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SYNTHESIS OF PROTON EXCHANGE MEMBRANE BASED ON SULFONATED POLYPHENYLSULFONE FOR FUEL CELL APPLICATIONS

MSc (FULL TIME) DISSERTATION

Prepared by

SWATHI BURLA

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering

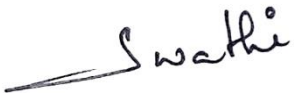
Supervisor(s):

Dr. Diakanua Nkazi and Dr. Jean Mulopo

April, 2017

DECLARATION

The dissertation work entitled "Synthesis of proton exchange membrane based on sulfonated polyphenylsulfone for fuel cell applications" is my own and unaided work, under the guidance of Dr. Diakanua Nkazi and Dr. Jean Mulopo. It is being submitted for the Degree of Master of Science in Chemical Engineering to the University of the Witwatersrand, Johannesburg. The work presented in the dissertation is original and not submitted in full or part for any degree or examination in any other body or organization or person outside the University.



…….

Signature of Candidate

…13…….day of……April……..year……2017……

ABSTRACT

This dissertation presents a detailed study on the synthesis of nanocomposite membranes of sulfonated polyphenylsulfone embedded with carbon nanoball fillers. The effect of various synthesis parameters such as temperature, time, and concentration of the sulfonating agent on sulfonation of polyphenylsulfone, and the production of carbon nanoballs by non-catalytic chemical vapour deposition method were investigated. The synthesized carbon nanoballs were added to the polyphenylsulfone membrane in order to optimize the mechanical properties of the membrane. Furthermore, the effect of addition of low volumes of carbon nanoballs on the morphology and membrane properties was investigated.

The sulfonation of polymeric membrane was characterized by Proton Nuclear Magnetic Resonance (^{1}H NMR) which confirmed the sulfonation of polyphenylsulfone. The Transmission Electron Microscopy (TEM) analysis showed that produced CNBs had necklace structure with almost uniform size ranging between 40 to 60nm. Bruner-Emmett-Teller (BET) analysis showed that CNBs had less impurities with pore volume and diameter of 0.0316 cm3/g and 16.7nm, respectively. From TGA result, it was observed that CNBs were thermally stable. Raman analysis indicates that CNBs were non conductive, a property which avoids unnecessary short circuits in the functioning of the fuel cells.

Nano composite membranes with varying loading levels from 0.25 wt% to 4 wt% were prepared using ultrasonication at varying amplitudes of 20%, 60% and 75%, and simple evaporative casting technique. The TGA graph shows that the addition of carbon nanoballs has significantly increased the thermal stability of SPPSU membrane and all the composite membranes prepared with varying CNB loading showed similar decomposition profile. The nanocomposites prepared at 60% amplitude produced homogenous membranes; and the membrane with 1.75wt% CNB loading had high percentage resilience and satisfactory water uptake capacity than other membranes. The results confirmed that the addition of CNBs in low volumes increase the thermal stability and percentage resilience which are very crucial for fuel cell applications.

DEDICATION

I dedicate this work to my family, friends and the Almighty God. Specially to my family members for supporting and encouraging me throughout this journey. They are my strength. I also dedicate this work to my supervisors, Dr. Diakanua Nkazi and Dr. Jean Mulopo**,** for helping, motivating and developing my skills throughout the academic program. They are the wonderful persons to work with.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisors Dr. Diakanua Nkazi and Dr. Jean Mulopo for the belief they have in me and for their guidance and motivation throughout my dissertation project work. I would like to thank University of Witwatersrand and NRF foundation for supporting me with financial assistance through Post Graduate Merit Award and NRF Innovation Scholarship.

