]

$$\% \text{ Water Uptake } = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{3.1}$$

3.2.6. Ion Exchange Capacity (IEC) Measurements

Method of titration was adopted to find the ion exchange capacity of the membranes. Small pieces of all the membrane samples (about 1 cm^2) were immersed in 1M hydrochloric acid (HCl) solution for 24 hours and then washed with distilled water to remove any excess H$^+$ ions from the surface of membranes. All the membrane samples were then placed in oven for 24 hours and weighed (W_{dry}). All the dried membrane samples were then soaked in 2M sodium chloride (NaCl) solution for 24 hours and titrated with 0.01M (C_{NaOH}) sodium hydroxide solution (NaOH) to determine equivalent volume (V_{NaOH}). Ion exchange capacity was calculated using the following formula [61]:

$$\text{Ion exchange capacity (meq/g)} = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \tag{3.2}$$

3.2.7. Electronic Conductivity Measurements

Standard four-point probe set up was used to find the electronic conductivity of the membranes. The set-up consists of a pair of current carrying outer probes and a pair of voltage sensing inner probes. Outer probes are connected with an ammeter (Keithley, Model 6220) for current supply and inner probes are connected with a voltmeter (Keithley, Model 2182A) for voltage measurement.

When the thickness of material is less than the half of the probes spacing, the resistivity is defined as [63]:

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot t \tag{3.3}$$

Where, ρ is the resistivity in ohm-centimeter, V is the voltage in volts, I is the current in ampere, t is the thickness of sample (membrane) in centimetre. Hence equation to find conductivity is:

$$C = \frac{1}{\rho} \qquad\qquad\qquad (3.4)$$

C is the conductivity in 1/ohm.cm.

3.2.8. Membrane Potential and Transport Number Measurements

Gamry® interface 1000 Potentiostat was used to measure membrane potential of the composite membranes. Two-compartment permeation cell was used where the membrane was interposed between the two halves as shown in figure 3.2. Sodium chloride (NaCl) and calcium chloride (CaCl$_2$) were used as an electrolyte to find transport number of composite membrane using membrane potentials. Platinum (Pt) electrodes were used in both halves of the cell to measure potential across membrane. The concentration of electrolyte was kept 1M in one half of the cell while concentration was varied from 1-0.001M in other half.
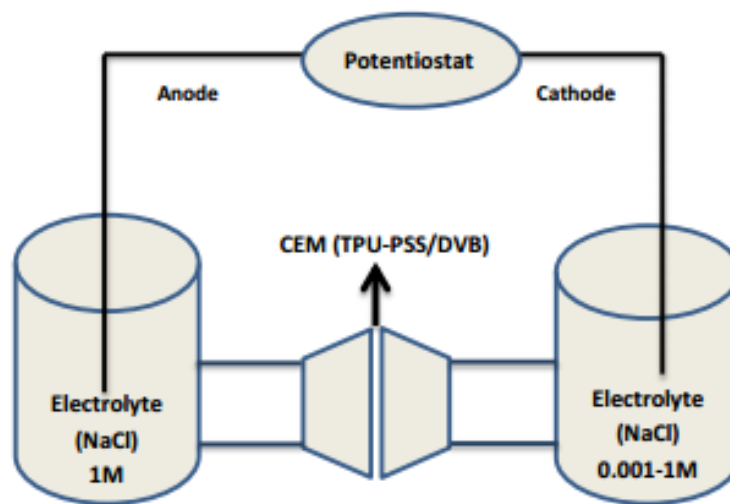

Figure 3.2: *Schematics of a two-compartment cell set up for membrane potential using Potentiostat.*

3.2.9. Electrodiaylsis Performance of the Membranes

Electrodiaylsis experiments were performed on a specially designed in-house built three-compartment electrodiaylsis cell to check the separation efficiency of TPU-PSS/DVB and TPU-PANI composite membranes. The cell was comprised of three compartments i.e. anodic, cathodic and middle compartment for the feed. For voltage application, platinum (Pt) electrodes were used. Synthesized TPU-PSS/DVB and TPU-PANI heterogeneous cation exchange membranes and commercial heterogeneous anion exchange membranes (supplied by Membranes International Inc. (model AMI-7001, IEC 1.3 meq/g by titration) were used for electrodiaylsis. Sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were used to prepare 3000 TDS solution used as a feed. Anodic and cathodic compartments were filled with distilled water while feed was introduced in the middle compartment. For electrodiaylsis experiments, DC voltage of 7, 8 and 10 volts (V) was applied. After each electrodiaylsis run, TDS content in each compartment was measured using HANNA portable TDS meter (model HI8734) and used as performance indicator of the electrodiaylsis cell. Electrodiaylsis experiments were evaluated in terms of percent salt rejection [64][65]. The schematics of this setup are shown in Figure 3.3.
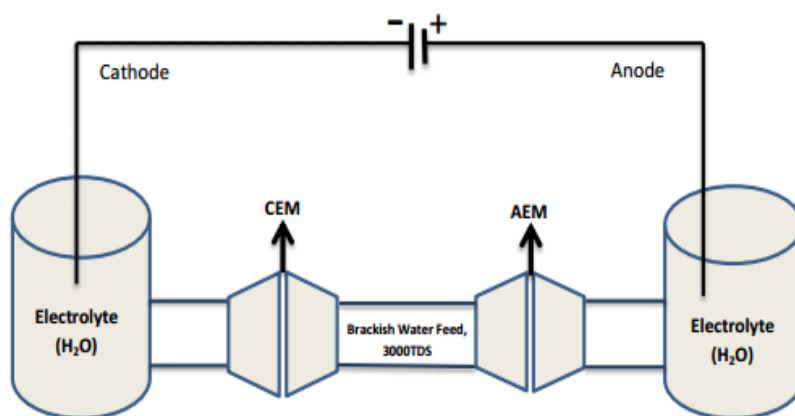
Figure 3.3: Schematics of electrodiaylsis set up.

