DEVELOPMENT AND CHARACTERIZATION
OF SULFONATED POLYETHERSULFONE
FOR
PROTON EXCHANGE MEMBRANE FUEL CELL APPLICATION

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DEVELOPMENT AND CHARACTERIZATION OF SULFONATED POLYETHERSULFONE FOR PROTON EXCHANGE MEMBRANE FUEL CELL APPLICATION

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A thesis submitted in fulfillment for the award of the Degree of Bachelor in Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering

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I declare that this thesis entitled "Development and characterization of sulfonated Polyethersulfone for Proton Exchange Membrane Fuel Cell Application" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature　　　: ....

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Dedicated, in thankful appreciation for support,

encouragement and moral advice.

To my beloved and understanding parents

Md Aris Hasbullah, Rahimah Nasir,

and my fellow friends

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ABSTRACT

Sulfonated polyethersulfone (SPES) with 20% concentration by weight were prepared with concentrated sulfonic acid at room temperature. Membrane solution developed in this study consisted of polyethersulfone dissolved in N,N – Dimethylformamide (DMF) as solvent, fuming sulfuric acid (36%) and concentrated sulfuric acid (95%-97%) as the sulfonating agent. The solution was cast manually at temperature between 25^oC-28 ^oC. The investigation on water uptake, TGA, CHNOS elemental analysis, and FTIR has been conducted. Successful introduction of the sulfonated groups was confirmed by using the FTIR spectra in the wave number range $1020cm^{-1}$-1030 cm^{-1} which attributed to the symmetrical stretch of the sulfonated group. It was found that sulfonated membrane produced from mixed sulfonating agent (98% H_2SO_4 and 36% $H_2SO_4.SO_3$) have higher degree of swelling. The type and ratio of the sulfonating agent has been identified as one of the most influential parameter in determining the bonding of -HCO_3 as well as the membrane performance thus, producing different morphology. The parameter such as sulfonating agent ratio and type used strongly affects the membrane performance.

ABSTRAK

Polyethersulfone sulfonat (SPES) dengan konsentrasi mengikut berat sebanyak 20% telah disediakan dengan menggunakan asid sulfurik pekat pada suhu bilik. Cecair membran yang disediakan dalam kajian ini mengandungi polyethersulfone yang di larutkan didalam N,N-Dimethylformamide(DMF) yang bertindak sebagai pelarut, asid sulfurik wasap (36%), asid sulfurik pekat (95%-97%) sebagai agen pensulfonasian. Cecair membran diacu pada suhu bilik dan tekanan bilik.Kajian terhadap penyerapan air, TGA, CHNOS analisa dan FTIR kemudian dijalankan. Pengenalan kumpulan sulfonat kepada rantai utama telah disahkan menggunakan sinaran FTIR pada jarak sinaran $1020cm^{-1}$-$1030cm^{-1}$. SPES-C dengan campuran asid sulfurik pekat dan asid sulfurik wasap sebagai agen pensulfonasian adalah paling larut kepada air dan mempunyai peratusan tertinggi untuk ujian tersebut. Dengan nisbah 1:2 (pekat:wasap), SPES-C adalah yang terbaik untuk ujian serapan air dan ini diikuti oleh SPES-B pada keadaan yang sama. Jenis dan nisbah agen pensulfonasian telah dikenal pasti sebagai salah satu factor utama dalam pengikatan HCO_3 begitu juga dengan prestasi lantas menghasilkan morfologi berbeza. Adalah dipercayai parameter seperti nisbah agen pensulfonasian dan jenis agen memberi impak besar kepada prestasi membran.

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Cp	-	heat capacity
Ft	-	feet
g/mol	-	gram per mol
hr/yr	-	hour per year
K	-	kelvin
Kg	-	kilogram
kg/hr	-	kilogram per hour
kg/kmol	-	kilogram per kilomol
kg/m3	-	kilogram per meter cubic
kJ	-	kiloJoule
km	-	kilometer
kmol/hr	-	kilomol per hour
m	-	meter
m3	-	meter cubic
ml	-	mililiter
ppm	-	parts per million
RM	-	ringgit Malaysia
s	-	second
sq	-	square
%	-	percentage
°C	-	degree Celcius
SPES	-	Sulfonated polyethersulfone
PES	-	Polyethersulfone

CHAPTER 1

INTRODUCTION

1.1 Background of study

Fuel cell represents a clean alternative to current technologies for utilizing hydrocarbon fuel resources. Polymer electrolyte membrane fuel call (PEMFCs) have acquired due to their importance as the best system for applications where a quick start up is required such as in automobiles. The prime requirement of fuel cell membranes are high proton conductivity, low methanol/water permeability, good mechanical and thermal per fluorinated ionomers, hydrocarbon and aromatic polymers and acid-base complexes. Although fuel cell are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent years and became the premiere candidate as a portable power source for small vehicles and buildings that replaces the rechargeable batteries(Georgi, 2005).

Polymeric membrane for fuel cell has been developed in recent years for wide range of industrial applications using porous and non-porous materials. The intrinsic properties of a material stem from its chemical structure as every single component have different structure that will determine its properties. All this chemical structures factors determines its basic mechanic properties, chemical resistance and permeability. The processing also affects in a certain way the properties because the morphology of the material obtained are related to the process by which the polymer was transformed. Therefore, there was a strong independence on the final properties between the polymer

structure and elaboration conditions. The performances of fuel cell are known to be influence by many parameters including operating temperature, pressure and relative humidity of the gas stream etc. In this context, a membrane that complies with the basic requirement of fuel cells has been the principal goal of the research.

1.2 Problem statement

Although PES has excellent physical performance characteristic, the hydrophobicity of this material has limited its application sometimes. Sulfonation is a frequently used means for polymer modification to improve their membrane properties

1.3 Objectives

The objectives of this project are to develop a membrane based on polyethersulfone for the use of Proton Exchange Membrane Fuel Cell (PEMFC) that can adapt with the basic requirement of a fuel cell application.

1.4 Scope of Study

In order to meet the objectives, some scopes of studies are needed to be focused.

(i) Preparations of the sulfonated polyethersulfone solution and fabrication of sulfonated membranes.
(ii) Physical and chemical characterization of the produced sulfonated membranes.

CHAPTER 2

LITERATURE REVIEW

A fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution. Fuel cell technology isn't new; NASA has used fuel cells for many years to provide power for space shuttles' electrical systems. In the near future, many vehicles may also be powered by fuel cells. Along the process of writing this literature review, a lot of fuel cell type will be introduced but the focused are more to the type of fuel cell typically used in automobiles that is the proton exchange membrane, also called a polymer electrolyte membrane fuel cell (Phair *et al*, 2001).

2.1   Fuel Cells

A new form of energy production has been in the works since the space race in the 1950's during the cold war between the Soviet and the United States of America. It's not eligibly introduced as a battery, but it practically isn't quite a combustion engine either. Fuel cells seem to be the wave of the future for electricity production. Some researcher even goes further and declared that no power generation system in the world one day can undo the efficiency of a fuel cell (Colleen, 2007).

2.1.1   History

The PEM fuel cell was first invented in the early 1960s, by Willard Thomas Grubb and Lee Niedrach of General Electric. Initially, sulfonated polystyrene membranes were used for electrolytes, but then were replaced in 1966 by Nafion ionomer. This new type of membranes proved to be superior in performance and durability to sulfonated polystyrene. PEM fuel cells were used in the NASA Gemini series of spacecraft, but they were replaced by Alkaline fuel cells in the Apollo program and in the Space shuttle Parallel. Pratt & Whitney Aircraft, General Electric developed the first proton exchange membrane fuel cells (PEMFCs) for the Gemini space missions in the early 1960s. The first mission to utilize PEMFCs was Gemini V. This had been since, become the turning point for the used of fuel cell.

Extremely expensive materials were used and the fuel cells required very pure hydrogen and oxygen. Early fuel cells tended to require inconveniently high operating temperatures that were a problem in many applications. However, fuel cells were seen to be desirable due to the large amounts of fuel available.

Despite the success in space programs, fuel cell systems were limited to space missions and other special applications, where high cost could be tolerated. It was not until the late 1980s and early 1990s that fuel cells became a real option for wider application base. Several pivotal innovations, e.g. low platinum catalyst loading and thin film electrodes drove the cost of fuel cells down, making development of PEMFC systems more realistic. However, there had been significant debate as to whether hydrogen fuel cells will be a realistic technology for use in automobiles or other vehicles (Bocarsly, 2002).

2.1.2 Fuel Cell Construction

Electricity are nothing more than flowing electrons. That means that power generation are nothing more than finding out how to free electrons. Fuel cells rely on hydrogen for its electrons. There are many different fuel cells for every kind of application. But every fuel cell has the same essentials. Each fuel cell have an anode (negative electrode) comprised of hydrogen gas, and a cathode (positive electrode) of oxygen. In the middle are electrolytes that only allow protons to pass through it. In between both electrodes and the electrolyte are catalysts that facilitate the reactions (Colleen, 2007).

2.1.3 The Chemistry of Fuel Cells

The fuel cell basically works by injecting molecular hydrogen (H_2) molecules into the anode. These are to allow the hydrogen molecules to react with the catalyst. The catalysts used are usually a thin coat of powdered platinum on carbon paper. The function of the catalyst was to break the hydrogen into a proton and an electron. The proton goes across the electrolyte, while the electrons are fed through the circuit and goes to work, and that creating electric power. Upon finishing this process, the electrons return to the cell through the cathode. There, the catalyst assists the oxygen molecules, the hydrogen protons and the hydrogen electrons in making water. The chemical reactions are as follows:

Anode:
$$2H_2 \longrightarrow 4H_+ + 4e\text{-} \qquad\qquad 2.1$$

Cathode:
$$O_2 + 4H_+ + 4e\text{-} \longrightarrow 2H_2O \qquad\qquad 2.2$$

The whole reaction ends up looking like this:

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad\qquad 2.3$$

This reaction only creates about 0.7 volts. These powers produced are still considered as small compared to the power that will be used to generate something as big as a car. Because of this, there are several cells built into a stack. This multiplies the voltage up to useable levels (Katsura, *et al*, 2008).

2.1.4   Types of Fuel Cells

The most important parts in fuel cells are electrolyte. Different electrolytes provide different voltages and different properties. The fuel cells destined to appear under car hoods are called a Proton Exchange Membrane Fuel Cell. The stacks that will be used to fuel the car are about the size of an average sized printer.