I profoundly thank Professor Herman Potgieter, Head of School of Chemical and Metallurgical Engineering, for giving an opportunity to carry out the project in the School. I also thank the School of Chemical and Metallurgical Engineering, the School of Chemistry, the School of Physics, the Biology Microscopy Unit and the Medical School and their staff for their help and support in providing laboratory facilities. I would like to extend my sincere thanks to Mr. Alain Mufula, Dr. Manoko Maubane, Dr. Zikhona Tetana, Dr. Rudolph Erasmus, Professor Neil Coville, Dr. Pradeep Kumar, Dr. Myron Johnson, Dr. Izak Kotze, Mrs Zama Mthabela and Mr. Edward Malenga (University of Johannesburg) for their assistance in completing the project.

I also thank Mr. Victor Boehme, Managing Director of Solvay Polymers and Chemicals South Africa (Pty) Ltd for donating Polyphenylsulfone for the research work. I have taken efforts in this project however; it would not have been possible without the kind support of fellow postgraduate students and Nanotechnology Research Group. Last but not least, special appreciation goes to my family for their constant support and faith in me.

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LIST OF ABBREVIATIONS AND SYMBOLS

PEMFC	Polymer Electrolyte Membrane Fuel Cell
DMFC	Direct Methanol Fuel Cell
SAP	Sulfonated aromatic hydrocarbons
PPSU	Polyphenylsulfone
SPPSU	Sulfonated Polyphenylsulfone
PSU	Polysulfone
DS	Degree of Sulfonation
CNB	Carbon Nanoball
MEA	Membrane Electrode Assembly
IEM	Ion Exchange Membrane
CSA	Chlorosulfonic acid
CVD	Chemical Vapour Deposition
PAES	Poly arylene ether sulfone
BuLi	Butyl Lithium
Pt	Platinum
CNTs	Carbon nanotubes
SFCVD	Swirled Floating Chemical Vapour Deposition Method
DCM	Dichloromethane
^{1}H NMR	Hydrogen-1 Nuclear Magnetic Resonance Spectroscopy
TGA	Thermogravimetric analysis
DMAc	N,N-dimethylacetamide
DMF	Dimethylformamide
NMP	N-methyl-2-pyrrolidone
DMSO	Dimethyl sulfoxide
NCCVD	Non Catalytic Chemical Vapour Deposition
TEM	Transmission Electron Microscope
SEM	Scanning Electron Microscope

CHAPTER 1: INTRODUCTION

The consumption of energy by modern societies in the form of heating, electricity production, transportation, industrial use is increasing. A substantial portion of energy production is met through fossil fuels derived from finite natural reserves and thus cannot be sustained indefinitely in the long run as there is a continuous energy demand (Sahu et al., 2009). The use of these resources is the main cause for carbon emission and greenhouse gases polluting the atmosphere and ultimately affecting the life on earth.

There is an urgent need for alternative sources of energy with more efficiency and less emission that result in the betterment of human society and cleaner environment. In response to these problems, interest in energy sources like solar, wind and hydro power is growing tremendously. Fuel cells, being sustainable, environmental friendly and renewable are gaining importance from governments and various industries as one of the alternative energy producing systems. They have the potential to provide cleaner, highly efficient and more fuel flexible operation than the conventional heat engines (Larminie et al., 2003).

1.1 BACKGROUND AND MOTIVATION

Fuel cells became commercial in a variety of applications in the fields of combined heat and power systems, offering significant advantage over conventional energy conversion systems. Among various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) are attracting increased attention as most promising candidates for the applications in small scale products such as automotive, portable power generation and stationary equipment with sustainability and reliability (Kim et al., 2015). They can also be scaled up in size to suit the demands of a variety of applications due to their simple design and quick start up. PEMFCs are based on solid polymers which act as proton conducting electrolyte membranes that transfer protons and act as a barrier to the passage of electrons and fuel (Zhang et al., 1998).

