

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

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**JUDUL : DEVELOPMENT & CHARACTERIZATION OF SULFONATED
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EXCHANGE MEMBRANE FUEL CELL APPLICATION**

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

**Faculty of Chemical and Natural Resources Engineering
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APRIL 2010

I declare that thesis entitled “Development & 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.

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Dedicated, in thankful appreciation for support, encouragement and understanding to
my beloved family and friends.

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Finally, I hope that this thesis will give the readers some insight as to maze of activities associated with the characterized and developed of polyethersulfone membrane from its planning stages until it is ready for start-up and commissioning.

ABSTRACT

Sulfonation process was used to produce ion exchange polymer from a commercial polyethersulfone. Sulfonations were achieved by varying the degree of sulfonation (DS) in reaction time. Water and methanol uptake analysis showed this SPES6 have the potential to use in proton exchange membrane fuel cell application compared to another membrane. Methanol uptake analysis showed Nafion 117 have no potential to use in direct methanol fuel cell application because the tendency of Nafion to swell is very high. FTIR analysis showed that the peak of sulfonic group was appeared at wavelength 1072 to 1074 cm^{-1} . TGA analysis showed that the range temperature that was assigned to the degradation of the polymer main chain at around 400°C.

ABSTRAK

Proses pensulfonan telah dikaji untuk menghasilkan polimer kapasiti penukaran ion dari polimer polietersulfona . Proses pensulfonan dijalankan dengan mempelbagaikan darjah pengulfonan dalam masa reaksi yang berbeza. Kaedah keberaliran dan kaedah kemetanolian menunjukkan SPES6 mempunyai potensi untuk digunakan dalam “PEMFC” jauh berbeza dengan membran- membran yang lain. Nafion 117 tidak mempunyai potensi untuk digunakan di dalam penggunaan “DMFC” kerana ianya mempunyai kebolehan untuk penyahairan adalah sangat tinggi Kaedah FTIR analisis menunjukkan kewujudan kumpulan sulfonic pada kadar gelombang antara 1072 cm^{-1} hingga 1074 cm^{-1} . Analisis TGA menunjukkan lingkungan suhu untuk pengurangan ikatan utama polimer adalah sekitar 400°C .

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CHAPTER 1

INTRODUCTION

1.1 Research Background

A fuel cell is an electrochemical device that converts the chemical energy of a reaction directly into electrical energy. Fuel cell also can be define as the chemical energy of a fuel and oxidant is convert directly into electrical energy.

The fuel cell is one of the electrochemical device that contain two electrodes and electrolyte that uses in chemical reaction to produce electricity. Many people thought that a fuel cell look like a battery. However, it didn't like a battery because a fuel cell never "goes dead" and never needs recharging. As long as a fuel cell has a constant supply of fuel and oxygen, it will continue to produce among or power. A fuel cell had been used since year 1839 till now.

Because of the role of coal as the major fuel at the beginning of the 20th century, the emphasis was put on coal-derived fuels first. Early 1960s, General Electric company produced the fuel cell-based electrical power system for NASA's

Gemini and Apollo space capsules. General Electric used the principles found in the 'Bacon Cell' as the basis of its design. Today, the Space shuttle's electricity is provided by fuel cells, and the same fuel cells provide drinking water for the crew. NASA decided that using nuclear reactors was too high a risk, and using batteries or solar power was too bulky to use in space vehicles. The fuel cell can be used in many sectors such as transportation and industrial. It is also used in space. It was also used in vehicle engine systems such as Toyota and Benz.

Generally, fuel cells also have their advantages and disadvantages too. Fuel cells have various advantages compared to conventional power sources, such as batteries and internal combustion engines. From all advantages that state in different books and journals, we can see that fuel cells eliminate pollution caused by the product of combustion of fossil fuel, which is only water. Fuel cells also can eliminate greenhouse gases if the hydrogen used comes from the electrolysis of water. Since hydrogen gas can be produced anywhere where there is water and electricity, production of potential fuel can be distributed. The installation of smaller stationary fuel cells leads to a more stabilized and decentralized power grid. As we know, fuel cells have a higher efficiency than diesel or gas engines. Compared to internal combustion engines, most fuel cells can operate silently.

Proton exchange membrane fuel cell (PEMFC) is one of the fuel cells that is used in automotive and stationary power applications. It is also used for lower power CHP systems. Proton exchange membrane fuel cells (PEMFCs) are also known as polymer electrolyte membrane fuel cells. Sometimes, proton exchange membrane fuel cells (PEMFCs) are also known as membrane fuel cells.

PEMFC is used in automobile applications. Some car manufacturers are working on their own fuel cell technology such as General Motors, Toyota, and Honda. Besides that, PEMFC is also used on scooters and bicycles. PEMFC is also used as power backup. Proton Energy Systems demonstrated regenerative fuel cells combining its own PEM electrolyzer technology with Ballard's Nexa units. PEMFC is also used by NASA in the future as an energy source in space. The electrolyte that is used in PEMFC is a polymer membrane. It was operated at a temperature range of 50-

100°C. PEMFC is types of the fuel cell that state in low temperature fuel cell section. Its used membranes as one of the fuel cell process.

In oder to get the most efficient system of PEMFC, the membrane develop need to have a good and stable membrane operating at desired temperature and pressure. The need of developing membrane that satisfies this condition with the minimum cost of production and maintenance are recommended.

1.2 Problem Statement

The increasing of the energy and the large demand of power generation can cause harmful to our environment. It can cause greenhouse and other pollutant to the environment. CO₂ will be produce during combustion process. CO₂ will be increase into our environment and cause emission. CO₂ emission from developing nations could account for more than half the world's CO₂ emissions. In the present of water and CO₂, it can cause solidification and corrosion.

In aspect transportation, the vehicle need electric that have high efficiency. Heat engine need to achieve a large temperature differential to achieve the same Carnot cycle efficiency. The combustion of engines, whether piston or turbine have good efficiency, but in present of fuel cell, it can be more efficient than that and can help to reduce the emission.

The batteries have their own limit. It need to recharge if it power is empty. Different with the fuel cell, it never goes dead and never need to recharge. As long as fuel cell has a constant supply of fuel and oxygen, it will continue to produce among of power.

Currently, common membrane for Proton Exchange Membrane Fuel Cell (PEMFC) is perflourosulfonic acid called NafionTM. Until now Nafion remains as standard for industry but it was very expensive to produce and require heat, high pressure and high level hydration in oder to perfom effectively. Thus the main

research in membrane fuel cell is to develop cost-effective material and membrane that can operate at low pressure and at high temperature.

1.3 Objective

The objective of this research is to develop and characterize of sulfonated polyethersulfone membranes using chlorosulfonic acid for Proton Exchange Membranes Fuel Cell (PEMFC) application.

1.4 Scope of the Research

In order to accomplish the set objectives, the following scope of works has been drawn.

- i. Development and fabrication the sulfonated polyethersulfone as a membrane for fuel cell.
- ii. Study the physical and chemical characteristic of sulfonated polyethersulfone membrane using Fourier Transform Infrared Spectroscopy (FTIR), Swelling Test and Thermal Gravimetric Analysis (TGA).

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Review

Membrane technology has become a common separation technique. The main attraction of membrane technology is that it consumes a relatively low amount energy and involves a simple and well-arranged set-up process (Conesa *et al*, 2007).

2.1.1 Definition of Membrane

Membranes are thin semi-permeable barriers that selectively separate some compounds from others. This definitions is necessarily broad because of the large variety of membrane materials separating an equally vast number of compounds in all phases (Dortmundt *et al*, 1999).

Membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100 µm to several mm (Nunes *et al*, 2003).

2.1.2 Type of Membrane

There are several types of membrane but most of them still have the same basic principle and structure.

2.1.2.1 Asymmetric Membranes

Asymmetric membranes are a vast improvement on homogenous membranes, they do have one drawback. Because they are composed of only one material, they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts. This difficulty is overcome by producing a composite membrane, which consists of a thin selective layer made of one polymer mounted on an asymmetric membrane, which is composed of another polymer (Dortmundt *et al*, 1999).

2.1.2.2 Composite Membranes

The composite membranes allows membrane manufacturers to use readily available materials for the asymmetric portion of the membrane and specially developed polymers, which are highly optimized for the required separation, for the selective layer. Composite structures are being used in most of the newer advanced CO₂ removal membranes because the properties of the selective layer can be adjusted readily without increasing membrane cost too significantly (Dortmundt *et al*, 1999).

2.1.2.3 Microporous Membranes

Membrane behaves almost like a fiber filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxide and polymers are used in making such membranes (Scott *et al*, 1998)

2.1.2.4 Homogenous Membranes

This type of membrane is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be depends on their concentration (Scott *et al*, 1998).

2.1.2.5 Electricity Charged Membranes

These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These are mainly used in the electro-dialysis (Nunes *et al*, 2003).

2.2 Membrane Separation Process

2.2.1 Separation Process

A separation process could be defined as a process that transforms a given mixture of chemicals into two or more compositionally distinct end-use products. One way to design these separation processes is to employ a model-based approach,

where mathematical models that reliably predict the process behaviour will play an important role (Soni *et al*, 2008).