3.3. Nomenclature

Table 3.1: *Nomenclature for TPU-PANI composite membranes*

Sr. No	Membrane Samples	Nomenclature to be used
1	Unmodified base membrane incorporating thermoplastic polyurethane and resin	TPU-PSS/DVB
2	Membrane modified with 2 hours polymerization time	TPU-PANI(2h)
3	Membrane modified with 4 hours polymerization time	TPU-PANI(4h)
4	Membrane modified with 8 hours polymerization time	TPU-PANI(8h)

Chapter Four

Results & Discussion

4.1. Scanning Electron Microscopy (SEM) of TPU-PANI Composite Membranes

Figure 4.1 is showing the SEM micrographs of pristine and PANI modified membranes surface at 2, 4 and 8 hours polymerization times at various magnifications.
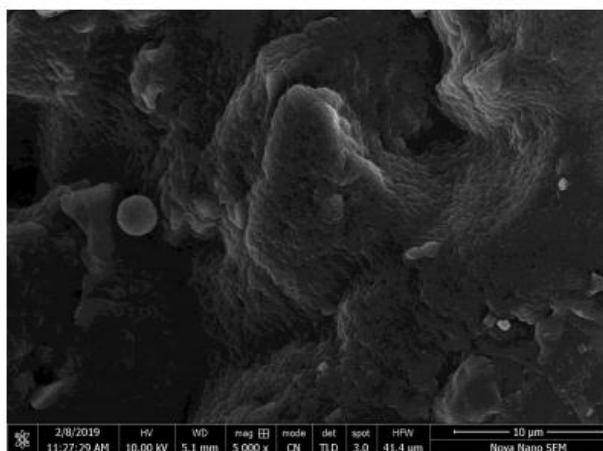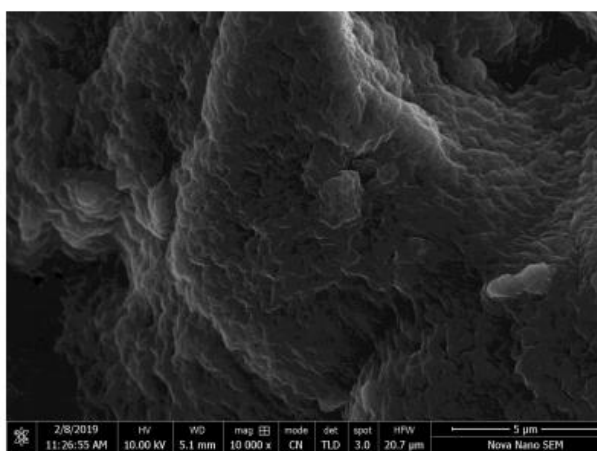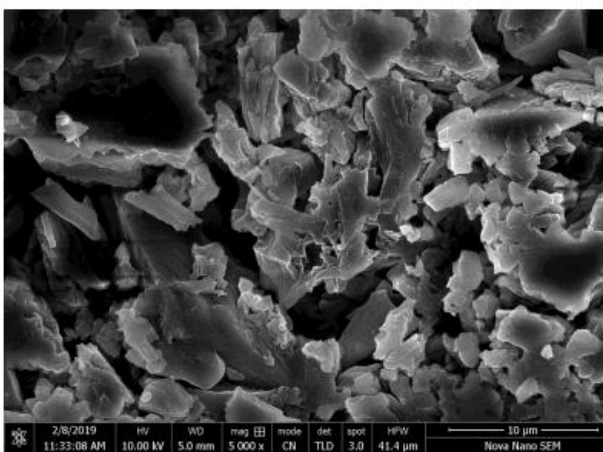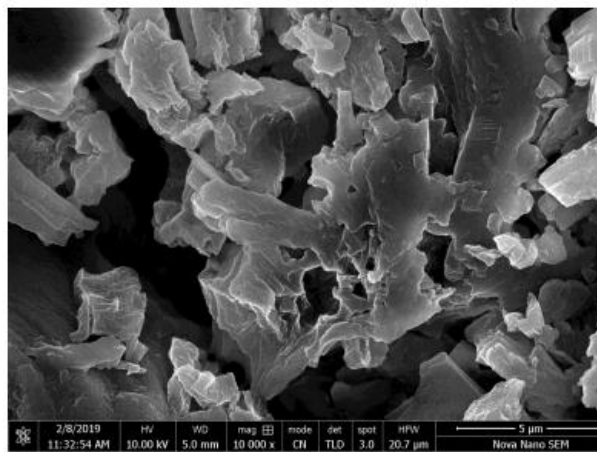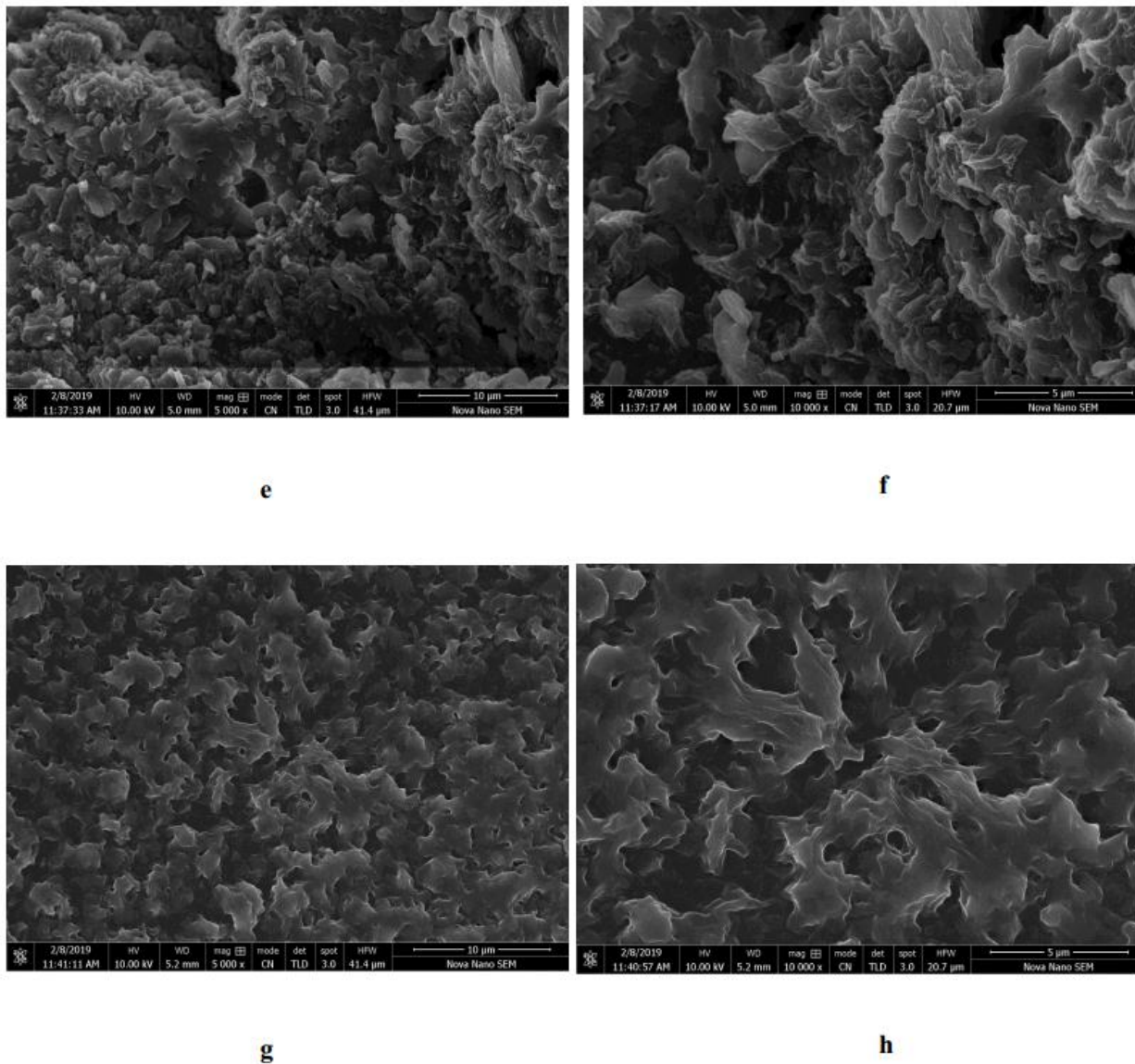
Figure 4.1: SEM micrographs of membranes surface at 5000 and 10000 magnifications, respectively, (a) & (b) pristine membrane (TPU-PSS/DVB); (c) & (d) TPU-PANI(2h); (e) & (f) TPU-PANI(4h); (g) & (h) TPU-PANI(8h).