Nafion (poly-perfluorosulfonic acid), manufactured by DuPont is the standard commercial proton exchange membrane (PEM) with outstanding chemical stability and performance at fully hydrated state (Grot, 1994). It has longevity of 50,000 hours at a working temperature of

80^{o}C with high ionic conductivity of 0.1 S/cm at fully hydrated stage (Zhang et al., 1998 and Ralph, 1997). However, the stability of Nafion is highly sensitive against the temperature and relative humidity of the operating fuel cell and the performance of the Nafion membrane start deteriorating at temperatures above 80^{o}C resulting in dehydration and low ionic conductivity of the membrane. It also has other barriers such as high cost, platinum poisoning by carbon monoxide (CO), high fuel permeability (methanol cross over in direct methanol fuel cell), and harmful production process with undesirable intermediates (Hickner et al., 2004 and Zawodzinksi, 1995). As the stated factors greatly affect the performance, durability and commercialization of Nafion membranes, a fuel cell with better performance that can operate at low humidity and withstanding higher temperatures without compromising proton conductivity is highly desirable. Apart from high performance, the selection of the membrane materials should also be cost effective, readily available and environmentally safe to make the fuel cells available to large parts of society without confining to specific groups or countries (Lypiridi, 2013).

Owing to the above mentioned drawbacks of Nafion, many attempts have been made to prepare alternative membranes that are more economical, safe and highly stable. As water and thermal management is highly complex in the operating fuel cell, a lot of work was devoted particularly in this regard (Li et al., 2008; Srinivasan et al., 1999; Kang and Wang, 1996 and Jannasch, 2003).

Sulfonated aromatic hydrocarbons (SAPs) are found to be the most promising materials for polymer electrolyte membranes, among various available polymer materials. They received a great deal of attention as they are relatively cheap, recyclable, easy to produce and can operate at temperatures above 100^{o}C (High Temperature PEM) (Zieren, 2011 and Maier and Meier-Haack, 2008). A lot of research has been focused on the studies of polyphenylsulfone (PPSU) membranes (Guiver et al., 1989; Ehrenberg et al., 1997; Chao and Kelsey, 1986 and Kerres et al., 1996), as they have good oxidative and thermal stabilities with an opportunity of desired chemical modification and showing large conductivity when sulfonated (Licoccia et al., 2007). Therefore, these features make PPSU considerably attractive for fuel cell application (Maier and Meier-Haack, 2008; Iojoiu et al., 2005; Xing and Kerres, 2006 and Di Vona et al., 2010).

1.2 PROBLEM STATEMENT

Even though the results obtained from sulfonated polyphenulsulfone (SPPSU) membranes appear promising, the stability of the membrane under fuel cell conditions is uncertain. The high degree of sulfonation (DS) exhibit increased water absorption which is expected to increase the proton conductivity, but according to the literature, the membrane shows excess swelling with increasing DS affecting the long term stability of the membrane due to decreased mechanical strength and hydrolytic property (Zhang et al., 1998). Despite these limitations, the research interest in developing polysulfone membranes has not reduced as they are economical and have good chemical and thermal stabilities that are important for them to be considered for the applications of fuel cells (Maier and Meier-Haack, 2008 and Naim et al., 2004).

1.3 NANOCOMPOSITE MEMBRANES IN FUEL CELL TECHNOLOGY

Numerous methods have been proposed to optimize the electrochemical and mechanical properties of the fuel cells but with the advent of nano technology, the synthesis of new proton conducting polymers and/or modifying the existing polymers with chemically engineered nano materials is found to be promising in designing fuel cells with desired properties. The incorporation of nano particles is proved to enhance membrane properties by acquiring the best qualities of both the polymer and nano particles (synergic interaction) and eliminate the drawbacks of individual components (Thiam et al., 2011).

Although SAPs showed low chemical stability compared to Nafion, some of the modifications to these membranes such as developing hybrid membranes have proved to show improved properties than the pure membranes (Kim et al., 2015). This shows that there will be a lot of scope in the future for nano technology in developing hybrid polymer membranes with improved performance and durability.