A membrane-based separation process separates an influent stream into two effluent streams known as permeate and retentate with the help of a membrane. A membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemical species in a selective manner. The stream that permeates through the membrane is the permeate stream while the one retained by the membrane is the retentate. Either of the two streams could be the end-use products in a membrane-based separation process.

Polymeric membranes can be classified as: porous and nonporous membranes (Mulder, 1996). A porous membrane is very similar in structure and function to a conventional filter (Baker, 2004). It has rigid, highly voided structure with randomly distributed, interconnected pores. Separation in these kinds of membranes is dependent on both the molecular size and pore size distribution. Non-porous membranes (also referred as dense membranes), consist of a dense film through which permeant molecules are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation is mainly determined by the diffusivity and solubility of the permeant molecules in the membrane material.

Membrane-based gas separation is an important process that has been extensively used for many tasks involving gas separations. For example, separation of hydrogen from gaseous mixtures of nitrogen and/or methane, and, recovery of hydrogen from product streams in ammonia production process. While non-porous polymeric membranes are usually used for membrane-based gas separations, porous membranes may also be employed. The pore diameter of the polymer must be smaller than the mean free path of gas molecules. Under normal condition (100 kPa, 300 K), it is about 50 nm, when, the gas flux through the pore is proportional to molecule's velocity, i.e., inversely proportional to square root of the molecule mass.

This transport phenomenon, commonly known as Knudsen diffusion, is an important factor in modelling and design of membrane-based gas separation processes.

Membrane-based separation processes have started to replace large scale conventional separation processes owing to their advantages over the conventional processes. They are often more capital efficient compared to conventional separation processes with appreciable energy savings. They are environmentally more benign and, in general, they are considered as a clean technology. The membrane units and devices are usually compact, modular, usually require less vapour spaces, and, operate at low pressures. The main disadvantages, which have prevented even wider applications of membrane-based processes, are the fouling of the membranes, the durability of membranes and the availability of suitable membranes for specific operations.

2.2.2 Type of Membrane Separation Process

There are several different type of membrane process and all based on the same principle which allowed the selected particle or ion pass through their body. But the way how it's operated will exactly differ with each other.

2.2.2.1 Ultrafiltration

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. In UF, the membrane pore size is larger allowing some components to pass through the pores with the water. It is a separation/ fractionation process using a 10,000 MW cutoff, 40 psig, and temperatures of 50-60°C with polyethersulfone membranes (Meier *et al*, 2000).

2.2.2.2 Microfiltration

Microfiltration designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. Membrane pore size allowing particles in the range of 0.2 to 2 micrometers to pass through. The pressure used is generally lower than that of UF process.

2.2.2.3 Reverse Osmosis or Hyperfiltration

Reverse osmosis (RO) designates a membrane separation process, driven by a pressure gradient, in which the membrane separates the solvent (generally water) from other components of a solution. The membrane configuration is usually cross flow. With reverse osmosis, the membrane pore size is very small allowing only small amounts of very low molecular weight solutes to pass through the membranes. It is a concentration process using a 100 MW cutoff, 700 psig, temperatures less than 40°C with cellulose acetate membranes and 70-80°C with composite membranes.

2.2.2.4 Electrodialysis

Electrodialysis is used for demineralization of milk products and whey for infant formula and special dietary products. Also used for desalination of water. Under the influence of an electric field, ions move in an aqueous solution. The ionic mobility is directly proportioned to specific conductivity and inversely proportioned to number of molecules in solution. $3-6 \times 10^2$ mm/sec charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are

permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations (Nunes *et al*, 2003).

Anion and cation exchange membranes are arranged alternately in parallel between an anode and a cathode. The distance between the membranes is 1mm or less. A plate and frame arrangement similar to a plate heat exchanger or a plate filter is used. The solution to be demineralised flows through gaps between the two types of membranes. Each type of membrane is permeable to only one type of ion. Thus, the anions leave the gap in the direction of the anode and cations leave in the direction of the cathode. Both are then taken up by a concentrating stream (Scott *et al*, 1998).

Table 2.1 shown that the characteristics membranes used in different membrane separation. The process that membrane can be applied which is microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation, pervaporation and nanofiltration.

Table 2.1:The characteristics membranes used in different membrane separation
(Nunes *et al*, 2003).

Process	Membrane type and pore radius	Membrane material	Process driving force	Application
Microfiltration	Symmetric microporous, 0.1-10 microns	Cellulose nitrate or acetate, Polyvinylidene difluoride (PVDF), Polyamides, Polysulfone, PTFE, Metal Oxides etc	Hydro-static pressure difference at approx. 10-500 kPa	Sterile filtration, Clarification
Ultrafiltration	Asymmetric microporous, 1-10 nm	Polysulfone, Polypropylene, Nylon 6, PTFE, PVC, Acrylic Copolymer	Hydrostatic pressure difference at approx. 0.1-1.0 Mpa	Separation of macromolecular solutions
Reverse Osmosis	Asymmetric skin-type, 0.5-1.5 nm	Polymers, Cellulosic acetate, Aromatic Polyamide	Hydrostatic pressure difference at approx. 2-10 Mpa	Separation of salts and microsolute from solutions
Electrodialysis	Cation and anion exchange membrane	Sulfonated crosslinked polystyrene	Electrical potential gradient	Desalting of ionic solutions
Gas Separation	Asymmetric homogeneous polymer	Polymers & copolymers	Hydrostatic pressure and concentration gradients	Separation of gas mixtures
Pervaporation	Asymmetric homogenous polymer (A non-porous membrane)	Polyacrylonitrile, Polymers	Vapour pressure gradient	Separation of azeotropic mixtures
Nanofiltration	Thin-film membranes	Cellulosic Acetate and Aromatic	9.3-15.9 bar	Removal of hardness and desalting

2.3 Fuel Cell Technology Review

2.3.1 Definition of Fuel Cell

A fuel cell is an electrochemical device which converts fuel energy directly into current (DC) without resorting to a burning process. In it, energy chemically stored is converted into electric current by means of an electrochemical process in the fuel cell. The chemical energy of the fuel is released in the form of a stream of electrons instead of heat when the fuel is oxidized in an ideal electrochemical cell. Fuel cells forego the traditional extraction of energy in the form of combustion heat, conversion of heat energy to mechanical energy (as with a turbine) and finally turning mechanical energy into electricity (e.g. using a dynamo). In contrast to it, the fuel cell is based on the chemical combination of the molecules of a fuel and oxidizer without burning and, thus, dispensing the pollution of traditional combustion (Chaurasia *et al*, 2001).

A fuel cell is an electrochemical device (a galvanic cell) which converts free energy of a chemical reaction into electrical energy (electricity); byproducts are heat and water/steam if hydrogen and air are the reactants; in some fuel cell types, the additional byproducts may be carbon dioxide and leftover lower forms of hydrocarbons depending on the fossil fuels used (Shah, 2007).

Since the fuel need not be burned in the fuel cell to generate the heat to produce the electric power, fuel cell systems are considered to be an efficient, non polluting power source, as it does not involve the intermediate steps like the burning process or associated processes. The power production from the fuel cell system is also free from the noise menace, as it has practically no rotating or moving parts. In principle, a fuel cell operates like a battery, which may be used for various applications in day to day life. In contrast to a battery, a fuel cell does not run down or require recharging. It produces the energy in the form of electricity and heat as long as fuel is supplied. The fuel cells are simple and compact in design, as well as having high power density and high energy efficiency (Chaurasia *et al*, 2001).

All these factors make fuel cell technology very attractive and have potential applications in numerous fields, such as in space, automobiles, individual power generation for remote homes, portable power sources in the army, emergency electricity supply (or as a backup power unit) for lighting, computers, medical equipment, computers, telephones, televisions etc. in case of power failure and now for future application for solar energy utilization through a solar thermal cell (Chaurasia *et al*, 2001).

2.3.2 Basic Concept of Fuel Cell

The concept of the conventional fuel cell is shown in Figure 2.1. A fuel cell consists of two electrodes sandwiched around an electrolyte. Most often, hydrogen is used as the fuel in the fuel cells. The hydrogen reacts with oxygen from the air in such a way that a voltage is generated between the two electrodes. The reactions occur in a chemical mediator known as an electrolyte (ion conducting membrane) in the presence of catalysts. The fuel cell consumes the hydrogen directly, which is fortunately one of the most abundant elements on Earth. Hydrogen fuel is fed to the “anode” of the fuel cell. Oxygen (or air) enters the fuel cell through the cathode. The hydrogen atom splits into a proton and an electron at the anode due to the presence of catalysts (see Fig. 2.1). These protons and electrons return to the cathode through the electrolyte and the outer path (external load), respectively. The electrons create a separate current in the outer path, which can be utilized before the electrons return to the cathode. These electrons are united with the protons and oxygen to form a molecule of water (waste of fuel cell emissions) (Chaurasia *et al*, 2001).