SEM micrographs of pristine (TPU-PSS/DVB) membrane surface at 5000 and 10000 magnifications are shown in Figure 4.1(a) & (b), respectively. SEM micrographs are showing that it is not a smooth surface morphology. Base membranes synthesized in this study are dense membranes with rough surface. Polymerization of aniline was conducted by using $FeCl_3.6H_2O$ as an oxidant in a two-compartment permeation cell. In this technique the polymerization of aniline started on aniline-facing side of the membrane and the deposition occurred in a continuous

linked up manner from bulk to the surface of the membrane throughout the polymerization time. Initially the 2 hours polymerization time resulted in a more open or protruding rods type structure (Figure 4.1 c & d) and PANI deposition started to create channels/voids between TPU and resin particles. With increased polymerization time i.e. 4 hours, (Figure 4.1 e & f) PANI started to fill the channels. At 8 hour deposition time, PANI has completely covered the surface and resulted in a more compact structure (Figure 4.1 g & h).

4.2. PANI Intercalation Levels in TPU-PANI Composite Membranes

The intercalation levels of PANI in the base ME membranes are shown in Table 4.1.

Table4.1: *PANI intercalation levels in the composite membranes*

Membranes	PANI %
TPU-PANI(2h)	13
TPU-PANI(4h)	16
TPU-PANI(8h)	24

Table 4.1 shows that PANI intercalation level is dependent upon the aniline polymerization time. Increase in the values of intercalation levels with increased polymerization times show the deposition of PANI in the bulk of the membrane along with the surface deposition. SEM images show complete coverage of membranes surface for prolonged polymerization times (Figure 4.1 g & h).

4.3. FTIR-ATR Spectroscopy of TPU-PANI Composite Membrane

FTIR is a useful technique to identify functional groups and to analyse the surface characteristics of materials up to the depth of few micrometres [66]. The ATR-FTIR (attenuated-total reflectance Fourier-transform infrared) spectra of TPU-PSS/DVB and PANI modified TPU-PSS/DVB membranes are shown in Figure 4.2. These spectra show various characteristic IR peaks, which can be attributed to certain functionalities in the membranes.
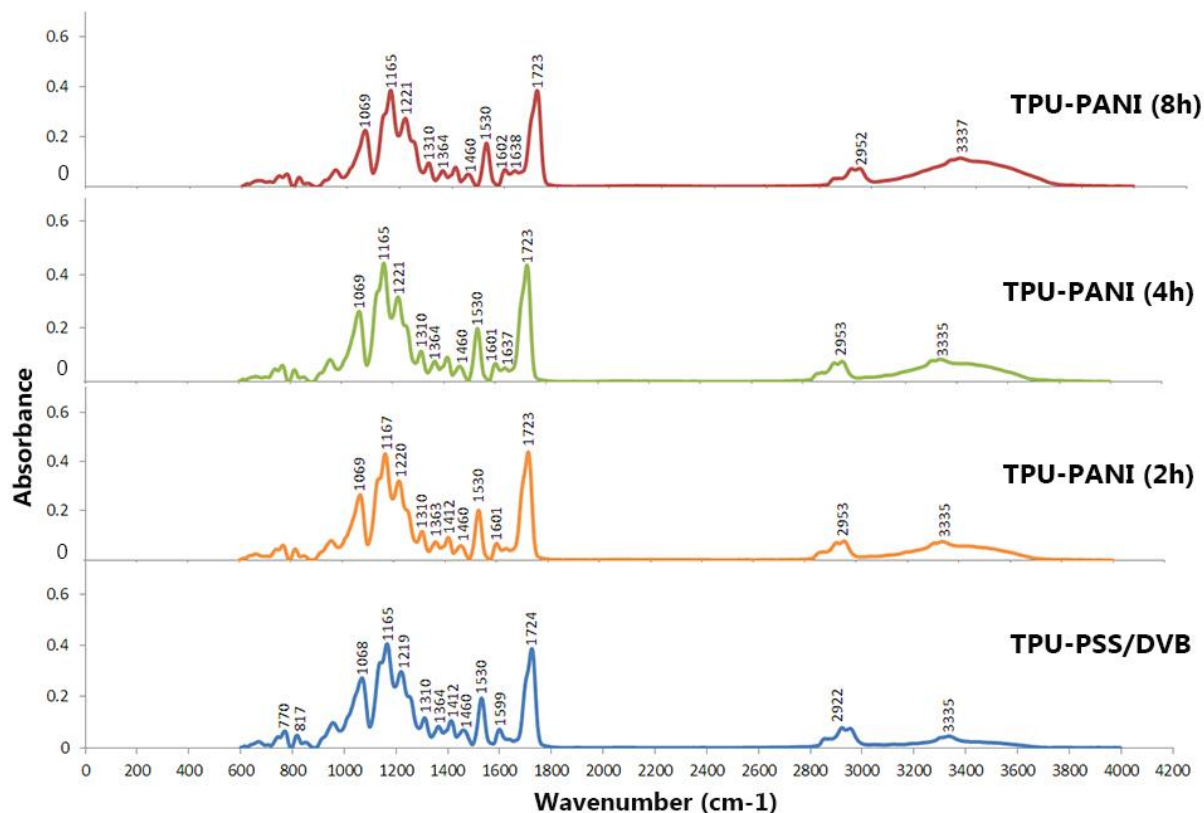
Figure 4.2: *FTIR spectra of unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.*