The concept of nanocomposite polymer was developed by Uchida et al. (2003) with the synthesis of self-humidifying PEM for fuel cells using hygroscopic metal oxides such as SiO_2 and TiO_2, to enhance the water absorbing capacity of the membrane without losing mechanical strength. Thereafter, several attempts were made to synthesize polymer

composites using Nafion incorporated with nano fillers (Ramani et al, 2004; Adjemian et al., 2002; Yang et al., 2001; Zaidi et al., 2000; Staiti et al., 2001; Thampan et al., 2005 and Mauritz et al, 1995) but the aforementioned limitations of Nafion led to the development of composite membranes with alternative non fluorinated materials which are more economical and easy to synthesize (Smitha et al., 2005). Therefore, PPSU with Carbon nanoballs (CNB) as nanofillers were selected to produce nanocomposite membrane as they are more economical and offer availability of diverse modification methods to prepare these composits (Zhang et al., 1998 and Kim et al., 2015).

1.4 SCOPE OF STUDY/ PROJECT

Synthesis of sulfonated polyphenylsulfone composite membrane with carbon nano balls as nano fillers for fuel cell application is the main focus of this study. The scope includes the synthesis of SPPSU, synthesis of CNBs, blending and casting techniques of polymer composite membrane and their characterization; studying the effect of the materials and synthesis techniques on the morphology and properties of the prepared SPPSU-CNB based composite membrane for the application in the fuel cell.

The present study will also help in understanding the use of CNBs in SPPSU and results obtained may be used in further study and development of efficient techniques and synthesis of valuable composites.

1.5 RESEARCH AIMS AND OBJECTIVE(S)

The aim of this research is to determine if the nanocomposites synthesized from simple, inexpensive materials such as PPSU and blended with CNBs can be used efficiently as proton exchange membrane for fuel cell applications.

The above aim could be achieved through the following objectives:

- Synthesis of ion exchange matrix material by sulfonation of the polyphenylsulfone.

- Synthesis of pure carbon nanoballs of uniform size and structure as the nanofiller for the polymeric membrane.
- Blending the sulfonated polyphenylsulfone with carbon nanoballs of different weight ratios in order to optimize the mechanical properties of the produced membrane.
- Casting the blended sulfonated polyphenylsulfone.
- Characterize the synthesized polymeric membrane and access its ion exchange capacity.

1.6 HYPOTHESIS

In this project, sulfonation of polyphenylsulfone with various parameters such as varying the concentration, time and temperature will be investigated along with the preparation of SPPSU-CNB composite membrane. As there are issues with solubility of polyphenylsulfone with organic solvents; and non-homogeneity of the reaction mixture while sulfonating, trying to find out suitable conditions for carrying out the experiments will be helpful in optimizing the conditions. These findings could simplify the approach of sulfonation and achieve a homogenous sulfonated polyphenylsulfone membrane. Blending sulfonated polyphenylsulfone with low levels of carbon nanoballs as nanofiller will improve the mechanical properties without affecting the ion exchange capacity.

CHAPTER 2: LITERATURE REVIEW

2.1 HISTORY OF FUEL CELLS

Humphry Davy introduced the concept of fuel cell in the early 19th century which was followed by the work carried out by Christian Friedrich and William Grove in 1838. However, William Grove is considered to be the father of the fuel cell for proposing a concept of reverse electrolysis and producing world's first gas voltaic cell using hydrogen and oxygen over platinum electrodes. He adopted this concept from electrolysis, a process of water decomposition producing hydrogen and oxygen (Carette et al., 2001).

Ludwig Mondand and Carl Langer (coined the term 'fuel cell') conducted experiments and designed fuel cells using air and coal gas. They developed the so called dry batteries using solid electrolyte as liquid electrolytes in fuel cells but had many issues (Srinivasan et al., 1999). Following this, several attempts were made to develop fuel cells (FC) that can convert coal or carbon into electricity, but the invention of internal combustion engine reduced further developments in fuel cell technology for many years.