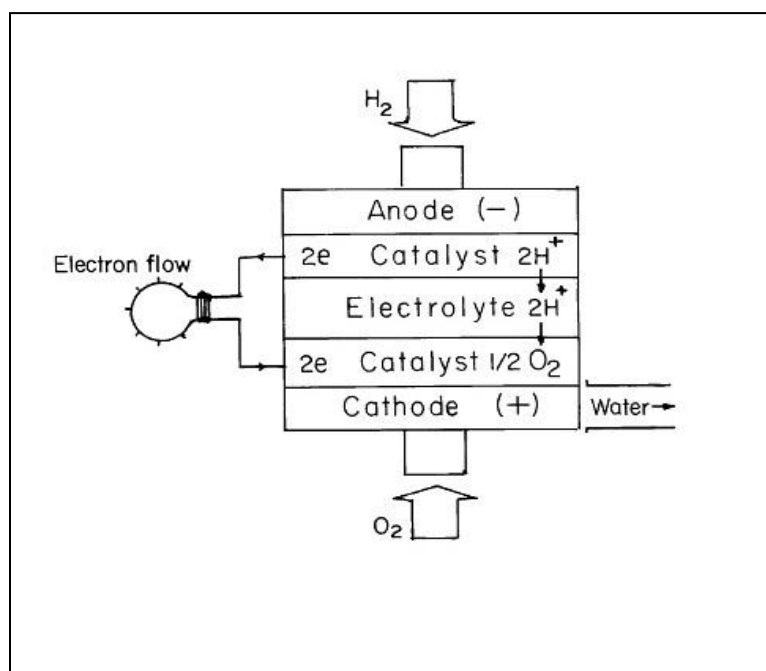


Figure 2.1: Concept of fuel cell system (Chaurasia *et al*, 2001)

2.3.3 History of Fuel Cell

The concept of the fuel cell was advanced by Sir William Grove in 1839, who is widely attributed as father of the fuel cell. Grove insights were gained from his experiments in 1839 on the basis of electrolysis of water. The electrolysis of water is a method whereby direct current is passed through water to separate it into hydrogen and oxygen. Grove argued that the electrolysis process of water may be reversed whereby hydrogen may be combined with oxygen to generate electric current, which ultimately became the principle of the fuel cell. Efforts were continued for development of fuel cells and Ludwing Mond and Charles Langer attempted to build the first practical device in 1889. Serious interest in fuel cell began from 1960 and onward when the US Space Program (National Aeronautics and Space Administration—NASA) chose fuel cells to provide on board power for an upcoming series of manned space missions after discarding the nuclear reactors as too risky, batteries as too heavy and short lived and solar power as too cumbersome and expensive. Fuel cells furnished power for the Gemini and Apollo spacecraft and played a key part in the landing of man on the moon. Electricity in many

installations, such as banks, hospitals, schools, buildings etc. in the USA, Japan and Germany are met by fuel cells. Apart from it, a few vehicles based on fuel cells are also in operation in various countries. There are more than 200 units based on fuel cell technology, which are in operation for power generation in various countries (Chaurasia *et al*, 2001).

2.3.4 Type of Fuel Cell

Various types of the fuel cells have been developed to generate power according to the applications and load requirements. Some fuel cells are the proton exchange membrane (PEM) fuel cell, phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). These fuel cells are normally distinguished by the electrolyte used, although the construction of the electrodes (fuel cell hardware) are also different in each case. The details of these different types of fuel cells are summarized in Table 2.2.

There is six major fuel cell technologies at varying stages of development and commercialization. There are alkaline, phosphoric acid, polymer electrolyte membrane, molten carbonate, solid oxide and direct methanol fuel cells.

Six of the fuel cell can be divide by followed between three section. First section is at low temperature of fuel cells, intermediate temperature fuel cells and the last one is high temperature fuel cells. For low temperature fuel cells, the fuel cells that in this categories is Alkaline fuel cell (AFC), Proton exchange membrane fuel cell (PEMFC), Phosphoric acid fuel cell (PAFC) and Direct methanol fuel cell (DMFC). For intermediate temperature fuel cells, the type of fuel cells that in this categories is Ceramic proton exchange fuel cell and Low temperature solid oxide fuel cells. And for the high temperature fuel cells is Molten carbonate fuel cell (MCFC) and Solid oxide fuel cell (SOFC).

Table 2.2: Typical characteristics and other essential features of fuel cell types

Fuel cell type	SOFC	PAFC	AFC	MCFC	DMFC	PEMFC
Characteristics						
Mobile ion	O_2^-	H^+	OH^-	CO_3^{2-}	H^+	H^+
Cell component	Ceramic	Graphite-based	Carbon-based	Stainless steel	Carbon-based	Carbon-based
Catalyst	Perovskites($Co-ZrO_2$ Ni- ZrO_2 anode, Sr-LaMnO ₃ cathode, Y ₂ O ₃ stabilized ZrO_2 electrolyte	Platinum	Nickel/Silver metal oxides, noble metals	Nickel anode, NiO cathode	Pt-Pt/Ru	Platinum
Operating temperature	700-1000°C	150- 220°C	50-200°C	600-700°C	0-60°C	50- 100°C
Electrolyte	Yttrium-stabilized Zirkondioxide	Concentrated 100% phosphoric acid	Concentrate (30-50%) KOH in H ₂ O	Molten Carbonate retained in a ceramic matrix of LiAlO ₂	Polymer (plastic) membrane	Polymer plastic membrane
Water management	Gaseous products	Evaporate		Gaseous products		Evaporate
Applications and notes	Vehicle auxiliary power, suitable for all sizes of CHP systems, 2kW to multi-MW	Stationary power, large power of 200-kW CHP systems in use.	Space vehicle (Apollo, Shuttle) and drinking water,	Stationary power, suitable for medium to large scale CHP systems, up to MW capacity	Portable power, suitable for portable electronic systems of low power, running for long times.	Automotive and stationary power, low power CHP systems
Density (kW/m³)	0.1-1.5	0.8-1.9	~1	1.5-2.6	~0.6	3.8-6.5
Combined cycle fuel cell efficiency	55-65%	55%	50-60%	55-65%	30-40%	50-60%
Advantages	High efficiency, flexibility of fuels, solid electrolyte reduces corrosion and management problem, internal reforming possible.	High efficiency for cogeneration, can tolerate impure hydrogen fuel	High performance, simple design	High efficiency, flexibility of fuel types, internal reforming possible CO/CO ₂ tolerant	Higher energy density than batteries, faster recharging	Low temperature, quick start up, solid electrolyte reduced corrosion and management problem
Primary fuel	H ₂ , CO	H ₂	H ₂	H ₂ , CO,	CH ₃ OH	H ₂

2.4 Sulfonation Process

In order to reduce difficulty in processing the aromatic polymers, more linking groups were often put between the aromatic rings. The linking added must have a good flexibility while it still maintained the polymers thermal properties. One of these linking groups was sulfonic group. Sulfonic can be added into the polymer structure via sulfonation. This sulfonation depends mainly on the polymer base unit and sulfonating agent. It was a very simple process and can help in reducing the cost of the membrane production (Jones *et al*, 2001).

The level of sulfonation was a key parameter or degree of sulfonation. The degree of sulfonation of the membrane was different with each other depending on how the membrane was produced. The operating temperature, molar acid ratio (type of sulfonating agent) and reaction time contributed to the differences.

2.5 Sulfonated polyethersulfone

Sulfonated polyethersulfone can be done by several sulfonation methods. Normally sulfonated polyethersulfone yield was known or called as the degree of sulfonation. From this degree of sulfonation leads to obtaining several information about membrane produced characterization. This characteristic can be such as thermal stability, the ion exchange capacity and the swelling effect.

The entire characteristic will be tested in different tests. Fourier Transform Infrared Spectroscopy (FTIR) to indicate the sulfonic acid group while the hydration level can be tested in swelling test such as water uptake test and methanol uptake test and the another one is Thermogravimetric Analysis (TGA) to determine the weight loss of sulphuric acid group that attached to the membrane after burned at 500°C.

2.6 Characteristic Studies

2.6.1 Swelling Test

From Nasef *et al*, (1999), the swelling test was run to observe the hydrophilicity of membrane samples. The water uptake and methanol uptake was found to increase gradually and linearly with increase in the degree of grafting. That also mean the water uptake and methanol uptake was found increase gradually and linearly with increase in reaction time. It is well known that the swelling test of the membranes is related to the reaction time and subsequently the amount of sulfonic acid groups available.

2.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

From Guan *et al*, (2005), FTIR spectra were explained to confirm the pendant SO_3H group on the polymer chain. The peak of sulfonic group appeared at peak approximately 1025 cm^{-1} shown that clearly exist at sulfonic acid group's peak range between 1020 to 1080 cm^{-1} . The others peak of aromatic ring, $\text{C}=\text{C}$ and aromatic structure, $\text{C}=\text{O}=\text{C}$ also exist at peak of approximately 1470 cm^{-1} and 1240 cm^{-1} . However, it still can get conclusion that the sulfonic acid groups has been introduced into the polymer chains.