Other fuel cells are much bigger (ranging in size from a large central air conditioning unit to a compact car.) These cells are stationary and can provide electricity to an apartment complex, an office building or 60 family homes. The types of fuel cell are:

2.1.4.1 Phosphoric Acid Fuel Cell (PAFC)

2.1.4.2 Molten Carbonate Fuel Cell (MCFC)

2.1.4.3 Solid Oxide Fuel Cell (SOFC)

2.1.4.4 Alkaline Fuel Cell (AFC)

2.1.4.5 Proton Exchange Membrane Fuel Cell (PEMFC)

All of these fuel cells are large and take a relatively long time to heat up (or "prime the hydrogen pumps") which became the reason why they are not suitable for automobiles. These large-scale fuel cells operate at high temperatures as well, (they range from about 1,000° F to 1,800° F) which allows engineers another way of

producing energy. The heat from the fuel cells can be used to boil water (perhaps the water it produces) and turn steam turbines for even more electricity.

2.1.4.1 Phosphoric Acid Fuel Cell (PAFC)

PAFC are the most developed fuel cell technology applied for power stations installed in buildings, hotels, hospitals and electric utilities in countries such as Japan, United States and European country. These types of fuel cell uses liquid acid as its electrolytes contains in silicone carbide matrix. These systems work at temperature higher than PEMFC or alkaline fuel cells yet still require platinum catalyst on the electrodes to promote reactivity. The anode and cathode reactions are same as any fuel cell system but it occur at a faster rate system due to the higher operating temperature (Weaver, 2002).

The efficiency of this system was proven to be lower than any of the fuel cell system, at around 40%. It also took longer time to warm up compared to PEMFC. Despites the lack of efficiency and warm up time, there are also advantages included in the system such as simple construction, stability, and lower electrolyte volatility.

Nowadays, the cost of the PAFC plant, which cost about US $ 3500 per KW, has appeared to be severe limitations for the widespread use and it seems that the possibilities for further technology improvements on such technologies are out of questions.

2.1.4.2 Molten Carbonate Fuel Cell (MCFC)

MCFC use either lithium sodium carbonate or molten lithium potassium as the electrolyte. The high temperature at which these cells operate means that they are able to internally reform hydrocarbons, such as natural gas and petroleum, to generate hydrogen within the fuel cell structure (Weaver, 2002).

2.1.4.3 Polymer electrolyte membrane fuel call (PEMFCs)

Polymer electrolyte membrane fuel call (PEMFCs) have acquired due importance as they are the best for applications where a quick start up is required such as in automobiles. The prime requirement of fuel cell membranes are high proton conductivity, low methanol/water permeability, good mechanical and thermal per fluorinated ionomers, hydrocarbon and aromatic polymers and acid-base complexes. Although fuel cell are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent past and became the premiere candidate as portable power source for small vehicles and buildings that replaces the rechargeable batteries.

Polymeric membrane for Fuel Cell has been developed in recent years for wide range of industrial applications using porous and non-porous materials. The intrinsic properties of a material stem from its chemical structure as every single component have different structure that will determine its properties. All this chemical structures factors determines its basic mechanic properties, chemical resistance and permeability. The processing also affects in a certain way the properties because the morphology of the material obtained are related to the process by which the polymer was transformed. Therefore, there was a strong independence on the final properties between the polymer structure and elaboration conditions.

The performances of fuel cell are known to be influence by many parameters including operating temperature, pressure and relative humidity of the gas stream etc.

A proton exchange membrane fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen and oxygen gases to produce thermal energy.

Streams of hydrogen were delivered to the anode side of the membrane electrode assembly (MEA). At the anode side it was catalytically split into protons and electrons. This oxidation half-cell reaction is represented by:

$$2H_2 \longrightarrow 4H + 4e \qquad\qquad 2.4$$

The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, thus creating the current output of the fuel cell. Meanwhile, a stream of oxygen is delivered to the cathode side of the MEA. At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction half-cell reaction is represented by

$$O_2 + 4H + 4- \longrightarrow 2H_2O \qquad\qquad 2.5$$

2.1.5   Applications of Fuel Cells

Fuel cells have the potential to slip into various kinds of electronic devices. A few applications could include:

(i)   Cars, as stated before, fuel cells the size of a printer could provide enough juice to power as well (if not better than) a combustion engine. Slightly larger units are already in place in several bus systems across the United States. The hydrogen for both forms of transportation may be provided through propane, methanol or natural gas.

(ii)   Personal devices (laptops, cell phones, and hearing aides) fuel cells have the tremendous potential to get into every electronic device we come in contact with. Fuel cells offer the possibility of laptops and cell phones with energy life measured in days or weeks, rather than hours. The fuel cell is scalable, which means it can go small enough to power medical devices that normally require battery replacement.

(iii)   Stationary power production and backup- larger-scale fuel cells could allow every city to have its own power station, rather than a centralized power grid. Power generation could become so decentralized that each housing development or apartment complex could be self-sustained with its own power. This would drastically cut down on pollution and ugly power lines. Hospitals and airports could (some already do) have backup power supplies that kick in, in the event of a power failure.

2.2   Membrane

Membrane science and technology are expending each and every day and without any doubt are becoming a prominent part of many activities within the process industry and power generation industry. This however does not justify with the wide fields of separations in which membranes are used.

The word separation conjures up a model of removing one component or species from a second component, for example a mass transfer process such as distillation. Separation in synthetic membranes has put the terminology separation in a wider context. A range of separation of the chemicals/mass transfer type have developed around the use of membranes including distillation, extraction, absorption, adsorption, and stripping, as well as separations of the physical type such as filtration. Synthetic membranes are an integral part of a device for analysis, energy generation and cells in the electrochemical industry.

Membrane technologies are in a state of rapid growth and innovation since the history of 40 years ago and becoming more active in the last decades. The world has watch numerous different separation processes have emerged in which synthetic membranes play a prominent role. Membrane separations are now routinely replacing separations which are unfortunately still referred as traditional. Go for a walk inside the research laboratory of many universities and industries to see membrane-based units supplying purified water (Jose Carlos *et al*, 2002).

A membrane are permeable or semi permeable phase, often a thin polymeric solid, which restrict the motion of certain species. These added phases are essentially function as a barrier between the feed stream for separation and one product stream. This barrier controls the relative rates of transport of various species through itself and thus, as with all separations, gives one product depleted in certain components and a second product that is concentrated in these components. The performance of a membrane had always been defined in few simple factors. It is defined as:

(i) Flux or permeation rate; the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time

(ii) Selectivity ; for solutes and particulates in liquids and gases ; retention are the fraction of solute in the feed retained by the membrane

(iii)Selectivity; for mixtures of miscible liquids and gases; Separation factor are the ratio of the concentration in the permeate divided by that in the feed for two components.

The uses to which membranes can be put are varied and include the separation of mixtures of gases and vapors, miscible liquids (organic mixtures and aqueous/ organic mixtures) and solid/liquid and liquid/liquid dispersion and dissolved solids and solutes from liquids. Thus virtually all separation requirements in industry can, in principle, be achieved with membranes. The main uses of membranes in industry are as the following areas:

(i) The filtration of micron and submicron size suspended solid (and dispersed liquid) from liquid and gases containing dissolved solid.

(ii) The removal of macromolecules and colloids from liquids containing ionic species.

(iii)The separation of mixtures of miscible liquids.

(iv)The selective separation of gases and vapors from gas and vapors from gas and vapors streams.

(v) The selective transport of ionic species only.

(vi)The virtually complete removal of all material, suspended and dissolved, from water.

The technical advantages of membrane separations which result in economic advantages are that they frequently achieve higher efficiency of separation, they often yield faster separations and the simplicity of operation in modern compact modules means operation with small or large plant are relatively easy.

Membrane technology has more recently been applied commercially to separate individual components from mixtures of liquids and gases, (area 3 and 4 above). The membranes here are non porous thin layers on porous substrates. The technical breakthrough, in terms of selectivity and rate of separation, in the membrane separation

of gases had made has permeation competitive with cryogenic separation, adsorption, absorption, etc. Pervaporation are membrane process which can essentially replace fractionation by distillation, although applications are restricted to the more difficult separations which typically involve azeotrope formation such as ethanol/water. These processes are somewhat unique within membrane separation involving a change in phase from feed (liquid) to permeate (vapor).

The final mentioned for liquid-based separations, which removes ions selectivity, are called electrodialysis. Market areas are again similar to the membrane filtrations with a principle application in the desalination of brackish water. The economic advantages gained by electrodialysis are through its specificity and efficiency of separation of separation achieved at low temperatures. A major application of electrodialysis-type membranes (ion exchange) are as electrolyte call separation (Keith, 1998).

2.2.1 History membrane

In 1850, separate papers appeared in the *Journal of the Royal Agricultural Society of England* by agriculturist Sir H.S.M. Thompson and chemist J.T. Way. Researches describe the phenomenon of ion exchange as it occurs in soils. In that paper, the researches addressed to the question of how soluble fertilizers like potassium chloride were retained by soils even after heavy rains. The Experiment took a box with a hole in the bottom, filled it with soil, and poured onto the soil a solution of potassium chloride, collecting the liquid that flowed out of the bottom. The soil was then washed with rainwater and analyzed, from both the solution and the rainwater. The water turned out to contain all of the chloride that had been originally added but none of the potassium; the potassium had been replaced by chemically equivalent amounts of magnesium and calcium. Researchers called the process "base exchange" because of the basic (nonacidic) character of the exchanged elements. That term persisted until after

1940, by which time the process had become universally known as ion exchange (Wang *et al*, 1998).

In modern days, the process would be described in the following way: potassium ions enter the soil and displace calcium and magnesium ions. The chloride ions have no part in the operation and pass through unchanged. In terms of a chemical equation, the process is

$$2K^+ + Ca^{2+} \text{ (soil)} \rightleftharpoons Ca^{2+} + 2K^+ \text{ (soil)}, \hspace{3cm} 2.6$$

in which the double arrow indicates that the exchange was reversible. In Way's experiment, the process was pushed to completion because the water trickling through the soil continually came in contact with fresh calcium-loaded soil. As Way also observed, the potassium could be regained by washing the soil with a solution of calcium chloride (Hann, *et al*, 1990).