In TPU-PSS/DVB sample, the characteristic IR bands for TPU are appeared at 3335 cm^{-1} (N–H stretch), 2922 cm^{-1} (C–H$_2$ stretch), 1724 cm^{-1} (C=O stretch), 1530 cm^{-1} (N-H bending), 1412 cm^{-1} (C-H$_2$ stretch), 1310 cm^{-1} (C-N stretch) and 1165 cm^{-1} (C-O-C stretch) [67]. For PSS/DVB, the characteristics IR peaks are appeared at 770 cm^{-1} (C-H plane bending), 817 cm^{-1} (aromatic C-H vibration), 1068 cm^{-1} and 1599 cm^{-1} (styrene C-C stretch) [66].

In the region below 2000 cm^{-1} the spectrum shows two main bands which reveal the presence of PANI. The deposition of PANI was identified by the absorption of additional bands at 1460 cm^{-1} that is associated with benzoid and 1602 cm^{-1} that is linked with quinoid in PANI [68]. The bands corresponding to C–H stretching vibration and N=Q=N stretching mode are appear at 1310 cm^{-1} and 1167 cm^{-1} respectively [61].

It is difficult to analyse the PANI deposition with respect to time because of overlapping IR

peaks of different functionalities. However by keen analysis of the single spectrum of each membrane (figure 4.2) one can see the changes produced in the spectrum after PANI deposition. The prominent emergence of IR peak corresponding to OH stretching in PANI modified membranes is shown at 1638 cm^{-1} [61]. The band corresponding to delocalization of π-electron in the polymer induced by protonation is appearing at 1310 cm^{-1} [49]. An IR peak with characteristics of the conducting protonated form is marked at the 1220 cm^{-1} (C–N$^+$ stretching vibration) [69].

Summarizing the analysis, it can be concluded in the light of above spectra that, as the PANI content is increased in the composite membranes it results in stronger hydrogen-bonded carbonyl group. It means that PANI molecules in the composite membranes have the groups that are able to induce H-bonding [70].

4.4. TGA of TPU-PANI Composite Membranes

Thermogravimetric analysis (TGA) is a useful characterization technique which shows the thermal stability of an organic material. TGA results for unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times are shown in figure 4.3.

Thermal degradation of TPU is a complicated process as hard and soft segments in TPU structure respond differently at high temperatures [71]. The TPU-PSS/DVB curve in figure 4.3 is showing three stages degradation behaviour. The weight loss up to ~80°C is attributed to the loss of water entrapped in resin, solvent (MEK) and other volatile components present in the membrane matrix. Then up to ~320°C the weight loss is constant for TPU-PSS/DVB membrane. The second degradation stage is starting from ~340°C is attributed to decomposition of hard segments in TPU. It involves the dissociation of urethane linkage into original polyol and isocyanate [71]. The third degradation stage around ~455° C is associated with the decomposition of soft segments. It involved the degradation of de-polycondensation and polyol [72].
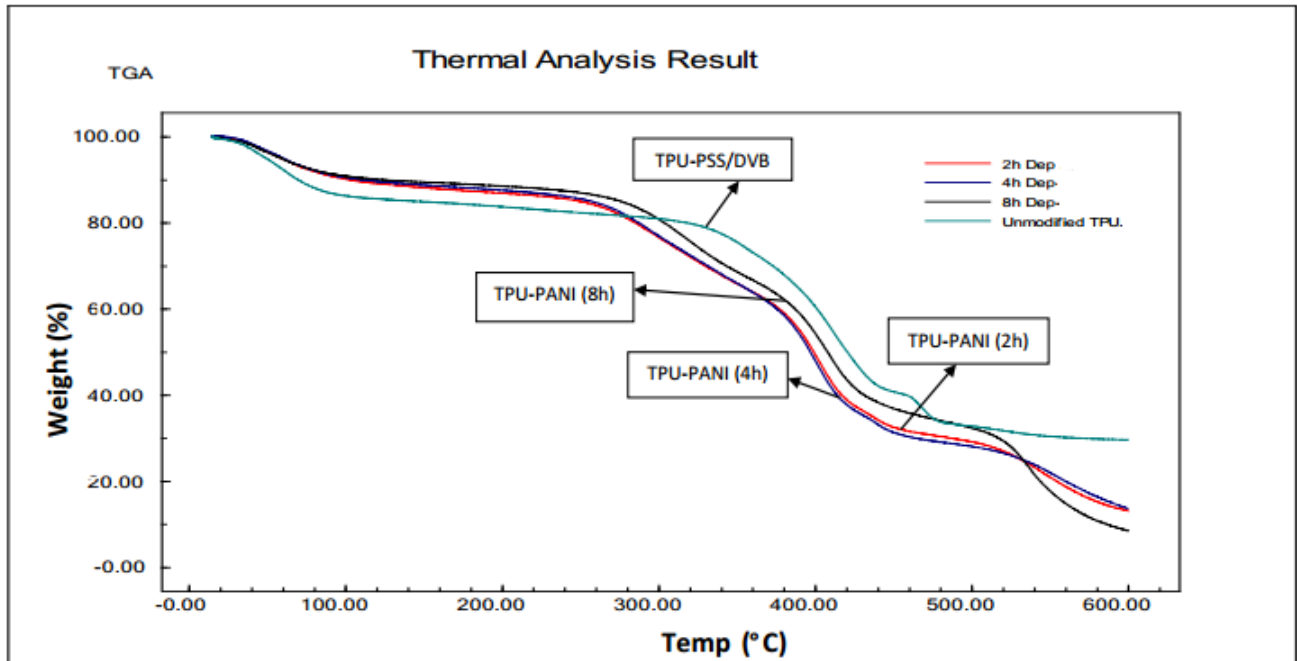
Figure 4.3: TGA curves of unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization.