2.6.3 Thermal Gravimetric Analysis (TGA)

From Guan *et al*, (2005), Thermal gravimetric analysis (TGA) were explained to measure weight loss of membrane samples after combustion. In this analysis, 3 transitions of loss in weight in three separate temperature ranges can be seen in TGA curves. The first, around $100\text{-}200^\circ\text{C}$ is related to the desorption of water bonded to the sulfonic group. The second one occurs at around 300°C and could be ascribed to

the decomposition of the sulfonic acid groups. The third thermal degradation of SPES at around 400°C to 500°C were assigned to the degradation of the polymer main chain.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Material Selection

3.1.1 Polyethersulfone

Polyethersulfone (PES) is a heat-resistance, transparent, amber, and non-crystalline engineering. PES is a tough and rigid resinsimilar to conventional engineering plastics, such as polycarbonate, at room temperature. The gratest characteristic of PES is that it has by far better high-temperature properties than conventional engineering plastics. Specificially, PES remains in satisfactory condition in long-term continuos use without causing any dimensional change or physical deterioration at temperatures as high as 200°C.

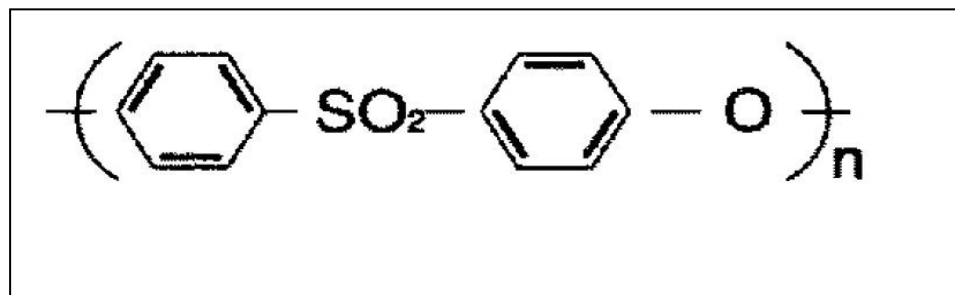


Figure 3.1: Polyetehrsulfone structure (Sato, 2004)

Table 3.1 below shown that the polyethersulfone properties which is density, water absorption, molding shrinkage, tensile strength and heat capacity.

Table 3.1: The polyethersulfone properties

Properties	Value
Density, kg/m ³	1500
Water absorption, %	0.6
Molding shrinkage, %	0.2/0.6
Tensile strength, MPa	127
Heat capacity, J/g.°C	1.2

3.1.2 Chloroform

Chloroform is a clear volatile liquid with a strong smell like ether, chloroform was once administered by inhalation to produce anesthesia and given as an analgesic (to relieve pain) and a remedy for cough. It is quite toxic to the kidney and the liver. Table 3.2 below shown that the chloroform properties.

Table 3.2: The chloroform properties

Properties	Value
Formula	CHCl ₃
Molecular weight	119.38
Specific gravity	1.48
Boiling point	62°C
Melting point	-63.5°C

3.1.3 Chlorosulfonic acid

Sulfonic acid is a compound with general formula RSO₂OH, where R is an aliphatic or aromatic hydrocarbon. It is a derivative of sulfuric acid (HOSO₂OH) where an OH has been replaced by a carbon group or a compound where a hydrogen atom has been replaced by treatment with sulfuric acid; for example, benzene is

converted to benzenesulfonic acid (water-soluble). Sulfonic acid has a sulfur atom bonded to a carbon atom of a hydrocarbon and bonded also to three oxygen atoms, one of which has been attached to a hydrogen atom. Sulfonic acid is acidic due to the hydrogen atom, stronger than a carboxylic acid. Sulfonic acid is one of the most important organo sulfur compounds in organic synthesis.

Chlorosulfonic Acid is a corrosive, clear liquid; melting point $-80\text{ }^{\circ}\text{C}$; boiling point $151\text{ }^{\circ}\text{C}$; soluble in chlorinated solvents. It is hygroscopic and lachrymatory strongly. It reacts with water to form HCl. Chlorosulfonic Acid is used to produce organic sulfonic acids for the end applications of detergent, pharmaceuticals, pesticides, and dyes. It was a starting material to produce saccharin. Table 3.3 below shown that the chlorosulfonic acid properties.

Table 3.3: The chlorosulfonic acid properties.

Properties	Value
Melting point	-80°C
Boiling point	$151\text{-}152\text{ }^{\circ}\text{C}$
Specific gravity	1.753
Solubility in water	Decomposes
Stability	Stable under ordinary conditions

3.1.4 Solvent Dimethylacetamide (DMAc)

The solvent in the sulfonation reaction must be able to dissolve the polymer base and inert to the sulfonating agent. In this study, Dimethylacetamide (DMAc) is used as the solvent. DMAc is a colorless, high boiling, mobile, polar liquid with a taint odor characteristic. Distillation process did not composed the DMAc and it is freely miscible with water, alcohols, ethers, ketones and aromatic hydrocarbons. Even at high temperatures aqueous solution of DMAc have little tendency to hydrolyze. Table 3.4 showed the properties of dimethylacetamide.

Table 3.4: Properties of dimethylacetamide (DMAc)

Properties	Value
Boiling point, °C	165
Molecular mass, g/mol	87
Relative density (water = 1)	0.9366
Solubility in water	miscible

3.1.5 Sodium Methoxide

To yield the desired sulfonated product, a solution of base is essential to cleave the trimethylsilyl group into the polymer backbone. In this study, sodium methoxide (CH_3ONa) was used. Table 3.5 showed the properties of sodium methoxide.

Table 3.5: Properties of sodium methoxide

Properties	Value
Density, g/cm ³	0.994
Molecular weight, g/mol	54
Flash point, °C	29
Viscosity, cPs	28
Boiling Point, °C	85

3.2 Research Design

There are several factors influencing the characteristic of the sulfonated membrane. There are sulfonating agent, polymer used and process condition. Figure 3.2 showed factor influenced characteristic of sulfonated membrane.

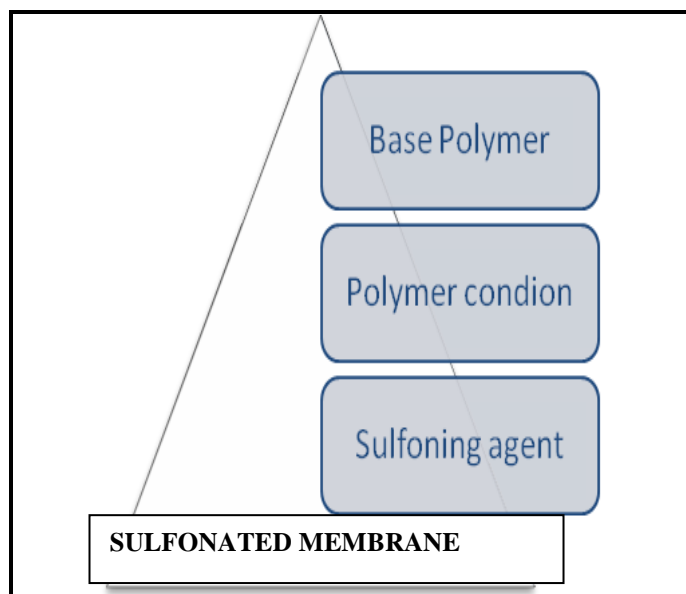


Figure 3.2: Factor influencing the characteristic sulfonated membrane

3.3 Experimental Stages

The experimental methods in this study involved several stages. Figure 3.3 showed the experimental stages in this study.

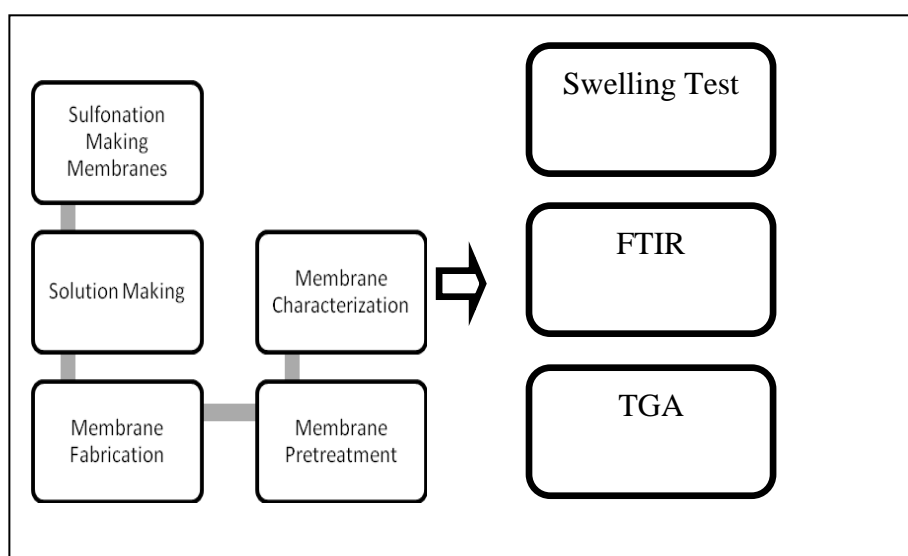


Figure 3.3: Experimental stages

3.3.1 Sulfonation Process

40 g of dried polyethersulfone was dissolved in 400 ml chloroform in a 1L 3 neck flask fitted with mechanical stirrer, condenser and nitrogen sparge tube. The solution was purged with nitrogen for 2 hours and chlorosulfonic acid (30 mL) was added from an additional funnel over 10 minutes. The solution then stirred at room temperature for 3, 4.5, 6 and 12 hours . The reaction solution was homogenous throughout this time. 70% solution (100 mL) of sodium methoxide in methanol was added to the reaction. After an hour the homogenous solution was added to the large excess of methanol in the stirrer and dried in vacuum oven. The recovered polymer was washed with water and methanol and dried in vacuum oven.