2.2.2   Membrane classification

The membrane, clearly the most important part of the separation process. This membrane material had been developed over the recent years to produce wide range of materials with different in structure and ways of functioning. Tables 2.1 regroup the types and properties of some synthetic membranes for technical interest. All these materials were generally classified into:

(i) Synthetic polymers; a vast source in theory although silicone rubbers, polysulphones, polyamides are prominent
(ii) Modified natural products; cellulose-based
(iii) Miscellaneous; include inorganic, ceramic, metals, liquid and dynamic membranes

The functioning of a membrane will depend on its structure as this essentially determines the mechanism of separation and thus the application. There are currently two types of structure generally found in membranes. It was symmetric and asymmetric. Symmetric membranes have three general types; with approximate cylindrical pores, porous and non porous. Asymmetric membranes are characterized by a non-uniform structure comprising of an active top layer supported by a sub layer. There are also divided into porous, porous with top and composites (Scott, 1998).

Table 2.1: Type, structure and preparation of synthetic membrane

Membrane type	Membrane structure	Preparation	Applications
Asymmetric CA,PA,PS,PAN	Homogenous or microporous, skin on a miroporous substructure	Casting and preparations	UF and RO, (MF) GP,PV
Composite CA,PA,PS, PI	Homogenous polymer film on a miroporous substructure	Deposition on microporous substructure	RO, GP, PV
Homogenous S	Homogenous polymer film	Extrusion	GP
Ion exchange DVB, PTFE	Homogenous or microporous copolymer film with positively or negatively charged fixed ions	Immersion of ion exchange powder in polymer, or sulphonation an amination of homogenouspolymer film	Ed
Microporous: Ceramic, metal glass	0.05-20 micrometer pore diameter 10-100 micrometer pore diameter	Moulding and sintering Leaching from two-component glass mixture	F(molecular mixtures)
Microporous: Sintered polymer PTFE,PE,PP	0.1-20 micrometer pore diameter	Moulding and sintering	F(suspensions, air filtration)
Microporous: Stretched polymer PTFE,PE	0.1-5 micrometer pore diameter	Stretching a partial crystalline film	F(air,organic solvents)
Microporous: Track-etched PC, PEsT	0.02-20 micrometer pore diameter	Irradiation and acid leaching	F(Suspension, Sterile filtration)
Symmetric microporous phase inversion CA	0.1-10 micrometer pore diameter	Casting and precipitation	Sterile filtration, water purification,dialysis

PTFE –polytetrafluoroethylene,   CA-Cellulosic esters,   PVC-Polyvinylchloride   PA-polyamide
PE-Polyethylene,   PS-Polysulfone,   PP-Polypropylene,   S-Silicon rubber,
PC-Polycarbonate,   PEsT-Polyester   PAN-polyacrylonitrile,   PI-Polyamide,
DVB-divinylbenzene,   UF-Ultrfiltration,   RO-Reverse osmosis,   GP-gas permeation,
MF-Microfiltration   ED-electrodialysis,   F-filtration,   PV-Pervaporation

2.2.3   Fundamentals of ion exchange reaction

Ion exchange are any of a class of chemical reactions between two substances (each consisting of positively and negatively charged species called ions) that involves an exchange of one or more ionic components (Vassilis *et al,* 2006).

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Ions are atoms, or groups of atoms, that bear a positive or negative electric charge. In pairs or other multiples they make up the substance of many crystalline materials, including table salt. When such an ionic substance was dissolved in water, the ions are freed from the restraints that hold them within the rigid array of the crystal, and they move about in the solution with relative freedom. Certain insoluble materials bearing positive or negative charges on their surfaces react with ionic solutions to remove various ions selectively, replacing them with ions of other kinds. Such processes are called ion-exchange reactions. They are used in a variety of ways to remove ions from solution and to separate ions of various kinds from one another. Such separations are widely utilized in the scientific laboratory in affect purifications and to aid in the analysis of unknown mixtures. Ion-exchange materials such as zeolites are also employed commercially to purify water and medically to serve as artificial kidneys and for other purposes *(*Edward, 1996).

Table 2.2: Characteristic and application of ion exchange membranes

Characteristic	Applications	Examples
Ion Conductivity	Electrodialysis	Concentration of electrolytes, separation between electrolyte and non electrolyte, bipolar ion exchange membrane process to produce acid and alkali, ion exchange reaction across membrane etc
	Separator for electrodialysis	Chloroalkali production, organics synthesis by electrolytes, etc
	Diffusion dialysis	Acid or alkali recovery from waste
	Neutralization dialysis	Separation of electrolyte and non electrolyte, desalination of water, etc
	Themo-dialysis	Desalination or concentration
	Battery	Alkali battery, redox-flow battery, concentration cell
	Fuel cell	Hydrogen-Oxygen, Methanol-Oxygen
Hydrophilicity	Pervaporation	Dehydration of water miscible organic solvents
	Dehumidification	Dehumidification of air and gases
	Sensor	Gas sensor(humidity,CO_2,NO_2, etc)
Fixed carrier (ion exchange group)	Facilitated transport (gas separations)	Removed of acidic gas, separation of olefins from alkanes, etc

2.2.4   Ion-exchange procedures

Only rarely are the ion exchangers used in stepwise procedures, in which the resin was mixed into a container of solution and then removed for further treatment. Much more frequently the exchangers are packed into a tube or column through which the solution made to flow. The column arrangement forces the ion-exchange reaction, which intrinsically reversible, to go to completion in the desired manner. The solution flowing down the column continually meets fresh exchanger, and a reaction that goes half way in the first centimetre of the column may be three-quarters completed in the second centimetre, seven-eighths in the third, and so on. In a short time, the exchangeable ions that entered the column have been adsorbed and become undetectable analytically. When the exchangeable ions do start to emerge from the end of the column, however, the column has become completely saturated with them. It may be restored to its original condition, or regenerated, by passing through it a solution of the ions that it originally contained (Zadowzinski *et al*, 1995).

Ion-exchange columns are easy to use, but the theories behind their use are extremely complicated. A column with a solution flowing through, are nonequilibrium system. Its interpretation must consider not only equilibrium distributions but rates of transfer of material and statistical variations in the paths of liquid flow between the granules that make up the exchanger. There are two chief theories of ion-exchange processes related to the two principal ways in which the columns are employed. In the first procedure, displacement, the column originally contains mobile ions of one kind that are pushed down the column by the steady flow of a solution of ions of a second kind. The theory for this procedure deals with the rate at which the "front" (the boundary between the different classes of ions) advances and its concentration profile (whether the front stays sharp as it moves down the column or whether it becomes progressively more diffuse). In the second process, elution, a thin layer of ions was introduced at the top of a column already saturated with ions of a second kind; it then is washed down the column with the same kind of ions that saturated the column at the start. In elution, the theory

must account for the rate of movement of the narrow band of ions and its spread as it proceeds down the column (Zadowzinski *et al*, 1995).

When a mixture of two kinds of ions that are held by the exchanger with differing strengths was introduced at the top of a column, the mixture of ions separates as it moves down the column, with the result that the original single band of ions is resolved into two separate bands. This process is called ion-exchange chromatography. Ion-exchange chromatographies are an important tool in chemical analysis because it permits separation of materials that are very difficult to separate by other means. It can be applied to organic and inorganic ions and even to substances that are not ionic. It is often used to separate mixtures of many components.

Ion-exchange columns are made in all sizes, from the large tanks used to soften the water supply of great cities to the tiny columns holding less than a cubic centimeter of resin that are used for recovering short-lived radioactive elements in the laboratory. Care is needed in preparing columns for the laboratory. Dry resin must be stirred with water to let it swell before it is poured into the column. Air bubbles must not be allowed to form in the resin bed, for they interfere with the liquid flow. It is desirable to backwash the column—that is, to pass liquid upward to expand the resin bed—in order to release air bubbles and to segregate the resin particles according to size before the column is used. The aim of the preparation procedure is to assure even packing and even flow. For difficult chromatographic separations, resins having uniform, very small particles are used to facilitate mass transfer and give sharper bands. As fine particles offer much resistance to flow, solutions must be forced through under pressure. One procedure is to use long, narrow columns of stainless steel (like those used in a related process called gas chromatography) and to hasten mass transfer by using, instead of resin beads, glass spheres coated with ion-exchange resin.

Ion exchangers, especially inorganic and cellulose-based exchangers, are used in thin-layer chromatography. Chromatographic papers for this purpose are manufactured

from finely ground resins and cellulose fibres. One use for this procedure is to filter small traces of metal ions from large volumes of solution.

Electrodialyses are processes somewhat similar to reverse osmosis. Ions are able to enter an ion-exchange membrane if they are simultaneously removed from it at the other side; the effects are the same as passing an electric current through the membrane. In practice, electrodialysis was carried out by placing a cation-exchange membrane on one side of the solution to be desalted and an anion-exchange membrane on the other and then passing an electric current through the system. The result shows that positive ions pass through the membrane on one side and negative ions pass through the membrane on the other. Pure water was left eventually in the area between the membranes (Conley, 1996).

Ion-exchange resins may also be fabricated into thin sheets, although it was not easy to make a sheet of ion exchanger that are strong and flexible and at the same time permeable; development of ion-exchange membranes has been slow for this reason. Ion-exchange membranes are used, however, to separate the electrodes of fuel cells and to remove salts from water by the physical processes termed reverse osmosis and electrodialysis. The former was the kind of filtration process—water was squeezed through the membrane under pressure while the dissolved salts are left behind. The reaction can be carried out, for example, by placing a membrane of cation-exchange resin loaded with sodium ions in contact with a dilute solution of sodium chloride. Because of the characteristics of the ion-exchange process, neither the sodium nor the chloride ions can enter the membrane. Water molecules can penetrate the membrane, however; and because of the pressure exerted on the system, they do so, crossing to the other side. The results are the removal of salt from the water without distillation (the usual desalting process) (Zagorodni, 2007).

2.2.5 Applications of ion exchange

Ion exchange was used for both analytical and preparative purposes in the laboratory, the analytical uses being the more common. Important uses of ion-exchange chromatography are in the routine analysis of amino acid mixtures. Columns of cation-exchange resin are used, and the solutions are maintained sufficiently acid so that the amino acids are at least partly in their cationic forms. The 20 principal amino acids from blood serum or from the hydrolysis of proteins are separated in a few hours, and their concentrations are determined automatically by light-absorption methods. Such analysis is used in clinical diagnosis (Inglezakis, 2006).

In a less routine and highly important application of ion-exchange chromatography, the products of hydrolysis of nucleic acids are analyzed. In this way, information was gained about the structure of these molecules and how it relates to their biological function as carriers of hereditary information. Cation-exchange resins are used for this purpose as well. Because of their use in analyzing the structures of complex biological materials, ion-exchange chromatographic procedures have been of great importance in the development of modern molecular biology—the explanation of biological processes in terms of the interactions of molecules(Zagorodni, 2007).