In HCl doped PANI the decline at ~290° C is attributed to the removal of HCl and degradation of main chains in PANI structure i.e. benzenoid (amine) and quinoid (imine) moieties. After ~450°C the weight loss is associated with the desulfurization of PSS/DVB probably due to strong hydrogen boding between ($-N^+=$) and SO_3^- moieties in PANI and resin respectively [67]. Overall the TPU-PSS/DVB membrane shows better thermal stability as compared to PANI modified membranes. The higher percentage of weight loss in PANI deposited composite membranes as compared to pristine membrane sample depicts the prominent effect of PANI on the thermal degradability of the membranes.

4.5. Water Uptake of TPU-PANI Composite Membranes

Water content is important for membranes in terms of ionic transport species and dimensional stability [73]. It can be seen from the figure 4.4 that water uptake value is decreasing with the increasing polymerization time of PANI.
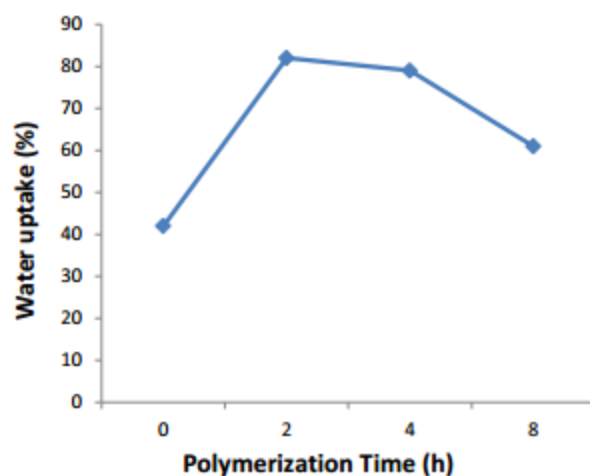
Figure 4.4: Water uptake (%) values for unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.

TPU is hydrophobic therefore does not absorb water but the addition of polystyrene sulfonated divinyl benzene resin is imparting hydrophilic character to the membrane because of sulfonic acid functionality ($-SO_3^-$) [61]. TPU-PSS/DVB membrane showed less amount of water because of the dense nature of membrane matrix. Hydrophilic ion exchange resin particles are not exposed to water contents completely.

Initially at small polymerization time (2h) PANI started to loosen the structure of membrane matrix and with increased polymerization times (4 and 8h) the membrane matrix structure became more compact and PANI stated to deposit in the form of layers. The water uptake is reduced significantly by increasing PANI deposition time. The decrease in water uptake with the increase in PANI deposition time shows the continuous and excessive layering of PANI on membrane matrix that results in loss of hydrophilic group ($-SO_3^-$) because of hydrogen bonding between PANI and sulfonic acid functionality of the resin ($-SO_3^-$). Also, by increasing deposition time, PANI blocked the channels and filled the voids between TPU and PSS/DVB resin particles. PANI coating around the resin particles resulted in loss of hydrophilic character.

The water uptake capacity also influences the dimensional stability of the membrane. The coating of PANI layer around resin particles is decreasing the affinity of membrane to water. As a result the dimensional stability of the membrane is enhancing [74].

4.6. Ion Exchange Capacity (IEC) of TPU-PANI Composite Membranes

Ion exchange capacity (IEC) is the representation of fixed charged groups in the bae membrane matrix. IEC is defined in terms of mille-equivalent of charged groups per gram of the dry membrane i.e. (meq/g) [73]. Figure 4.5 is showing the IEC values that are indicating the deviation in the amount of amine or imine groups compensated by sulfonate groups in the CEM [75]. IEC is usually tested by finding the number of counter-ions, cations in case of CEM, after converting CEM to H^+ [76].

IEC values are decreasing with increasing PANI polymerization time. Trend of IEC is proportional to water uptake. The unmodified TPU-PSS/DVB membrane showed an IEC value 1.35 while TPU-PANI membrane with 2 hours deposition time shows maximum ion exchange capacity value. This is because ionizable groups (H^+) in the sulfonic acid functionality of resin are not exposed completely for disassociation in unmodified membrane because of dense nature of the membrane.

But the 2 hour PANI deposition has created the pathways between TPU and PSS/DVB resin and making the availability of H^+ ions more convenient. Beyond 2 hour polymerization time, PANI started to envelop the resin particles with increased PANI coating on PSS/DVB particles with 4 and 8 hour polymerization time. It has reduced availability of H^+ ions for exchange because of their replacement with secondary amine group in PANI. This resulted in lower ion exchangeability of PSS/DVB resin at prolonged polymerization times [77].
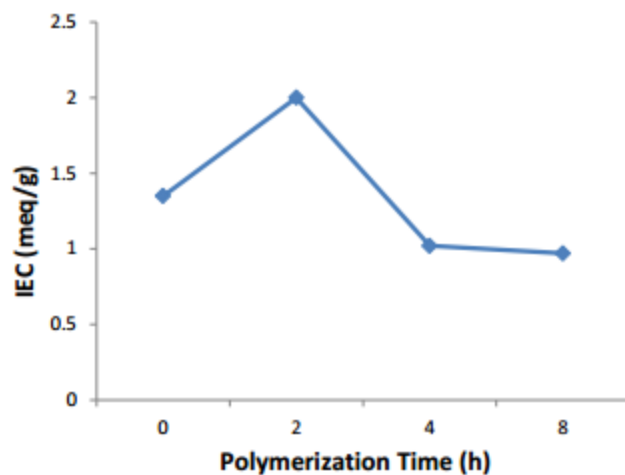
Figure 4.5: Ion Exchange Capacity values for unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.