3.3.2 Polymeric Solution Making

The making of polymeric solution was been conducted by dissolving the identified amount of sulfonated polysulfone in dimethylacetamide (20%w/w) under continuous stirring at room temperature over hours to get the dilute solution of the mixed matrix. Then the solution degassed in an ultrasonic bath to eliminate the air bubble. Figure 3.4 showed the sulfonation process and solution making apparatus.

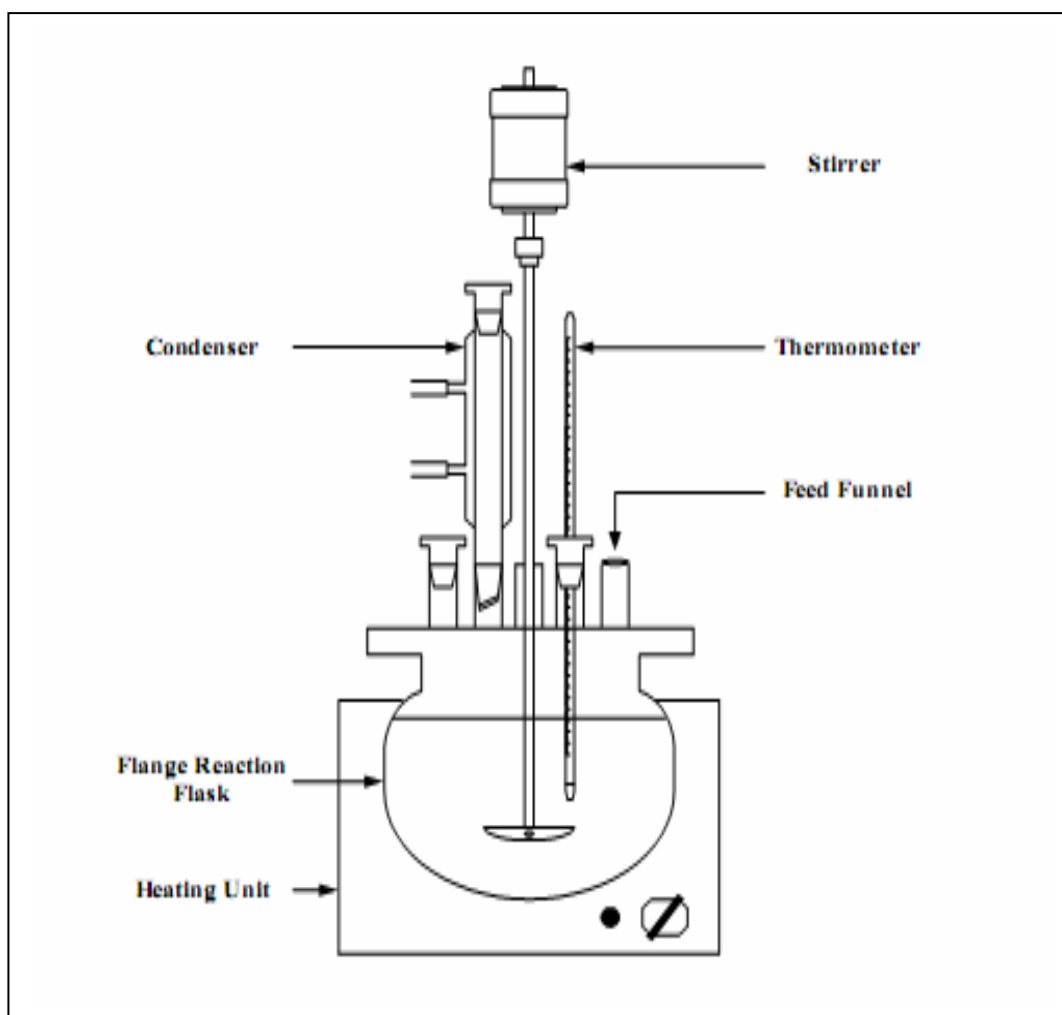


Figure 3.4: Sulfonation process and polymer making apparatus (Nunes *et al*, 2003)

3.3.3 Membrane Fabrication

The membrane was casted on a flat glass plate using a manual casting knife. After the casting process, the membrane was immersed in a water bath and dried at ambient temperature for approximately 24 hours.



Figure 3.5: Casting knife

3.3.4 Acid Membrane Pretreatment

The dried membrane was been pretreated by doping it into a 1M HCl solution for 1 hour to convert it into acid membrane for experimental analysis.

3.3.5 Membrane Characterization

3.3.5.1 Swelling Test

The swelling characteristic was determined by water uptake measurements. The membrane samples was dried under vacuum for 17 hrs at 35°C and 65°C and weighed in scaled lass weighing bottles. The membrane then placed in distilled water at different temperature (between 35°C to 90 °C). The water uptake then calculated using this equation;

$$SW = \frac{M_w - M_d}{M_d}$$

where M_w was the wet weight of the membrane and M_d was the dried weight of the membrane. The result can be considered as number of water molecules associated with each SO_3H group.

3.3.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was conducted in order to verify the success of the sulfonic group that attach to the polymer. The sample of membranes were analyzed to see the existence of sulfonic group, aromatic ring and aromatic structure at different peak of wavelength.

3.3.5.3 Thermal Gravimetric Analysis (TGA)

The thermal stability of various SPESs and Nafion 117 were investigated using Thermo Gravimetric Analysis (TGA) from room temperature to 500°C . The purpose for using TGA was to determine the weight loss for each membrane after combustion.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Sulfonation and Dope Solution Making

Sulfonation process had been conducted several times by varying the reaction time to 3 hours, 4.5 hours, 6 hours and 12 hours. Sulfonation process was conducted at room temperature (25 to 28°C) by utilizing chlorosulfonic acid as sulfonating agent. The sulfonation process cannot be operated at high temperature because the boiling point of the solvent was too high and vaporized the solvent. Some of the sulfonation process were successful conducted and some were not. The problem occurred when some of the precipitation did not dissolved in the same solvent.

Table 4.1 below, shows that the sulfonation and dope solution making observation.

Table 4.1: Sulfonation and dope solution making observation

Reaction Time (Hours)	Amount				
	PES (g)	Chloroform (mL)	Chlorosulfonic Acid (mL)	Sodium Methoxide (mL)	Mass of Particle (g)
3	40	400	30	70	42.20
Observation					
When the SPES3 solution was added into large excess of methanol, the solution change from liquid to solid (particle like tissue). SPES3 particle was replaced into a bath of distillation water twice and soak for one night. SPES3 particle was dried at surrounding temperature for 24 hour and dried again in furnace at 100°C for 12 hour. The particle of SPES3 was weighted and was diluted in 300 mL of DMAc. SPES3 solution was degases into supersonic wave to remove air bubbles.					
4.5	40	400	30	70	42.43
Observation					
When the SPES4.5 solution was added into large excess of methanol, the solution change from liquid to solid (particle like tissue). SPES4.5 particle was replaced into a bath of distillation water twice and soak for one night. SPES4.5 particle was dried at surrounding temperature for 24 hour and dried again in furnace at 100°C for 12 hour. The particle of SPES4.5 was weighted and was diluted in 300 mL of DMAc. SPES4.5 solution was degases into supersonic wave to remove air bubbles.					
6	40	400	30	70	42.86
Observation					
When the SPES6 solution was added into large excess of methanol, the solution change form liquid to solid (particle like tissue). SPES6 particle was replaced into a bath of distillation water twice and soak for one night. SPES6 particle was dried at surrounding temperature for 24 hour and dried again in furnace at 100°C for 12 hour. The particle of SPES6 was weighted using analytical balance and was diluted in 300 mL of DMAc. SPES6 solution was degases into supersonic wave to remove air bubbles.					

4.2 Characteristic Studies of Sulfonated Membrane

4.2.1 Swelling Test (Water Uptake)

The sample of membrane size 5 cm x 5 cm each was weighted before soaked into distillation water for 24 hours. After 24 hours, the each sample of membrane were weighted for wet membrane and the result was shown at Table 4.2.

Table 4.2: Average water uptake % for membrane samples

Type of membrane	Water Uptake percentage (%)
Nafion 117	3.09
PES	0.72
SPES3	1.48
SPES4.5	1.72
SPES6	2.91

From the Table 4.2, Nafion 117 showed the highest % compared to others membrane. The other alternatives to replace Nafion 117 were replacing SPES6 as replacement. SPES6 showed that the highest % compared to others sulfonated membrane with 2.91 %, followed by SPES4.5 was 1.72 % and so on. The lowest % for water uptake was PES with 0.72 %. This was showed that the % of water uptake depend on the quantity of sulfonic group in the membrane. If sulfonic group increased the % of water uptake also increased.

4.2.2 Swelling Test (Methanol Uptake)

The sample of membrane size 5 cm x 5 cm each was weighted before soaked into methanol for 24 hours. After 24 hours, the each sample of membrane were weighted for wet membrane and the result was shown at Table 4.3.