Inorganic ions also can be separated by ion-exchange chromatography. The lanthanides, or rare-earth elements, are separated on columns of cation-exchange resin. Solutions of citrates, lactates, or other salts whose anions form negatively charged complexes with the lanthanide ions are used to wash the ions from the column. The metal ions themselves are held by the resin; the complexes are not. Those ions that form more stable complexes do not adhere to the resin and therefore move off the column more quickly than the ions that do not form complexes (or complex only weakly). Cation exchange in general are not a selective process, but the above process, termed differential complex formation, renders it more so. In lanthanide separations the exchanger was like an undiscriminating sponge that simply holds the metal ions,

whereas the real separation of the various metals was accomplished by the weakness or strength of the complexes formed (Zagorodni, 2007).

Anion exchanges in hydrochloric acid are the effective way to separate metal ions. Most metals form negatively charged chloride complexes that can be held by anion-exchange resins carrying quaternary ammonium groups (NR_4^+). These complexes differ greatly in their stabilities in solution and in their affinities for the resin. The distribution of metal ions between the solution and the resin depends on the hydrochloric acid concentration and the identity of the metal ion. Impressive separations of metal ions can be achieved by manipulating the hydrochloric acid concentration.

Ion-exchange separations of this kind are widely used; they can be modified by using mixed solvents, like acetone–water, and great selectivity is possible. In the process called "activation analysis," an unknown sample to be analyzed is bombarded with neutrons, and the radioactive elements thus formed are separated by anion-exchange procedures. Such analyses are especially valuable in separating minor metallic constituents from samples containing large amounts of other substances. The technique has been used to analyze lunar rocks.

Preparative uses of ion exchange in the laboratory are not many, but on occasion unusual acids, such as hydroferrocyanic acid or unusual bases, like cesium hydroxide, are prepared from their salts by passing solutions of the salts through the appropriate resins. Resins also are used to purify acids or bases that contain nonionic contaminants and to remove ionic contaminants from solvents (Inglezakis, 2006).

CHAPTER 3

RESEARCH METHODOLOGY

This chapter describes the experimental method that had been used to develop and characterized the produced sulfonated polyethersulfone that had been produced. The membranes was first prepared and thus characterized through several analytical equipment and test such as swelling test, Thermogravimetry Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and CHNOS elemental analysis. Finally, the obtainable results were evaluated.

3.1   Polyethersulfone (PES)

Polyethersulfone are heat resistant, transparent, amber, non crystalline engineering plastic having the molecular structure shown in Figure 3.1.
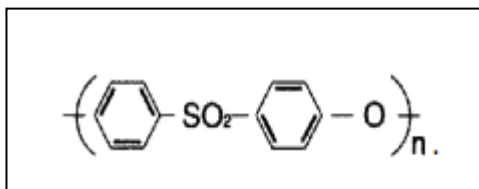
Figure 3.1: Polyethersulfone (PES) structure

Polyethersulfone (PES) are a tough and rigid resin similar to conventional engineering plastics, such as polycarbonate, at room temperature.

The greatest characteristics of polyethersulfone (PES) are that it has by far better high-temperature properties than conventional engineering plastics. Specifically, polyethersulfone (PES) remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C. It has poor fatigue characteristics and was prone to environmental stress cracking but has good long term thermal ageing resistance and reasonable radiation resistance.

Polyethersulfone have been applied widely in automotive electrical/electronic, automotive fuel systems, automotive lighting, as a coatings, composites, additives for gas separation, cookware, electrical contactors, switches and as a membranes for water purification, waste water recovery and hemodialysis.The physical properties and thermal properties of polyethersulfone are shown in Table 3.1.

Table 3.1: Physical and thermal properties of polyethersulfone (PES)

| Physical and ThermalProperties	Unit
Density	1.37 g cm^{-3}
Flammability	V-0 @ 0.4mm
Limiting oxygen index	34-41%
Radiation resistance	Good-Fair
Water absorption – equilibrium	2.2 %
Water absorption - over 24 hours	0.4-1 %
Coefficient of thermal expansion	55 x10^{-6} K^{-1}
Heat-deflection temperature - 0.45MPa	> 260 °C
Heat-deflection temperature - 1.8MPa	203 °C
Lower working temperature	- 110 °C
Thermal conductivity @23°C	0.13 – 0.18 W m^{-1} K^{-1}
Upper working temperature	180 – 220 °C
Elongation at Break	20 – 150 %
Flammability	VTM-0 @ 25µm

3.2   Solvent

The solvents used in the sulfonation reaction must have the ability to dissolve the base polymer and must be inert towards sulfonating agent. Preferred solvents are chloroliphatic hydrocarbons such as chloroform, methylene chloride and 1, 2-dichloroethane, N, N-Dimethylformamide. In this study, N, N-Dimethylformamide was preferably added between 15 to 25 ml per gram of polymer.
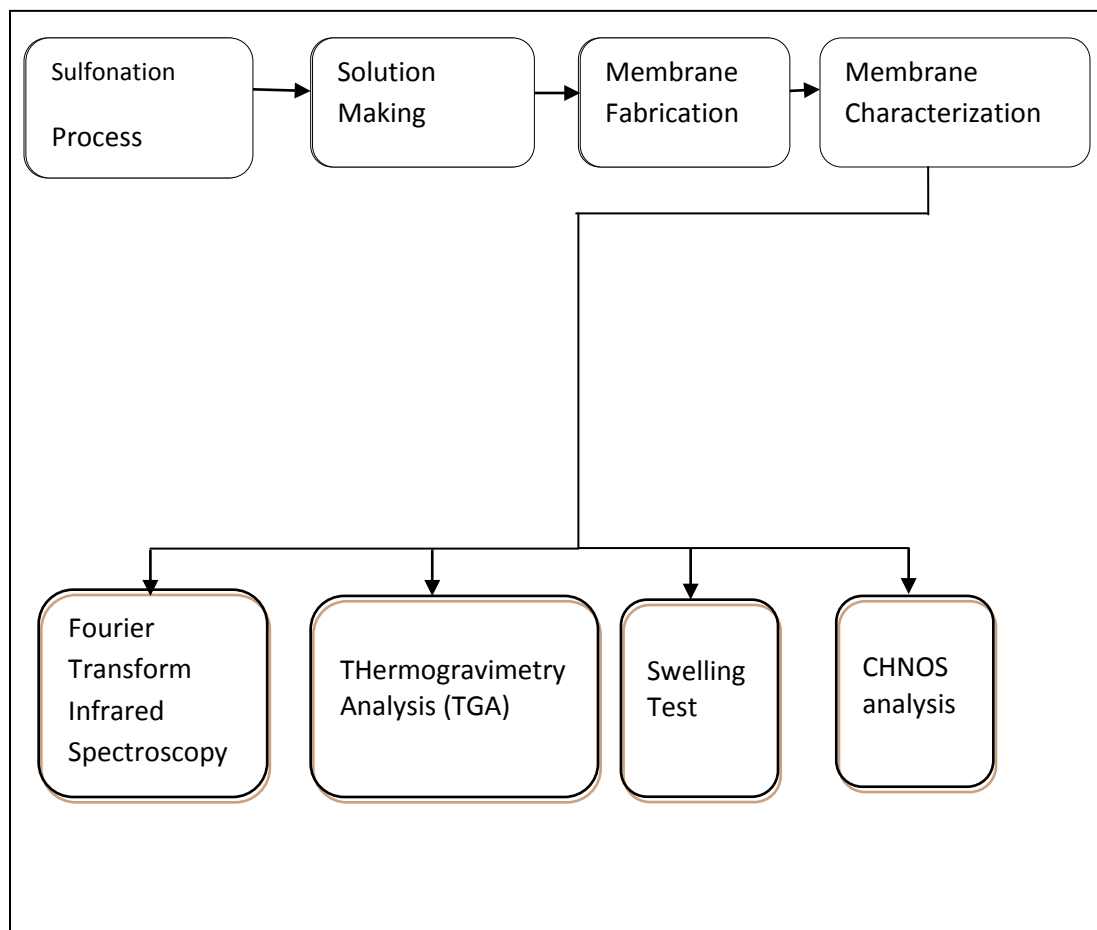
3.3   Research Design

Several factors have been identified for influencing, the characteristic of sulfonated membranes include the sulfonating agents, the base polymer and the process condition applied.
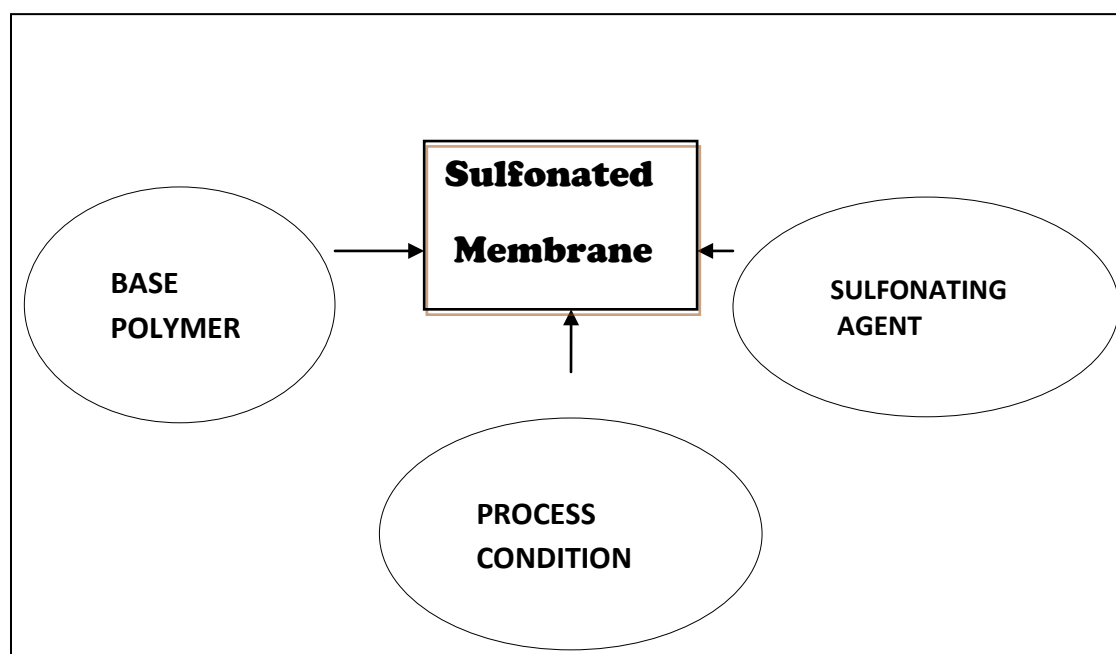
Figure 3.2: Research design

3.4 Experimental stages

Figure 3.3 below shows the steps that were involved during the experimental work.