In addition, PANI modifies resin structure by bonding with negatively charged group ($-SO_3^-$). As a result of this bonding the ion exchangeability of PSS/DVB resin reduced to the minimum. This is due to the interaction of positively charged $-N^+=$ with $-SO3^-$ of PSS/DVB resin figure 4.6 [61].
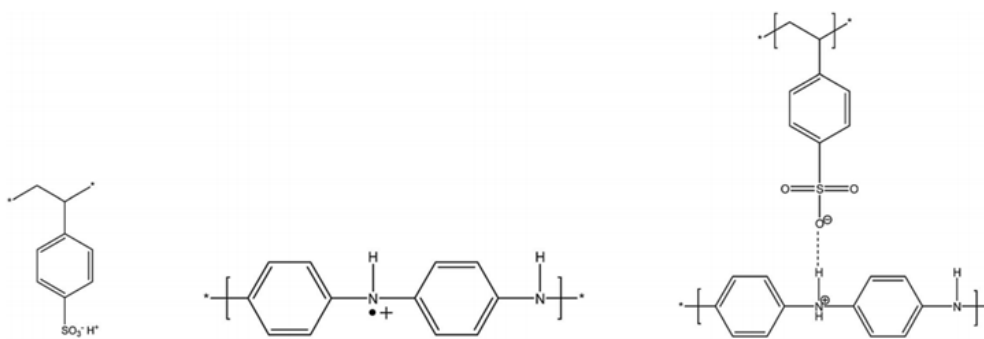
Figure 4.6: Molecular interactions between PSS/DVB resin and PANI.

4.7. Electronic Conductivity of TPU-PANI Composite Membranes

Electronic conductivity, the capacity of the material to allow the flow of electric current, of TPU-PSS/DVB and PANI modified TPU-PSS/DVB membranes at different polymerization times is shown in Figure 4.7.
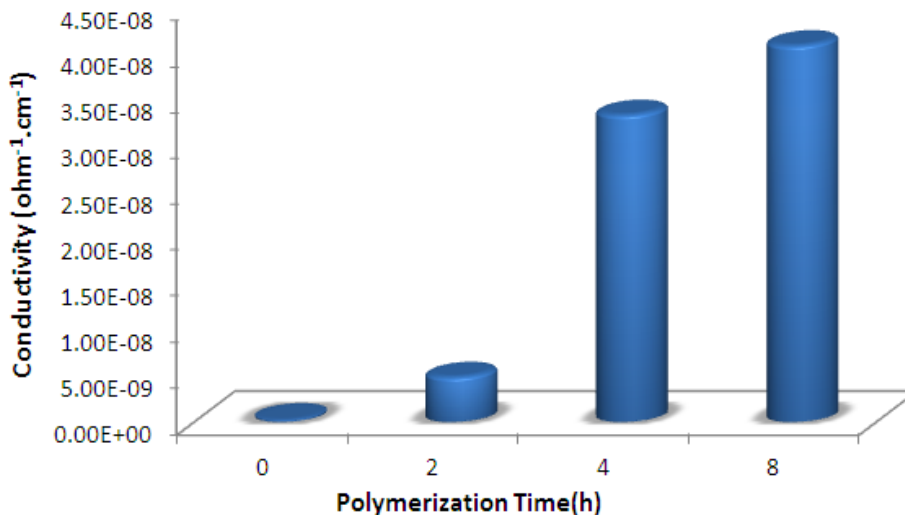
Figure 4.7: *Electronic conductivities of unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.*

Electronic conductivity, the capacity of the material to allow the flow of electric current, of TPU-PSS/DVB and PANI modified TPU-PSS/DVB membranes at different polymerization times is shown in Figure 4.7. It can be observed from that as the polymerization time is increasing, the conductivity of the TPU based composite membrane is also increasing. TPU based cation exchange membrane in pristine form is insulating [78]. This trend verifies the deposition of higher fraction of PANI content within the membrane bulk as emeraldine-salt form, as it is the only conducting state of PANI [79].

PANI exists in three oxidation states namely, leucoemeraldine-base (completely reduced), emeraldine-base (partial oxidized) and pernigraniline-base oxidation state (completely oxidized) [78] (figure 2.4). In all these oxidation states PANI exist as an insulating material. To obtain conducting state of PANI, emeraldine-base is converted to emeraldine-salt by doping emeraldine-base with an acid [80]. Frequently used acids for doping are hydrochloric acid [81]

and camphorsulfonic acid [81]. The ideal oxidation state of PANI, emeraldine-base contains an equal amount of repeating benzenoid (amine) and quinoid (imine) units [82]. When emeraldine-base is doped with an acid, the protonation occurs on the imine nitrogen sites to emeraldine-salt [78]. Hence, increasing PANI content results in higher conductivities.

4.8. Membrane Potential and Transport Number of TPU-PANI Composite Membranes

The membrane potentials were measured using NaCl and $CaCl_2$ as an electrolyte in a two-compartment cell [83]. The membrane potential across the ion exchange membrane in two compartment permeation cell is given by equation (4.1):

$$V_{Measured} = V_{Don1} + V_{Diff} + V_{Don2} \tag{4.1}$$

Generally, across ion exchange membrane, the membrane potentials are the sum of three sub-potentials showing in the equation (4.1). Here, $V_{Don}{}^n$ denotes Donnan potentials at both faces of the membrane facing the electrolyte solution, while V_{Diff} is the diffusional potential due to the diffusion of ion through membrane. At higher concentrations of electrolyte the Donna potentials can be neglected. In this scenario the expression for Donnan free (diffusion dominant) membrane potential can be written by following the Nernst equation [84]:

$$V_{Diff} = -\frac{RT}{F} \int \left(\sum \frac{t_i}{z_i} d \ln a_i + t_w d \ln a_w \right) \tag{4.2}$$

Here R, T and F denote ideal gas law constant, absolute temperature and Faraday's law constant, respectively. Whereas t_i and t_w represents the transport numbers of ions and water, and z_i, a_i shows valence number, activity constant of ith ion and water, respectively. For the purpose of simplification, transport of water can be ignored in equation (4.2) and can be written as:

$$V_{Diff} = -\frac{RT}{F} \int \left(\sum \frac{t_i}{z_i} d \ln a_i \right) \tag{4.3}$$