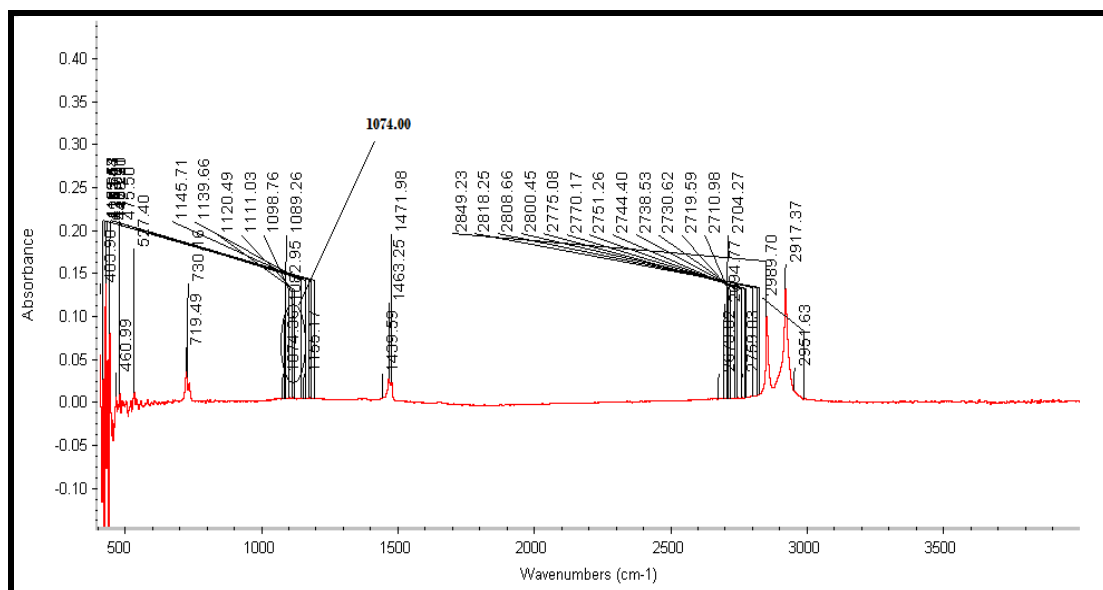
Table 4.3: Average methanol uptake % for membrane samples

Type of membrane	Methanol Uptake percentage (%)
Nafion 117	1.56
PES	1.00
SPES3	1.34
SPES4.5	3.26
SPES6	3.94

From the Table 4.3, SPES6 showed the highest % compared to others membrane with 3.94 %. This showed that SPES6 have the potential that can be used in Direct Methanol Fuel Cell (DMFC). The lowest % for methanol uptake was PES with 1.00 %. The result showed that the % of methanol uptake depend on the quantity of sulfonic group in the membrane. If sulfonic group is increased so the % of methanol uptake also increased. The % of methanol uptake for Nafion was low due to Nafion 117 was weak absorption that cause the rate of methanol absorbed were low. This result showed that Nafion 117 suitable in PEMFC application but not suitable for DMFC application.

4.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was conducted in order to determine the sulfonate group in the membrane whether the sulfonation process succeeded or not. However the sulfonation process confirmed by FTIR was only qualitative. The FTIR results from the study were showed below for each samples at Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4 and Figure 4.5.



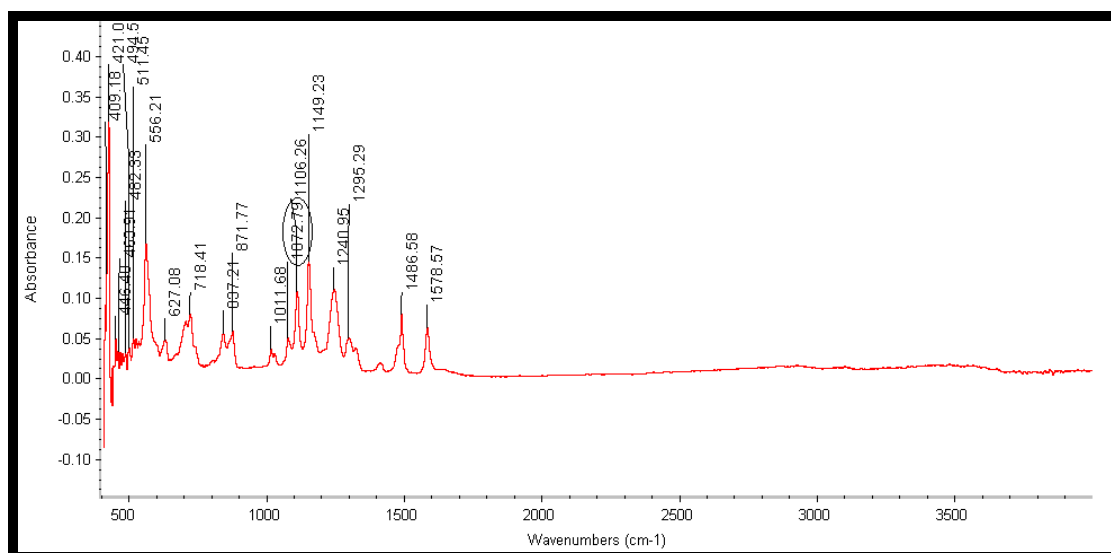


Figure 4.3: FTIR result for SPES3

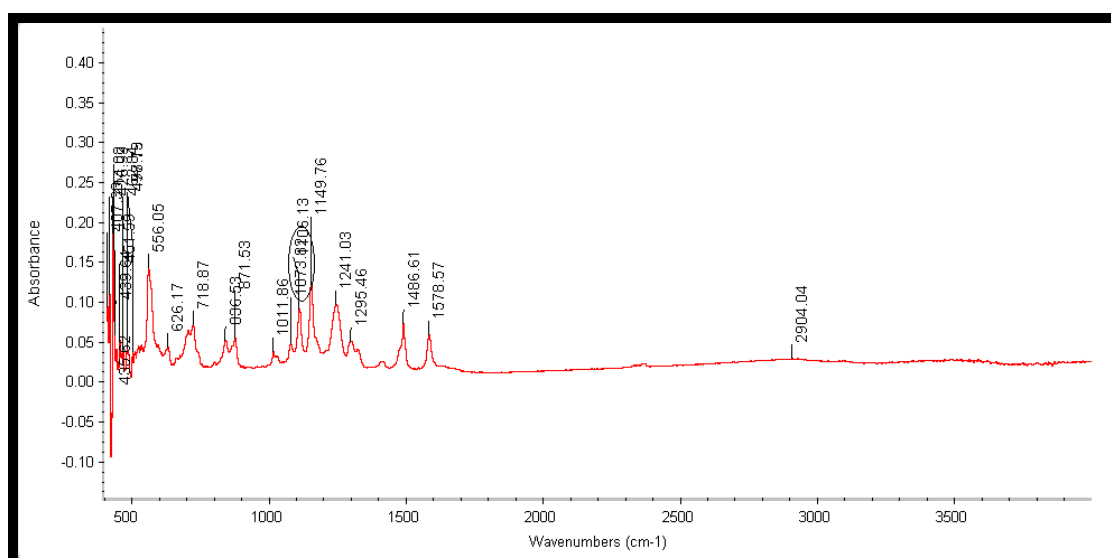


Figure 4.4: FTIR result for SPES4.5

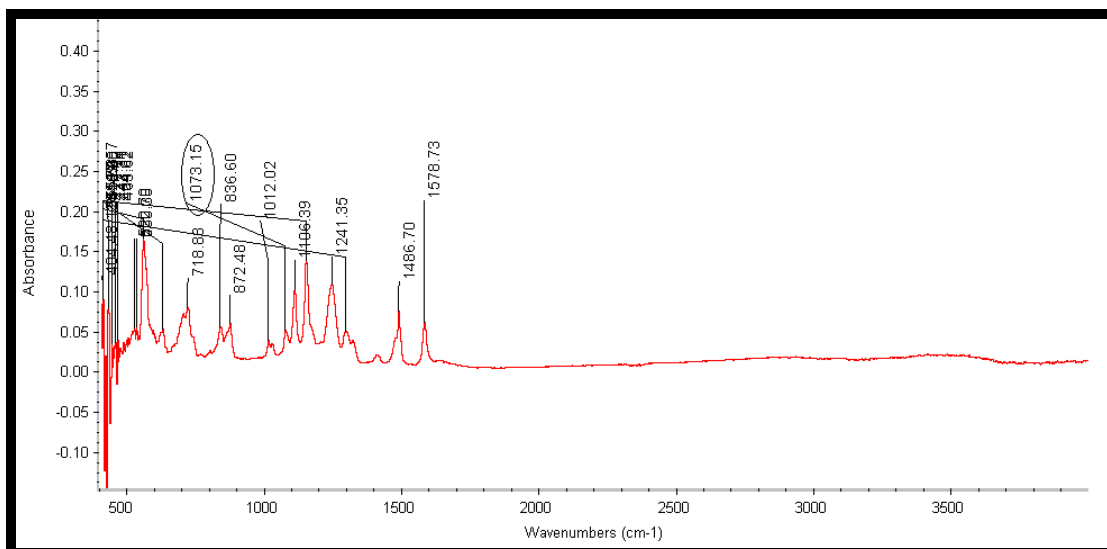


Figure 4.5: FTIR result for SPES6

The data of each result were summarize into Table 4.4 for more detail and clearly. In this result, the symmetric $\text{O}=\text{S}=\text{O}$, aromatic ring $\text{C}=\text{C}$ and aromatic structure $\text{C}=\text{O}=\text{C}$ were simplify into Table 4.4.