Francis Thomas Bacon successfully developed alkali fuel cells by modifying the work of Ludwig Mond and Carl Langer. His work led to the first commercial use of fuel cells in the U.S. space program (1960s) to supply electricity and drinking water to the astronauts Srinivasan et al., 1999). This success eventually led to the extensive research on fuel cell applications for terrestrial use (Hickner et al., 2004). Unfortunately, fuel cell technology did not gain much importance till recent times as it was confined to small group of research industries and companies. But the growing concern over the issues of depleting natural energy sources, environmental pollution has demanded large scale research on fuel cells as they run quietly, have much more energy conversion efficiency over conventional methods (steam engine, gas turbines) with no emission (pollutants) and water (and heat) being the only product (Smitha et al., 2005 and Carette et al., 2001).

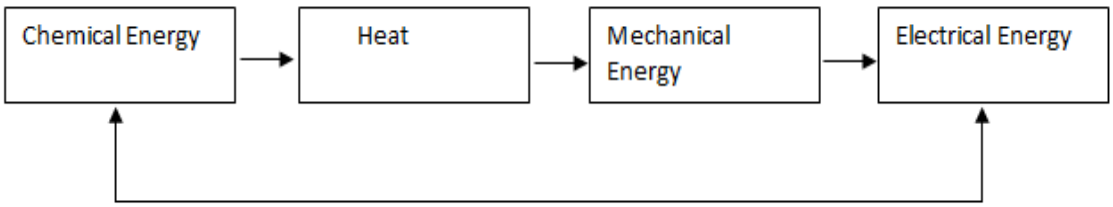


Figure 2.1: Scheme of electrochemical energy conversion in a fuel cell (Gubler and Scherer, 2008)

2.2 BASIC PRINCIPLE

The basic principle involved in fuel cell working is the simple combustion reaction converting chemical energy directly into electrical energy as long as hydrogen (fuel) and oxygen are provided as inputs. Methane, methanol and gasoline can also be used as fuels (Larminie et al., 2003 and Laberty-Robert et al., 2011).

2.2.1 Membrane Electrode Assembly (MEA)

The main cell components include two porous carbon electrodes (one cathode and one anode); a proton conducting electrolyte that separates the two electrodes to avoid direct contact of the fuel and oxygen and allowing rapid proton transport (De - Bonis, 2009). The membrane and the electrodes together form membrane electrode assembly (MEA) with graphitic bipolar flow plates and gas channels arranged on each side of the MEA as shown in the Figure 2.2. Hydrogen (fuel) and oxygen (air) are supplied to the anode and cathode electrode surfaces respectively. Bipolar plates supply the reactants through the flow channels to the electrodes and connect one cell to another electronically in the fuel cell stack. Protons and electrons are produced by hydrogen in the presence of oxygen resulting in water and heat as by-products. PEMFCs have porous gas diffusion electrodes to supply the reactant gases to the active sites in presence of thin Platinum or Platinum/Ruthenium alloy catalyst coating at electrode-electrolyte interface. An external load circuit connected to the catalyst of the fuel cell results in the generation of electricity via the electrons produced by the fuel cell reaction

and helps in electrons getting away from the reaction site (Larminie et al., 2003 and Laberty-Robert et al., 2011).