For NaCl solution on both faces of the membrane, a simplified version of membrane potential (equation 4.3) can be written by using the electro-neutrality condition i.e. $t_{Na}{}^+ + t_{Cl}{}^- = 1$:

$$V_{Diff} = (2t_{Na^+} - 1)\left(\frac{RT}{F}\right) \ln\left(\frac{a_1{}^s}{a_2{}^s}\right) \tag{4.4}$$

The ratio $\left(\frac{a_1}{a_2}\right)$ can be replaced by $(\frac{C1}{C2})$, by assuming concentration independent activity coefficients (γ_i). Equation (4.4) suggests that the transport number can be calculated by evaluating the slope of the straight line. The slope can be obtained by plotting V_{Diff} vs. $ln(\frac{C1}{C2})$. Transport numbers for both monovalent (NaCl) and divalent (CaCl$_2$) ions were determined by using equation 4.4.

Figure 4.8 is showing the membrane potentials of unmodified and PANI modified TPU-PSS/DVB membranes for different concentration ratios ($\ln C_1/C_2$) of both monovalent and divalent ions. With increasing PANI deposition times, the membranes with Na$^+$ ions showed decreasing membrane potential trends and the membranes with Ca^{+2} ions showed increasing membrane potential trends. Overall, for the case of NaCl, the membranes showed higher membrane potential values than CaCl$_2$. This trend can be attributed to the smaller radius of sodium ions as compared to calcium ions. Hence, membranes are more permselective for Na$^+$.
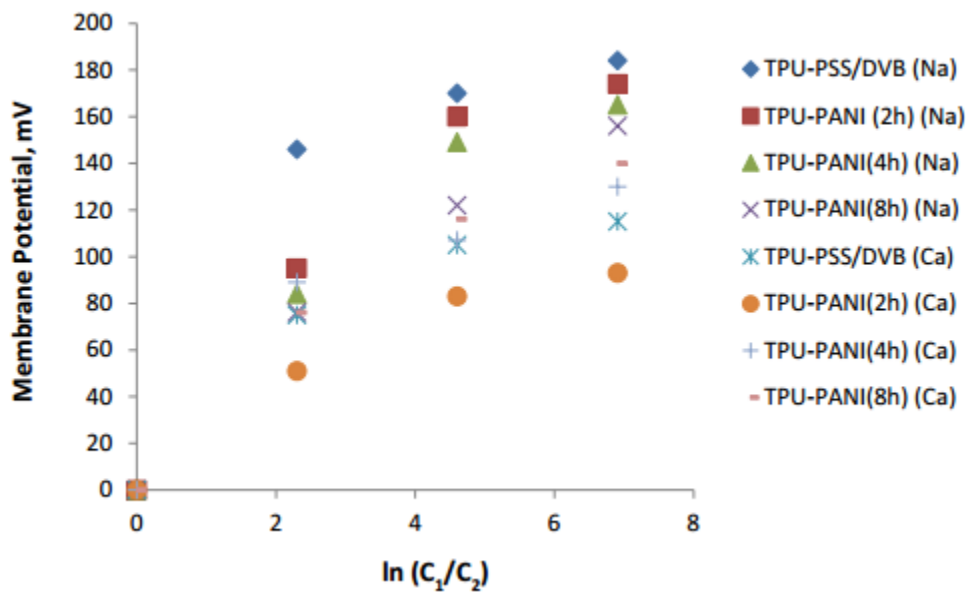
Figure 4.8: *Membrane potentials of unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.*

The transport numbers of Na^+ and Ca^{+2} for unmodified and PANI modified membranes calculated using equation (4.4) are given in figure 4.9. Overall the transport number for Na^+ ions is higher than that of Ca^{+2} ions. Figure 4.9 shows that the increased PANI deposition time resulted in decreasing transport number values for the membrane with Na^+ ions and increasing transport number values for the membrane with Ca^{+2} ions.
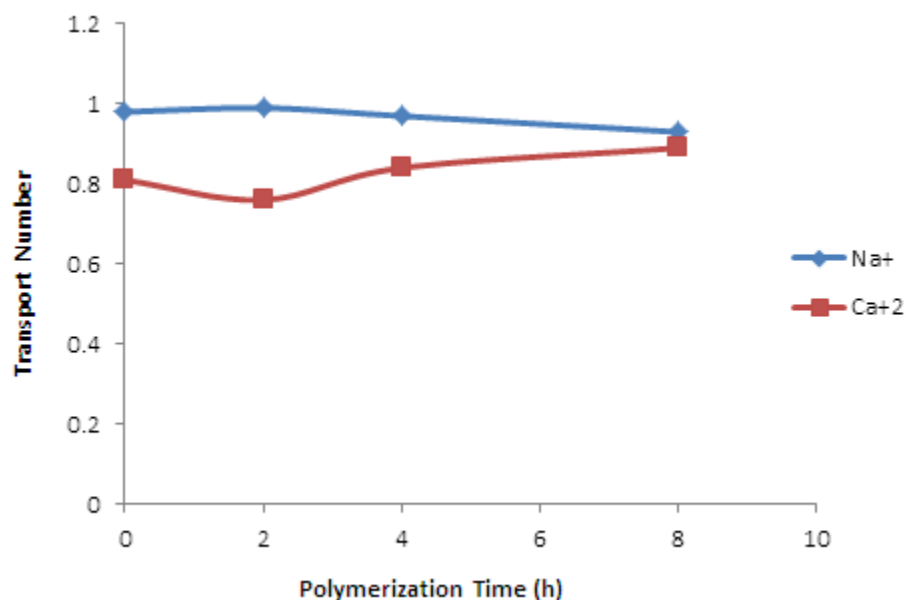
Figure 4.9: *Transport number of Na^+ and Ca^{+2} ions in unmodified and PANI modified TPU-PSS/DVB membranes at different polymerization times.*

Initially for the case of unmodified membrane, the membrane structure was compact hence the cation exchange resin was not exposed to aid the transport of Na^+ ion. The 2 hour PANI deposition resulted in more open structure and interaction occurred between Na^+ ion and cation exchange resin which resulted in increased transport number. At 4 and 8 hours polymerization times, PANI started to fill the channels due to which the membrane transport number is decreasing [61]. Increasing transport number trends for Ca^{+2} ions is because of its larger size and hence more electropositive character. With excessive PANI layering, dopant anion (Cl^-) character becomes prominent which resulted in the increased transport number of Ca^{+2} ions [61].