Table 4.4: Wavelength of membrane samples

Samples	Reaction time (hour)	Symmetric (cm^{-1}) $\text{O}=\text{S}=\text{O}$	Aromatic ring (cm^{-1}) $\text{C}=\text{C}$	Aromatic structure (cm^{-1}) $\text{C}=\text{O}=\text{C}$
Nafion 117	-	1074.86	1471.98	-
PES	-	-	1488.25	1243.58
SPES3	3	1072.79	1486.58	1240.95
SPES4.5	4 $\frac{1}{2}$	1073.82	1486.61	1241.03
SPES6	6	1073.15	1486.70	1241.35

From FTIR analysis above, each of the samples shown the peak of sulfonic group accept PES. Each of the samples have a peak of sulfonic group at range 1072 to 1074 cm^{-1} . From this FTIR, another peak also had been analysed which is at peak approximately 1240 cm^{-1} . From this peak, it is proved that the existent of aromatic C-O-C structure in the membrane itself. From the analysis above, the membrane that

have this peak was PES, SPES3, SPES4.5 and SPES6. All samples also showed the existent of C-C aromatic ring at peak of approximately 1480 cm^{-1} . From FTIR analysis above, each of the samples shown the peak of sulfonic group accept PES. Each of the samples have a peak of sulfonic group at range $1072\text{ to }1074\text{ cm}^{-1}$. PES didn't have sulfonic group because during the particles making, no chlorosulfonic acid was be added into this solution. So this make the dope solution of PES didn't have sulfonic acid group. From this analysis, the another peak also had been analysed which is at peak approximately 1240 cm^{-1} . From this peak, it proved that the existent of aromatic C-O-C structure in the membrane itself. From the analysis above, the membrane that have this peak was PES, SPES3, SPES4.5 and SPES6. All samples also showed the existent of C-C aromatic ring at peak of approximately 1480 cm^{-1} .

4.2.4 Thermal Gravimetric Analysis (TGA)

TGA was conducted in order to determine the weight loss of membranes after combustion. The TGA results from the study were showed below for each sample at Figure 4.6, Figure 4.7, Figure 4.8, Figure 4.9 and Figure 4.10.