Figure 3.3: Flow of experimental stages

3.4.1 Sulfonation process

The PES polymer was dried in a vacuum oven at 100 °C overnight. Mixtures of 15–30% fuming sulfuric acid and 95–98% of concentrated sulfuric acid was used to conduct sulfonation reactions at room temperature. A different acid ratio was used in order to obtain sulfonated PES with different DS. The mixture of 25 g PES polymer and 400 ml of total sulfonating agent use was constantly stirred at room temperature and under nitrogen atmosphere at a certain reaction time. The total time for polymer dissolution and reaction is the reported reaction time. After a prescribed time, the sulfonated PES polymer should be recovered by precipitating the acid polymer solution into a large excess of ice water. Then filtrated and washed the sulfonated PES polymer thoroughly with deionized water until the pH ~6–7. Use the drying oven at 80–100 °C for 24 h to dry the sulfonated PES.

3.4.2 Preparation of casting solution

At a temperature of 150°C, the polymer was dry for at least 4 hour in a vacuum oven in order to remove all absorbed water vapor. The polymer was then dissolved in N,N-Dimethylformamide and nonsolvent additive which is distilled water. The solution was then heated at 40°C - 60°C and stir about 4 to 6 hours to achieve complete homogeneity. After that, the solution had been kept in a storage bottle and was degasses by using ultrasonic bath to remove any traces micro bubbles present in the solution. The apparatus assembled are shown in Figure 3.4:
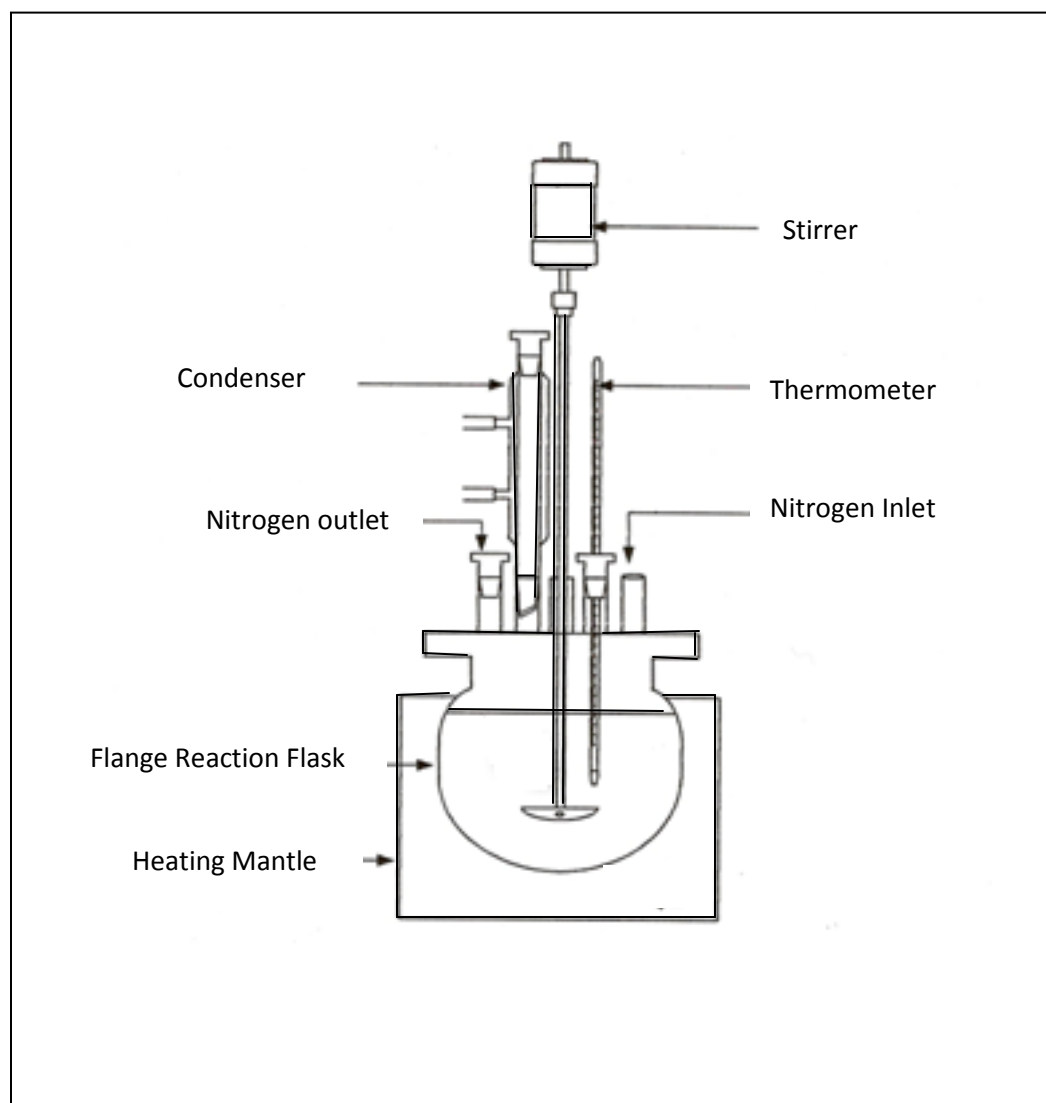
Figure 3.4: Preparation of casting solution system.

3.4.3 Membrane casting

Manually casted, sulfonated polyethersulfone membranes were prepared according to dry/wet phase separation process. Four steps procedure involved in this experiment was shown in figure 3.5;
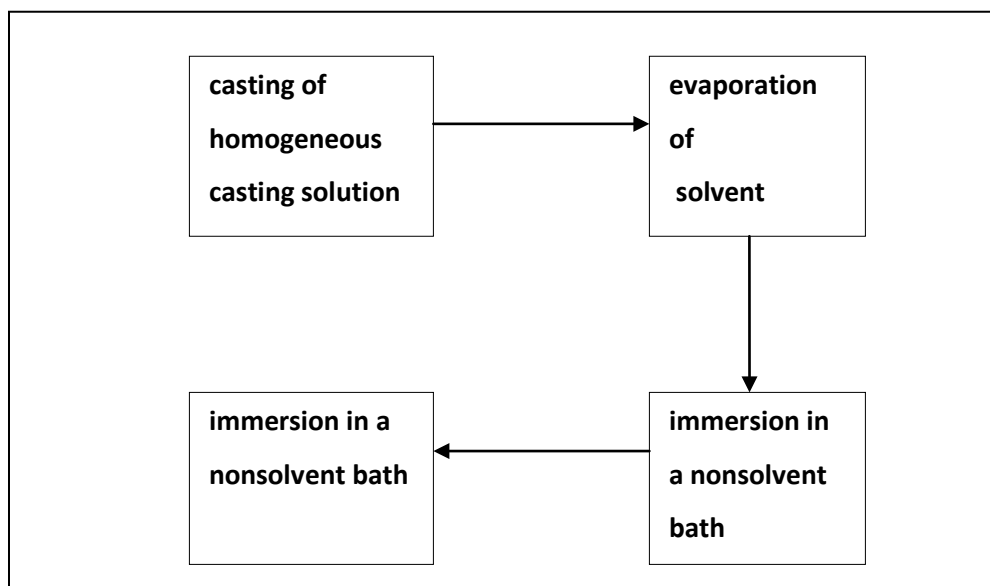
Figure 3.5: Stages of membrane casting

Casting process was conducted at room temperature (30°C±2) and approximately 84% relative humidity. A small amount of casting solution was pour onto a glass plate with a casting knife gap setting of 150µm and at an appropriate casting shear of 223.33 s^{-1}. Before being immerse into the coagulation medium, a force convective evaporation was induced on membrane during the casting process. A specified exposure time of 10s, an inert nitrogen gas stream was blown parallel and across the cast membrane surface which enable a sufficient amount of the easily volatized solvent to be evaporate. Both glass plate and the membrane was then had to be immersed into the coagulation bath (compose of water as the coagulant medium). The membrane is transfer to a water bath for 1 day after the coagulation process completes and finally wash with methanol for 1 day before being air dry for at least 48 hr at room temperature to remove any residual organic compounds.

3.5   **Membrane Characterization**

Membrane characterizations are all the experimental test that had been done in this study in fulfilling the objective to characterized the membrane.

3.5.1   CHNOS Elemental Analysis

CHNOS elemental analysis was conducted to determine the theoretical amount of elements for each sample. The data was then used for degree of sulfonation calculation. The analysis gives number of carbon, hydrogen, nitrogen, oxygen and sulfur content in the sample. For this test, the samples were cut into very fine pieces and were sent to Rubber Research Institute Malaysia (RRIM) to conduct the test.

The result from CHNOS analysis can later be used to calculate the degree of sulfonation by using this formula:

$$\% SO_3H = \frac{(s/c)\exp erimental}{(s/c)theoretical} x100\%$$

3.1

3.5.2   Water Uptake/ Swelling Test

The swelling characteristic are determine by using water uptake measurements. The membrane sample was first immersed in deionized water at $80^{o}C$ for 24 hours. The wet membrane then bottled dry to remove surface droplets and quickly weighted. The wet membrane was dried at $80^{o}C$-$100^{o}C$ and weighted again. The water uptake of the membranes are calculated by weight gain of absorbed water with reference to the dry membrane and reported as weight percent water absorption. The water uptake can be calculated as follows (Jaafar, 2005).

$$\text{Water Uptake} = (M_{wet} - M_{dry})/M_{wet} \qquad 3.2$$

Where,

M_{wet}=weight of wet membrane

M_{dry}=weight of dry membrane

3.5.3 Fourier Transform Infrared (FTIR)

FTIR was conducted in this experiment to study the chemical structure of organic molecules and potential structural changes that occur as a result of the membrane's chemical treatment or degradation.

3.5.4 Thermal Gravimetric Analysis (TGA)

Dynamic TGA was performed in nitrogen to assess the thermal stability of sulfonated polyether sulfone membrane. The samples are then heated at rate of 5C/min from 30°C to 900°C. Weight are measured and reported as function of temperature. The thermal stability of the polymers was generally reported at the observed temperature of 5% weight loss.