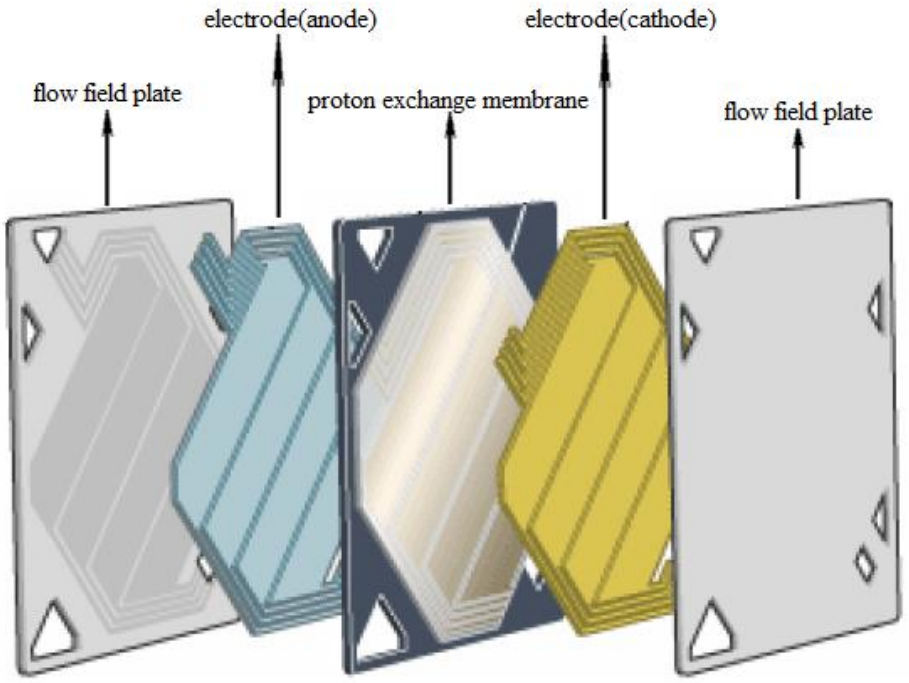


Figure 2.2: Membrane Electrode Assembly (De - Bonis, 2009)

2.2.2 Chemical Reaction

The type of conducting ions produced by the fuel cell depends on the type of fuel incorporated into it. According to Grove's fuel cell that used acid electrolyte, the following reactions take place:

At Anode (Negative Electrode)

Hydrogen is ionized (oxidation) in presence of a catalyst to produce electrons and protons (H^+).

$$2H_2 \rightarrow 4H^+ + 4e^-$$

At Cathode (Positive Electrode)

Oxygen reacts with the electrons coming from the electrode and the protons from the electrolyte to form water (and heat).

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

Overall Reaction

The reaction shows that for each oxygen molecule, two hydrogen molecules are required for the system to be balanced and to produce water as product.

$$2H_2 + O_2 \rightarrow 2H_2O$$

Only protons are allowed to pass through the electrolyte and not the electrons because the electrons would be lost if they got in contact with the electrolyte.

2.2.3 Applications of Fuel Cells

Fuel cells are very efficient and are cleaner source for power generation with many commercial, industrial and residential primary and backup power generation applications. They are used in variety of fields such as: spacecraft, remote weather stations, airplanes, boats and submarines, military applications, combined heat and power generation (CHP), fuel cell electrical vehicles (manufactured by Toyota, Mercedes Benz , Buses from Ballard) ; fuel cell fleets operated by companies like Sysco Foods, GENCO etc., (Larminie et al., 2003).

The fuel cell design is shown in Figure 2.3. Fuel cells operate at relatively low temperatures, and contain two main components (electrode and proton exchange membrane). The MEA consists of porous catalyst-coated electrodes layered with an electrolytic membrane. The system facilitates the supply of oxygen (cathode) and hydrogen (anode) through flow passages.