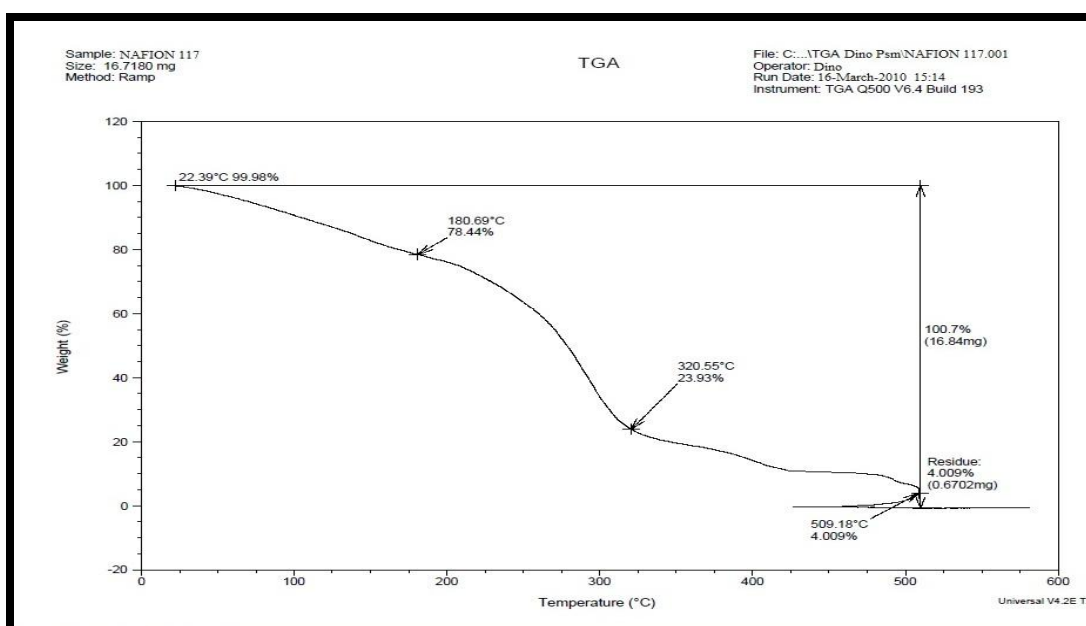


Figure 4.6: TGA result for Nafion 117

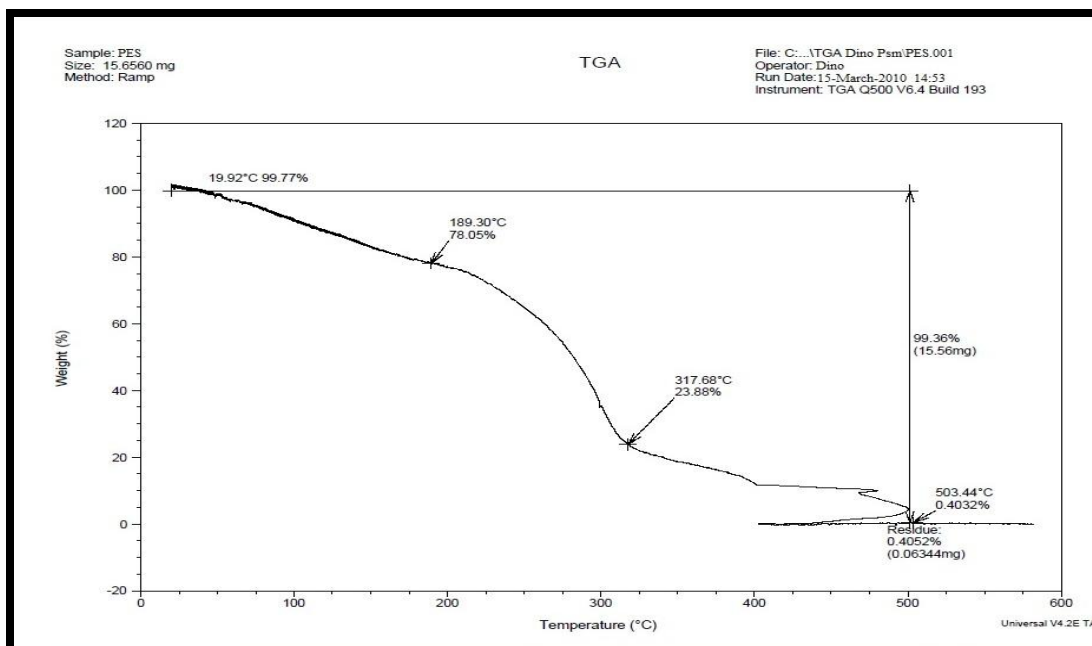


Figure 4.7: TGA result for PES

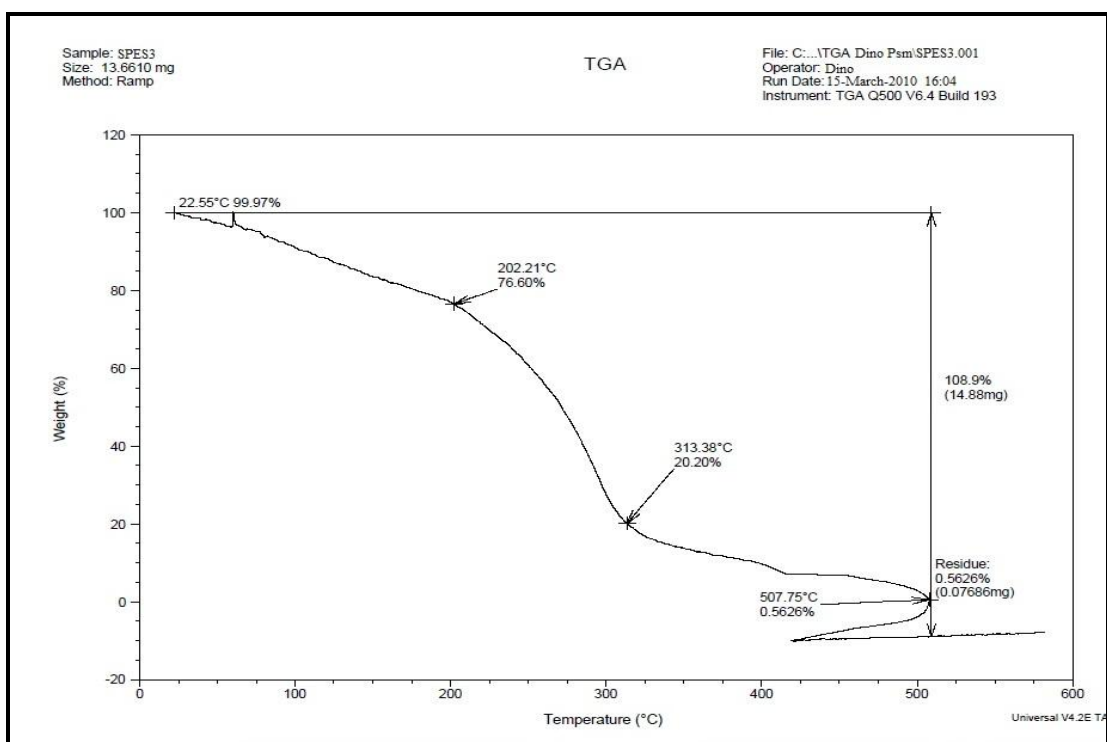


Figure 4.8: TGA result for SPES3

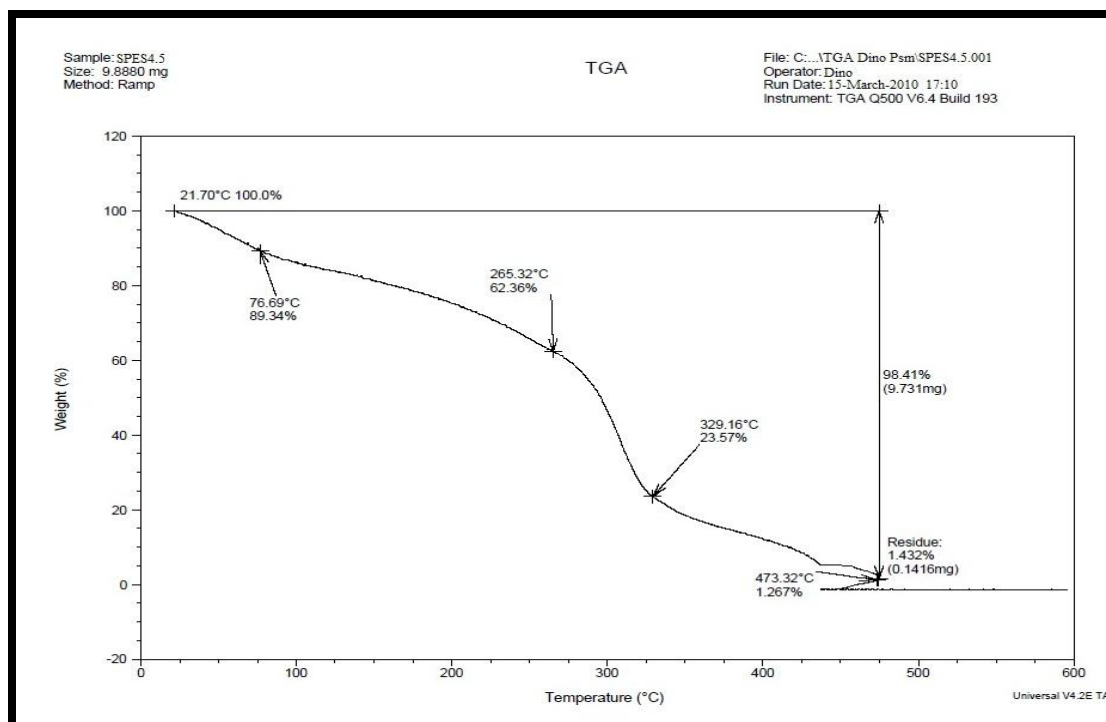


Figure 4.9: TGA result for SPES4.5

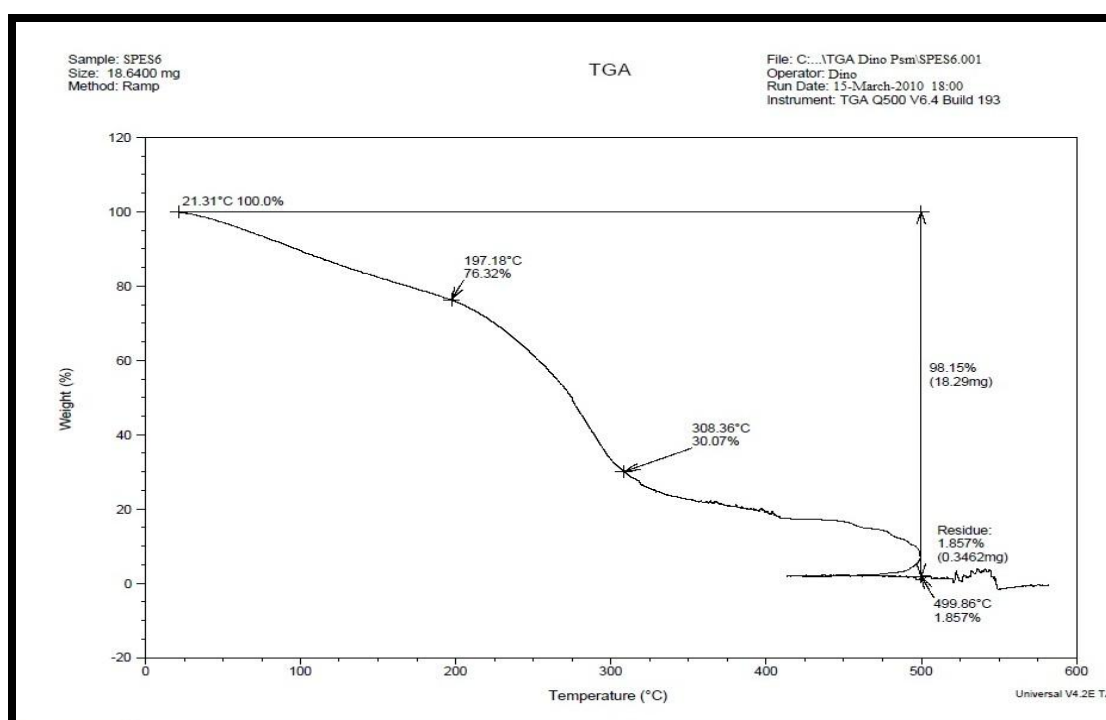


Figure 4.10: TGA result for SPES6

Table 4.5: Weight lost of membrane samples

Samples	Initial weight of membranes, (mg)	Final weight of membranes, (mg)	Percentages of weight residue, (%)
Nafion 117	16.7180	0.6702	4.0090
PES	15.6560	0.0634	0.4032
SPES3	13.6610	0.0769	0.5626
SPES4.5	9.8880	0.1416	1.4320
SPES6	18.6400	0.3462	1.8570

From this TGA analysis, the result showed that the Nafion 117 is the highest % of weight residue. This is because the range of temperature that occur during the analysis is not enough to burn the sample completely. In this analysis, the temperature range that had been set up was 500°C, but for Nafion 117, the temperature range supposed to be from room temperature to 600°C. PES is the lowest % of weight residue because the sample itself not stable compared to others samples. From this analysis, have 3 transitions of loss in weight in three separate temperature ranges can be seen in TGA curves. The first, around 100-200°C is related to the desorption of water bonded to the sulfonic group. The second one occurs at around 300°C and could be ascribed to the decomposition of the sulfonic acid groups. The third thermal degradation of SPES at around 400°C was assigned to the degradation of the polymer main chain. Moreover, sulfonate samples show lower decomposition temperatures with respect to PES. This difference could be explained by an enhanced asymmetry in the polyethersulfone structure due to the introduction of SO₃ groups that renders it less regular and then less stable.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The sulfonated polyethersulfone (SPES) was successfully synthesized by sulfonation process. This sulfonation was determined succeeds by Fourier Transform Infrared Spectroscopy (FTIR) analysis. Result from FTIR showed that all the samples were in the range of sulfonate group 1072 to 1074 cm^{-1} . The intensity peaks tends to broadening as the increasing of reaction time for sulfonation process. The swelling test result showed the water and methanol uptake % were directly proportional to the reaction time of sulfonation. The introduction of bulky sulfonate groups into the polymer backbone contribute in increasing the hydrophilicity of membrane. The thermal gravimetric analysis (TGA) analysis showed the graph of weight loss for different type of membrane after combustion at 500°C . The TGA analysis showed that have 3 stage occur during combustion of different membrane. The first stages showed that the desorption of water bonded to the sulfonic groups. The second stages showed the decomposition of sulfonic acid groups and the third stages showed that the degradation of polymer main chain. The TGA analysis also showed that the weight of residue after analysis. The different % weight of residue at the end of analysis showed that the reaction time of sulfonation process effect the weight of each membrane and also effect the weight loss during combustion.

5.2 Recommendation

In order for future improvisation in sulfonate polyethersulfone membrane studies, some recommendations were withdrawn.

- (i) Reaction time of sulfonation process should be longer but not exceeded 12 hour.
- (iii) The surface area of membrane must be large and the membrane must be immerse in distillation water and methanol for 24 hours so that membrane can absorb a lot of water.
- (iv) The characteristic of membrane can be more variety of result if the sulfonation process was conducted with different reaction time, temperature and composition.

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APPENDICES



Appendix 1: Polymer dissolved process



Appendix 2: Sulfonation process



Appendix 3: Sulfonated polyethersulfone particle



Appendix 4: Sulfonated polyethersulfone dissolved process



Appendix 5: Degases process



Appendix 6: Sulfonated polyethersulfone dope solution after degases



Appendix 7: Casting apparatus



Appendix 8: Sulfonated polyethersulfone membrane produced



Appendix 9: FTIR analysis



Appendix 10: TGA analysis