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CHAPTER 4

RESULT AND DISCUSSION

This chapter discussed the experiment that had been done in this study. The characterization of SPES was successfully done by FTIR, water uptake as well as the thermal stability of the sulfonated membrane by using TGA. Three samples was fabricated with different acid ratio as the sulfonating agent fuming sulfuric acid (36%), concentrated sulfuric acid (98%) and mixture of both acid.

4.1   Sulfonation reaction

In sulfonation reaction of PES, the SO_3H group was influenced to attach to the aromatic ring (1) as compared to ring (2). This was due to the characteristic of SO_3H group that prefers to attract the electron. There was no effect on sulfonation reaction if the SO_3H group attacks the ring (2) since the carbonyl group in that rings was also influenced to attract electron. Atomic oxygen in carbonyl group are more electronegative as compared to atomic carbon. This situation promotes the carbonyl group to attract the electron from the neighboring aromatic rings. Consequently, the carbonyl functional group deactivates the sulfonation substitution at the other ring. The sulfonation reaction was influenced by more active site in the polymer backbone which referred to the position that possesses higher electron density as compared to other positions. Therefore, the ether group will activate the ring (1) to the sulfonation reaction. This is another reason for the SO_3H group preferable attached to the aromatic ring.
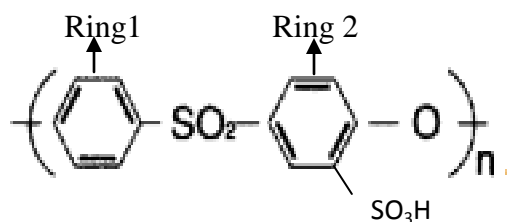
Fig. 4.1: Chemical structure of PES before and after sulfonation process.

Jaafar, *et al*, had stated that under ordinary sulfonation conditions (for example, at room temperature and with concentrated sulfuric acid used as solvent), there is only one SO_3H group (first type substitution) attached to each of the PES repeating units. However, at higher reaction temperatures or with long reaction times, the second type substitutions (the substitution in the two other aromatic rings or in the attached preferential aromatic ring) are also possible.

As a matter of fact, there was no clear-cut boundary between the first and second types of electrophilic substitution reaction. The second type substitution may be initiated when the first type substitution nearly comes to the end. Consequently, it was very important to decide the reaction time, operating temperature and also the sulfonating agent used in order to obtain desired degree of sulfonation (DS). Several other researchers also reported that the first type substitution reaction are more favorable since their experiment results showed that sulfonated PES became water-soluble when the sulfonation degree was approaching 100% (Jaafar,2005). Evidently, the second type substitution sulfonated PES was not suitable to be used as membrane materials. Therefore, the first type substitution was used in this study.

4.2 FTIR analysis

FTIR spectra for sample C at figure 4.4 with the mixture of sulfonating agent with the ratio of fuming sulfuric acid to concentrated sulfuric acid by 2 : 1 indicated the presence of two new absorption peaks at $1022\ cm^{-1}$ and $1071\ cm^{-1}$, representing the aromatic SO_3H symmetric and asymmetric stretching vibrations, respectively. This was in close agreement with $1020\ cm^{-1}$ and $1080\ cm^{-1}$ as reported by Gao *et al*,2000. The intensity of these peaks seemed to broaden as the degree of sulfonation (DS) is increased. This broadband confirmed the presence of sulfonic acid group in the parent PES. The peak identified at $1500\ cm^{-1}$ proved the presence of C–C aromatic ring in the PES, which referred to the 1,2,4-substitution aromatic ring. This peak was almost similar to the peak reported by Jaafar which was $1490\ cm^{-1}$. The broad absorption band of hydroxyl group appeared at $3415\ cm^{-1}$ was due to the hydrogen bonding between the SO_3H groups with absorbed water molecules. This peak could only be observed in the sulfonated PES membranes due to the attachment of SO_3H into the aromatic ring. The intensity of this peak would be remarkably enhanced with increasing SO_3H concentration. The presence of SO_3H group in the sulfonated PES membranes increases the amount of absorbed water and thus increased the number of hydrogen bonding involved. Thus, the FTIR spectra confirm the rule of sulfonation reaction in enhancing the hydrophilicity of the membrane. The peak observed in PES and sulfonated PES was at $1228\ cm^{-1}$ which referred to the aromatic C–O–C absorption.

FTIR spectra for sample B at figure 4.3 with the sulfonating agent by using concentrated sulfuric acid indicated the presence of two new absorption peaks at $1022\ cm^{-1}$ and $1066\ cm^{-1}$, representing the aromatic SO_3H symmetric and asymmetric stretching vibrations, respectively. This was in close agreement with $1020\ cm^{-1}$ and $1080\ cm^{-1}$ as reported by Gao *et al*,2000. The intensity of these peaks seemed to broaden as the degree of sulfonation is increased. This broadband confirms the presence of sulfonic acid group in the parent PES. There is no peak identified at $1486\ cm^{-1}$. This peak is supposedly to proved the presence of C–C aromatic ring in the PES, which

referred to the 1,2,4-substitution aromatic ring. There is however a slight peak absorption band of hydroxyl group appeared at 3423 cm^{-1} was due to the hydrogen bonding between the SO$_3$H groups with absorbed water molecules. This peak could only be observed in the sulfonated PES membranes due to the attachment of SO$_3$H into the aromatic ring.

FTIR spectra for sample A at figure 4.2 with the sulfonating agent of fuming sulfuric acid indicated the presence of two new absorption peaks at 1029 cm^{-1} and 1064 cm^{-1}, representing the aromatic SO$_3$H symmetric and asymmetric stretching vibrations, respectively. This was in close agreement with 1020 cm^{-1} and 1080 cm^{-1} as reported by Gao *et al*. The intensity of these peaks seemed to broaden as the degree of sulfonation is increased. This broadband confirms the presence of sulfonic acid group in the parent PES. However,no peak was identified at 1486 cm^{-1} that should proved the presence of C–C aromatic ring in the PES, which referred to the 1,2,4-substitution aromatic ring. The broad absorption band of hydroxyl group appeared at 3415 cm^{-1} was due to the hydrogen bonding.
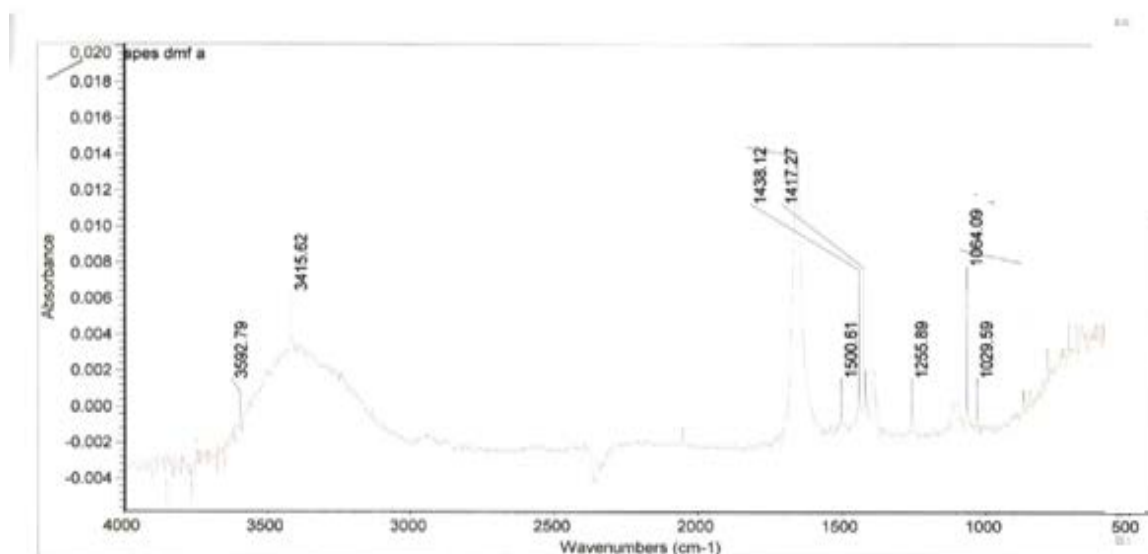
Figure 4.2: FTIR for sample SPES A
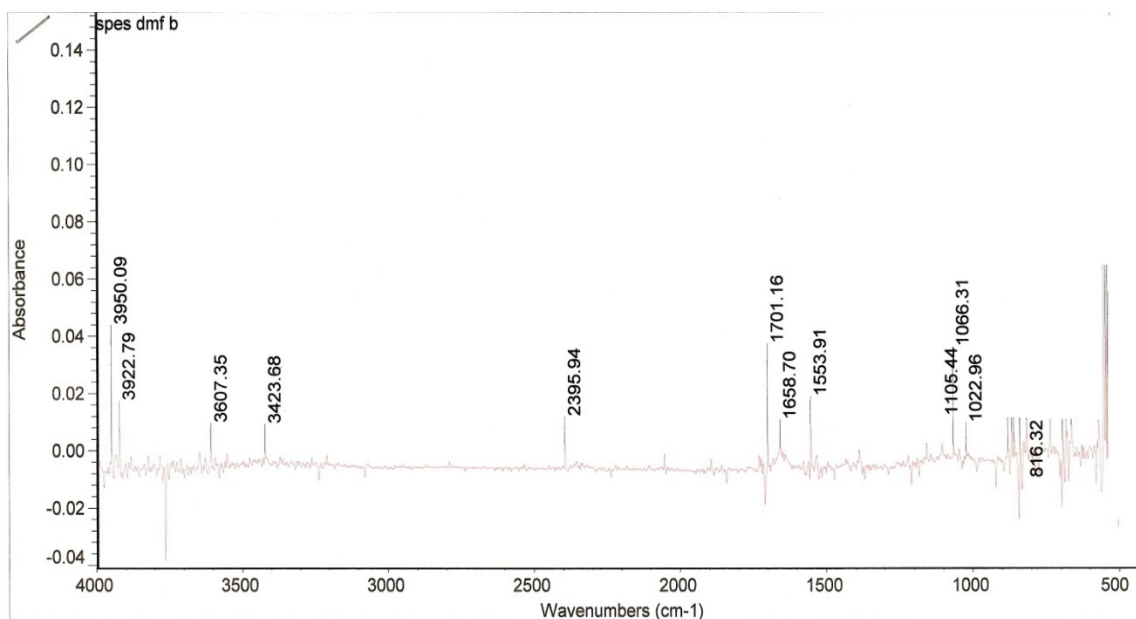
Figure 4.3: FTIR for sample SPES B
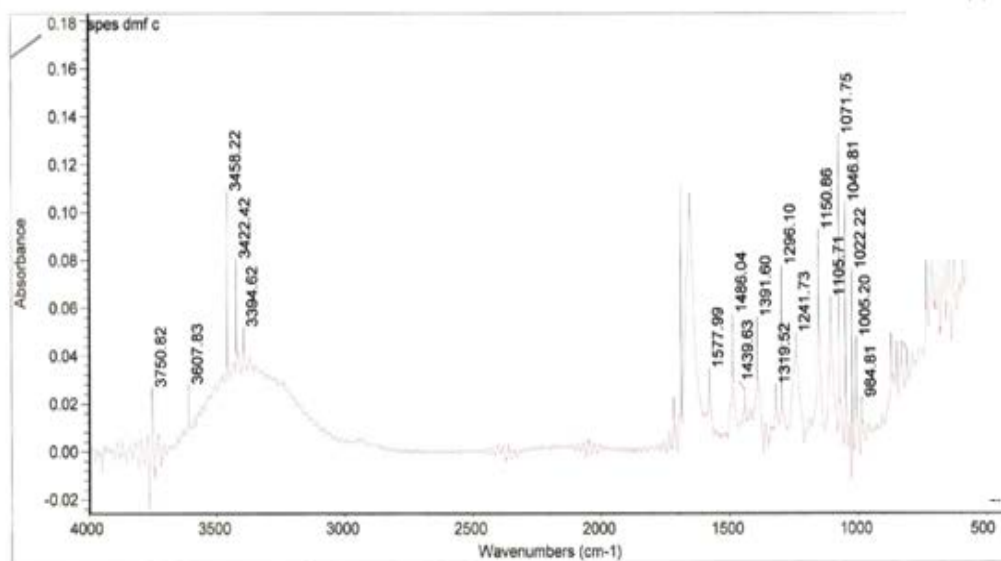
**Figure 4.4:** FTIR for sample SPES C