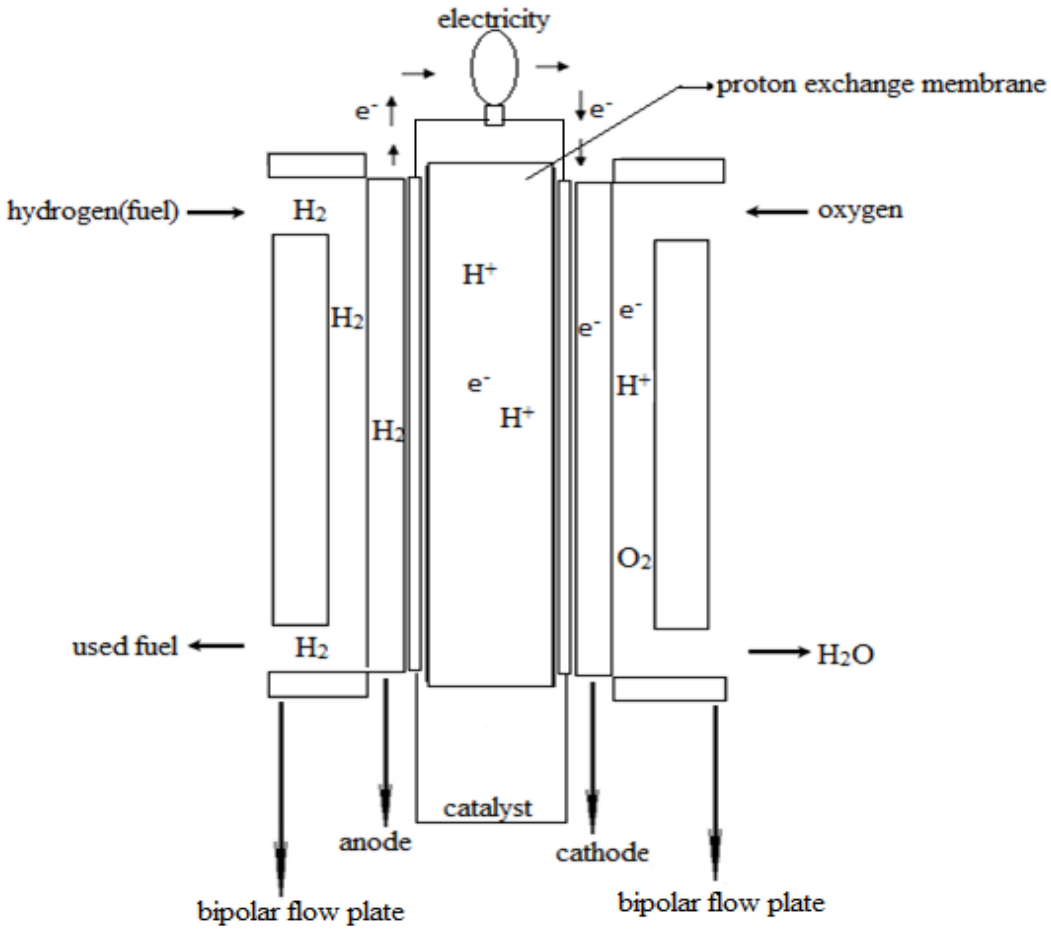


Figure 2.3: Fuel cell design (Sahu et al., 2009)

2.2.4 Types of Fuel Cells

The fuel cells are categorized into six types based on various factors such as type of electrolyte, conducting ions and the fuel used. They can also be divided into low (up to 100^{o}C), medium (up to 200^{o}C) and high temperature (up to 1000^{o}C) fuel cells based on the temperature at which they are being operated (Larminie et al., 2003 and Gubler and Scherer, 2008). This paper does not explain much about the types of fuel cells because the main focus of this paper to synthesize nanocomposites based on PEMFCs. The following table 2.2 shows a generalized view of different fuel cells and their applications. All the types have a generalized function but with their own advantages, limitations and potential applications.

Table 2.1: Types of fuel cells (Larminie et al., 2003 and Lypiridi, 2013)

Type of fuel cell	Electrolyte material	Charge carrier	Operating Temperature (^oC)	Applications
Solid Oxide fuel cell (SOFC)	Yttria stabilized zirconia	O^{-2}	700-1000	Auxillary power, electricity utility, cogeneration, distributed generation
Molten Carbonate fuel cell (MCFC)	Solution of potassium, lithium, sodium carbonates	CO_3^{-2}	600-700	electricity utility, cogeneration, distributed generation
Phosphoric Acid fuel cell (PAFC)	Phosphoric acid	H^+	150-200	distributed generation
Alkaline fuel cell (AFC)	Aqueous solution of Potassium hydroxides	OH^-	90-100	Space missions, military uses
Direct Methanol fuel cell (DMFC)	Perfluorosulfonic acid	H^+	20-90	Portable electronic systems
Proton exchange membrane (PEM)	Perfluorosulfonic acid	H^+	50-100	Back-up power, portable power, distributed generation, transport (vehicles)

2.3 ION EXCHANGE MEMBRANE AND ION EXCHANGE CAPACITY

The importance of the ion exchange property in separation processes has acted as a driving force for the research and development of the ion exchange membranes (IEM) in various fields (Sata, 1991). The significant technical and commercial importance resulted in the evolution of IEMs from laboratory experiments to industrial products resulting in the development of new functionalized materials with (Sata, 1991).