4.9. Electrodiaylsis Performance of TPU-PANI Composite Membranes

Electrodiaylsis is an electro-membrane process used for brackish water desalination and for the recovery of NaCl from sea water [8]. Electrodiaylsis is carried out under the influence of electric potential as a driving force. Cation and anion exchange membranes are arranged alternately in electrodialysis assembly. When the potential applied between the electrodes, cations move towards cathode through cation exchange membranes and anions move towards anode through anion exchange membranes [40]. This arrangement results in desalinated and concentrated streams as shown in figure 2.1.

Electrodiaylsis performance was evaluated in terms of % salt rejection using the following equation: [64][65]

$$\% \text{ Salt rejection} = \frac{C_0 - C}{C_0} \times 100 \tag{4.5}$$

Where, C_0 and C are representing the concentrations of feed and permeate respectively. Figure 4.10 is showing the % salt rejection of unmodified and PANI modified TPU-PSS/DVB membranes at different values of applied voltage using electrodiaylsis.
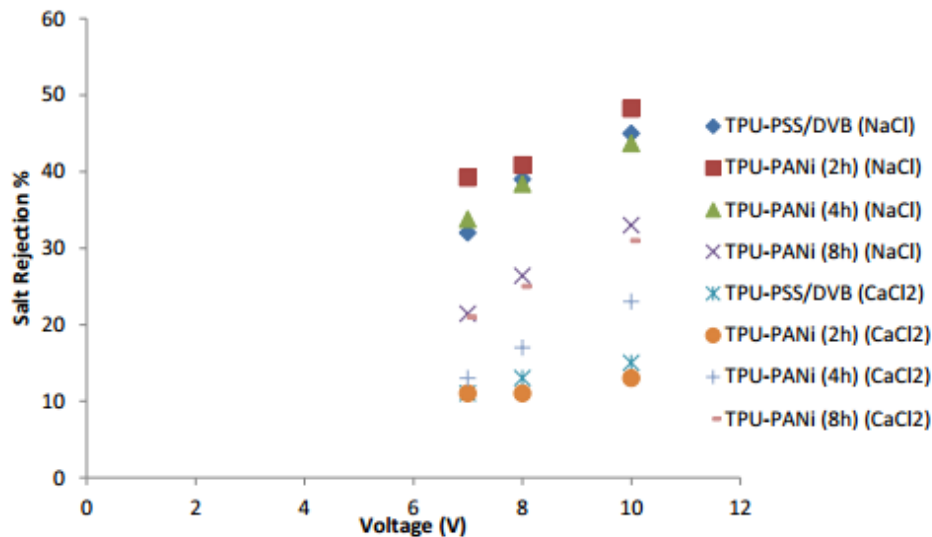
Figure 4.10: *% salt rejection of unmodified and PANI modified TPU-PSS/DVB membranes using electrodiaylsis.*

It can be observed that membrane with high transport number (TPU-PANI (2h)) in figure 4.9 is showing the highest increasing trend of % salt rejection Figure 4.10. As the PANI content is increasing the percentage of salt rejection is decreasing. This is because of the excessive layering of PANI deposition on the base membrane for prolonged polymerization times. The continuous PANI layering causes the desulfurization of PSS/DVB resin which is responsible for cation exchange character of IEM, due to strong hydrogen boding between ($-N^+=$) and SO_3^- moieties in PANI and resin respectively as shown in figure 4.6. This reduction in exchangeability of resin, surrounded with uniform PANI coating resulted in reduction of % salt rejection of cation (Na^+). The desulfurization of PSS/DVB resin is probably due to strong hydrogen boding between ($N^+=$) and SO_3^- moieties in PANI and resin respectively [61].

Chapter Five

5.1. Conclusions

ICPs based composite ion exchange membranes are the integral part of various separation processes such as pervaporation, gas separation, fuel cell and electrodialysis. In the present study, PANI modified composite membranes have been developed with the aim to improve the mechanical and electrochemical properties. In the light of experimental work and the characterizations that have been performed for the development of composite ion exchange membranes, certain conclusions can be summarized as follows:

- Heterogeneous CEM were developed by incorporating polystyrene sulfonated divinyl benzene (PSS/DVB) resin particles (400 mesh size) in base polymer matrix, thermoplastic polyurethane (TPU).

- Membranes were prepared by solution casting and phase inversion method.

- PSS/DVB incorporated polymer matrix (TPU) membrane was modified with polyaniline (PANI) as a conducting component of membrane, at varying deposition times (2, 4 and 8 hours) using in-house built two-compartment permeation cell technique.

- SEM images showed that the polymerization of aniline started on aniline-facing side of the membrane and the deposition occurred on the surface and in the bulk of the membrane throughout the polymerization times.

- Higher intercalation values with increased polymerization times showed the PANI deposition in the bulk of the membrane along with the surface deposition.

- Increased polymerization time of aniline also affected water uptake and ion exchange capacity values of composite membranes. Water uptake decreased because of increased PANI coating around resin particles that resulted in the loss of hydrophilic ion exchange particles because of hydrogen bonding between PANI and sulfonic acid functionality of

the resin ($-SO_3^-$). Reduction in ion exchange capacity values occurred due to the replacement of H^+ ions with secondary amine group in PANI.

- Increased values of electronic conductivities with prolonged polymerization times showed the presence of PANI in emeraldine salt form as it is the only conducting form of PANI.

- Electrochemical study in a two-compartment permeation cell showed a decreasing trend of transport numbers with increased polymerization time for monovalent ion (Na^+) and increasing trend of transport numbers for divalent ions (Ca^{+2}). The decrease of transport number for Ca^{+2} found significant as compared to Na^+ ions. This trend can be attributed to the smaller radius of sodium ions as compared to calcium ions. Hence, membranes are more permselective for Na^+ at 2 hour polymerization time.

- Trends of % salt rejection of composite membranes using electrodiaylsis were also in accordance with trends of transport number. Membrane with high transport number showed the maximum % salt rejection that decreased with increased deposition time.

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