4.3   Thermal stability study

The thermal stability study involved the determination of the degradation temperature of pure polyethersulfone) and sulfonated polyethersulfone membranes using thermogravimetric analysis. The TGA analysis of SPES indicates the extent of which SPES can be thermally stable when subjected to various degree of sulfonation. The temperature at which SPES started to be thermally degraded was known as degradation temperature. The degradation temperature can be determined from the derivative thermogravimetry (DTG) The DTG curve shows that the degradation temperature of SPES decreased with increasing degree of sulfonation. The parent PES was a thermostable polymer, of which the maximum weight loss temperature was only observed at 590 °C. This temperature was corresponded to the decomposition temperature of the polymer chain. Meanwhile, all the SPES samples started to lose weight in the range of temperature 100–300 °C. The SPES membrane was predicted to undergo thermal degradation when the membrane loses water that interacts with sulfonic acid group during the sulfonation process (Wang *et al*, 2005).

From the observation form figure 4.5,figure 4.6 and figure 4.7, there seem to be two weight loss steps observed for SPES with 38%, 55% and 72% degree of sulfonation (DS), as indicated by two broad peaks in the DTG curve. The first weight loss peak was believed due to the decomposition of sulfonic acid group in the parent PES. The first maximum weight loss for SPES with the DS of 38% occurred at about 360 °C. Meanwhile, the first weight loss for SPES with the DS of 55% and 72% was observed at around 430 °C. The maximum value of the second peak for all the SPES samples appears to move away from the degradation temperature of PES (i.e. 590 °C) as the DS decreased. Interestingly, SPES with the DS of 72% seems to have three weight loss steps. Nevertheless, the present study indicates that they may have been at 400 °C and 460 °C, respectively previous studies also shows that SPES with the higher degree of sulfonation has bigger range of the weight loss temperature (i.e. 300–460 °C) as compared to that of the lower degree of sulfonation in the temperature range of 360–430 °C. This circumstance indicated that the weight loss during this period for the higher DS was due

to the elimination of residual sulfonic acid group. This was also could be explained by an enhanced asymmetry in the parent polymer structure due to the introduction of sulfonic acid groups that rendered it less stable. Although the degradation temperature was observed relatively at a low temperature, such thermal decomposition was well above the normal operating temperature of direct methanol fuel cell (i.e. 60–120 °C). It had been proven that the thermal stability of SPES membranes was sufficient and thus thermally stable for fuel cell application.
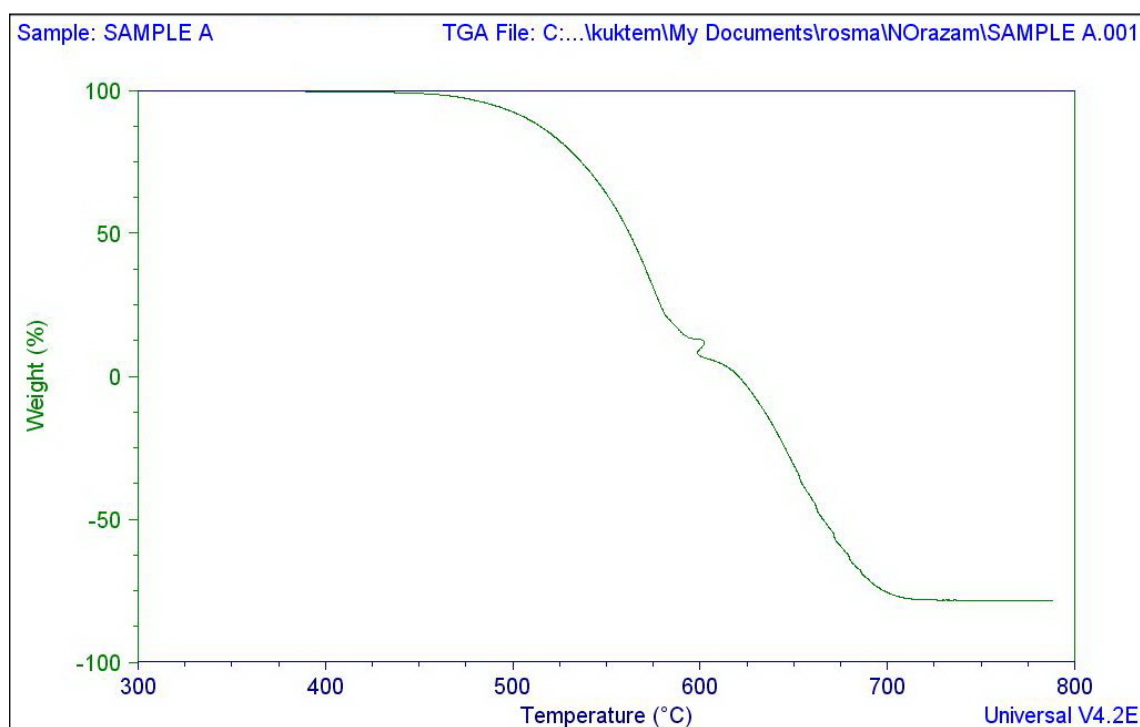
Figure 4.5: TGA analysis for sample A
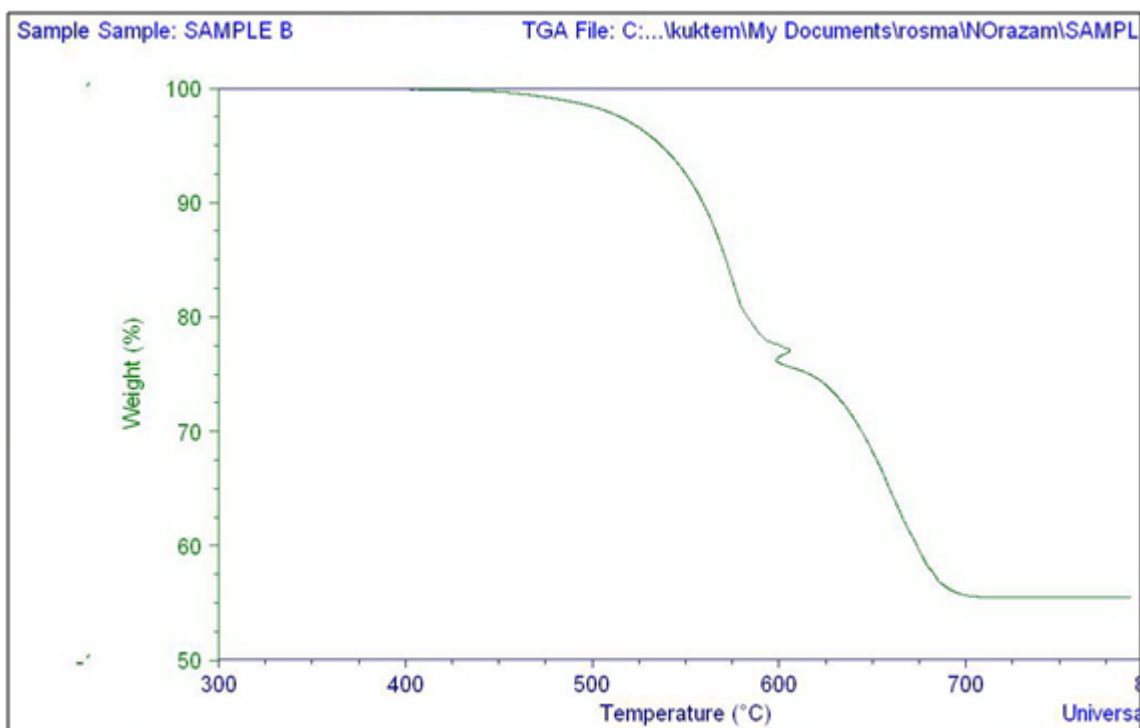
Figure 4.6: TGA analysis for sample B
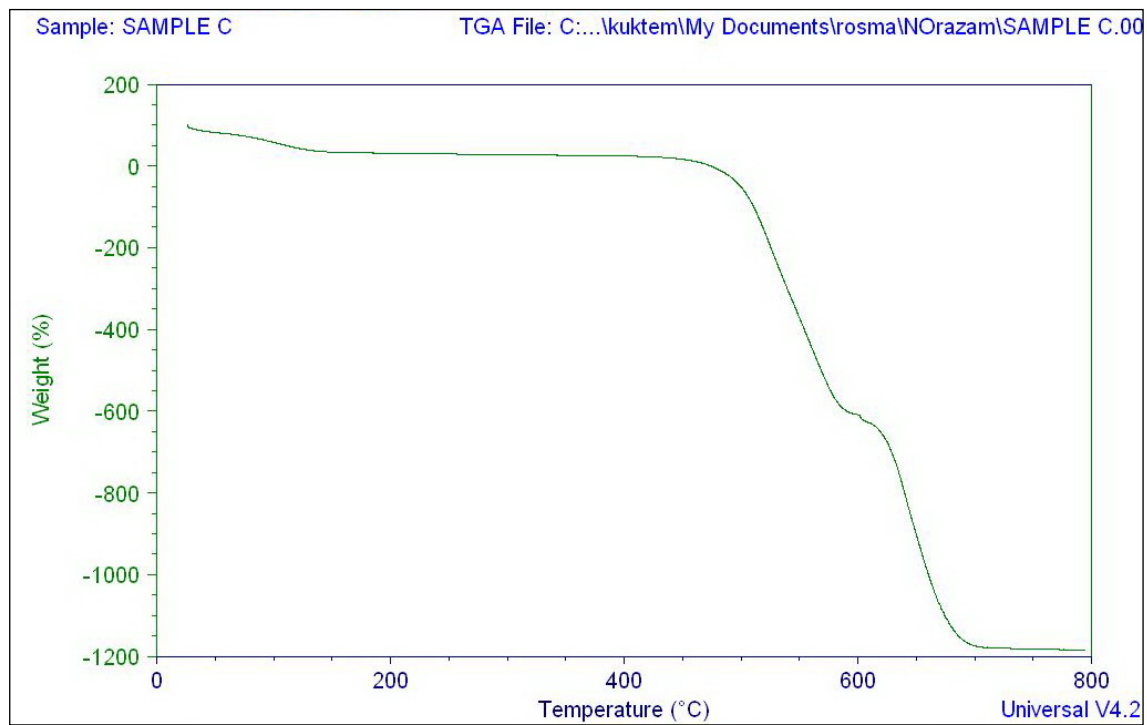
Figure 4.7: TGA analysis for sample C

4.4   CHNOS Elemental Analysis

CHNOS elemental analysis had been conducted to obtain experimental data for degree of sulfonation calculation. The samples were sent to Rubber Research Institute of Malaysia (RRIM) to undergo the analysis needed. The results were grouped in Table 4.1:

Table 4.1: Summary of CHNOS Elemental Analysis

Sample	Elemental Analysis (%)				
	C	H	N	O	S
PES	67.631	5.300	0.613	16.133	7.324
SPES A	62.241	5.321	0.098	19.553	8.955
SPES B	59.242	5.328	0.075	21.336	9.522
SPES C	56.872	5.361	0.058	24.057	11.138

The results show that sample SPES C has the highest sulfur, oxygen and hydrogen content due to the minture of fuming sulfuric acid and concentrated sulfuric acid that were used as the sulfonating agent added. The data of sulfur and carbon content of each sample was used to calculate degree of sulfonation.

4.5   Degree of Sulfonation Calculation

Degrees of sulfonation are quantitative analysis based on the data obtained from CHNOS elemental analysis. Degree of sulfonation can also be defined as the percentage of SO_3H group associated with the polymer ($\%SO_3H$). The formula has been used to calculate degree of sulfonation:

$$\%SO_3H = \frac{(s/c)\exp erimental}{(s/c)theoretical} x100\% \qquad 4.1$$

where the value of (S/C) theoretical are considered as the amount of sulfur content over the amount of carbon content in the PES membrane while the value of (S/C) experimental are the value of sulfur content over the amount of carbon content in the sulfonated samples (SPES A, SPES B and SPES C) minus the (S/C) theoretical value. Table 4.2 summarizes the sulfur and carbon content obtained from CHNOS elemental analysis for each sample:

Table 4.2: Sulfur and Carbon Content Summary

Sample	Carbon Content (%)	Sulfur Content (%)
PES	67.631	7.324
SPES A	62.241	8.955
SPES B	59.242	9.522
SPES C	56.872	11.138

The value of (s/c) theoretical is calculated as follows:

$$\left(\frac{S}{C}\right) Theoretical = \frac{Spes}{Cpes} = \frac{7.324}{67.631} = 0.108$$

Then the experimental values for each sample were calculated:

$$\left(\frac{S}{C}\right) Experimental\ SPESA = \frac{SpesA}{CpesA} = \frac{8.955}{62.241} = 0.144$$

$$\left(\frac{S}{C}\right) Experimental\ SPESB = \frac{SpesB}{CpesB} = \frac{9.552}{59.242} = 0.161$$

$$\left(\frac{S}{C}\right) Experimental\ SPESC = \frac{SpesC}{CpesC} = \frac{11.138}{56.872} = 0.196$$

After all the calculation had been done, the degree of sulfonation was calculated by using:

$\%SO3H = [(s/c)_{experimental} - (s/c)_{theoretical}]/ (s/c)_{theoretical} \times 100\%$ 　　　　4.2

The results were tabulated in Table 4.3 below:

Table 4.3: Degree of Sulfonation for each Sample

Sample	Degree of Sulfonation (%)
PES	-
SPES A	38.46
SPES B	55.49
SPES C	72.53

From the result gained, the sample with both fuming and concentrated sulfuric acid achieve the highest degree of sulfonation of 72 % which should be more superior amongst the other sample as been stated by a research conducted by Jaafar,2005.
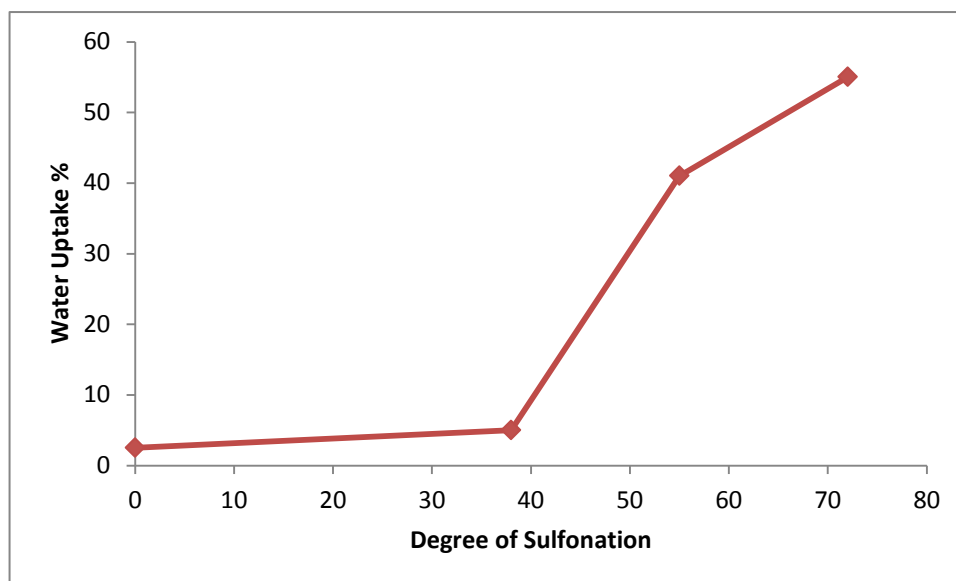
4.6   Water uptake

The sulfonation of PEEK polymer was also aimed at improving its water uptake capability which are important in fuel cell system. A strong relation between the DS and water uptake was illustrated in Fig. 4.8. The results showed that the water uptake of the sulfonated PES C membrane at the 72% DS was superior to that of SPEEK membrane studied by Jaafar, 2007. This was due to the microstructure of the polymer which distributed to two domains; hydrophobic domain represented by the polymer backbone and hydrophilic domain represented by the functional group attached to the polymer ring.

SPES B which uses concentrated sulfuric acid as the sulfonating agent has the water uptake reading as high as 41 %. It is still considered a very good result compared to standard PES which is only at 2.5 %.

The SPES A meanwhile gave the lowest water uptake percentage at only 5 %. This evidently shows that fuming acid can be used as sulfonating agent but there are better alternatives like SPES C and SPES B. From the SPES membranes point of view, the presence of aromatic group in the SPEES polymer backbone presented less

pronounce of the hydrophobic domain. Hence, hydrated hydrophilic domain of the SPES membranes could be expanded. A comparable finding of water uptake for the SPES membranes with 80% DS was reported by Jaafar, 2007.

Fig. 4.8: Water uptakes for sulfonated PES membranes as a function of the degree of sulfonation.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

SPES membranes with different degrees of sulfonation were successfully prepared using different mixtures of fuming sulfuric acid and sulfuric acid as the sulfonating agent. The formation of sulfonic acid group in SPES membranes was successfully confirmed by FTIR. SPES films showed a continuous increase in the water uptake with DS. The degradation temperatures of the SPES membranes are well above the standard polyethersulfone membrane. Amongst all three membranes, samples C with incorporating mixture sulfonating agent evidently showed comparison with results done by other researchers. Sample C fulfills all the criteria in FTIR and give the best result for degree of sulfonation as well as water uptake. Sample C also give a satisfied result for thermal stability test. Hence SPES C membranes exhibited higher overall performance than SPES A and SPES B membrane.

5.2   Recommendation

Throughout the experiment in fabricating and characterizing of the membranes, most of the problem faces are while sulfonating the membranes and fabricating the membranes. This problem can be settled with this few suggestions:

(i) Pneumatically casting machines should be used rather than manual casting machine. This is to ensure that the thickness of the membranes are same and the weight reading for water uptake is more precise.

(ii) Nitrogen gas should be prepared automatically so that we can fixed the flow for the nitrogen.

(iii)More test should also be conducted so that more characterized of the membranes can be studied.

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GANT CHART

Activity / Project	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
1. Literature Review	■	■	■	■	■	■	■	■	■	■		
2. Sulfonation Process				■	■	■	■	■	■			
3. Membrane Fabrication i. Membrane Solution Preparation (Dope) ii. Membrane Fabrication (Dry /Wet Phase Inversion)					■	■	■	■	■	■		
4. Membrane testing i. Water uptake (Swelling) ii. Ion Exchange Capacity							■	■	■	■		
5. Membrane Characterization i. Thermo gravimetric Analysis (TGA) ii. Differential Scanning Calorimetric (DSC) iii. Fourier Transform Infrared (FTIR) iv. Scanning Electron Microscopy (SEM)									■	■	■	
6. Data analysis and report writing										■	■	■
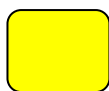
■ Project activity

APPENDIX

Fig A.1: Mixing of membrane solution

Fig A.2: Degassing of sulfonated solution

Fig A.3 : Ultrasonic Cleanser

Fig A.4: Sulfonated solution