2.3.1 Ion Exchange Membranes

Ion Exchange Membranes are semi-permeable membranes with an ionic functionality fixed to the backbone of the membrane enabling the concentration, separation, or exclusion of the ionic species in the membrane.

IEMs are classified into anion and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contain negatively charged groups, such as $–SO_3^-$, $–COO^-$, $–PO_3^{2-}$, $–PO_3H^-$, $–C_6H_4O^-$, etc., fixed to the membrane backbone and allow the passage of cations but reject anions. While anion exchange membranes contain positively charged groups, such as $–NH_3^+$, $–NRH_2^+$, $–NR_2H^+$, $–NR_3^+$, $–PR_3^+$,$–SR_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations (Strathmann et al., 2011).

2.3.2 Properties

The most desired properties of ion-exchange membranes are:

- High perm selectivity
- Low electrical resistance
- Good mechanical and form stability and
- High chemical and thermal stability

However, the properties are dependent on various factors determined by the parameters such as the membrane material, polymer network density, hydrophilic and hydrophobic nature of the polymer matrix, type and concentration of ions.

2.4 POLYMERIC MEMBRANES USED IN THE FUEL CELL

Polymeric membranes gained substantial importance in recent times as alternative energy sources resulting in the development of solid conducting membrane fuel cells. The immobilized electrolyte as a fuel cell has many promising features such as fast start up, immediate response to changes and high tolerance to shock and vibration (Laberty-Robert et al., 2011). Initially, aqueous electrolytes were used in fuel cells but owing to the high cost and permeability issues leading to undesirable reactions, they have been replaced with inexpensive and more durable solid polymers (Maier and Meier-Haack, 2008). Before the invention of PEMs, solid-oxide fuel cells were in use, but the limiting factor is that they are expensive, involve in extreme reaction conditions and have size issues.

Thomas Grubb and Leonard Niedrach of General Electrics developed a solid polymer electrolyte which was used in the U.S space mission applications. It was named as polymer electrolyte membrane fuel cell, or proton exchange membrane fuel cell (PEMFC). NASA utilized a cross-linked polystyrene divinyl benzene sulfonic acid (PSSA) membrane which showed high stability among the highly diverse family of fuel cells. But, they were soon replaced by Nafion (DuPont, 1960s) synthesized by Walther Grot by modifying commercially available Teflon polymer, due to its superior performance and durability.

The initial research aimed at using solid electrolyte has started with a class of polymers known as engineered thermoplastics that are mouldable at specific temperatures. They are generally light, flexible, can be sterilized, and have good resistance to water and chemicals. These properties vary in each of them based on their chemistry. Some polymers can withstand extreme temperature up to $350^{o}C$ while others may have low thermal resistance. Most of the thermoplastic members are excellent insulators for electricity but can be made electrically conductive with the addition of suitable materials.

2.4.1 Properties of Polymeric Membranes for fuel cell applications

The polymeric membrane is the heart of the fuel cell as it serves as the main component for conduction of protons and effective separation of the electrodes and reactants (Larminie et al., 2003). In general properties such as (a) heat and chemical resistance, (b) fire safety, (c) light weight, (d) high strength and accuracy and (e) the feasibility of manufacturing in high volumes with low processing costs make them well suited for broad range of applications.

Particularly, for the fuel cell performance, an ideal membrane should possess the following properties as described by De - Bonis (2009):

- A proton conductivity of more than 10^{-2} S cm^{-1} in a fully hydrated membrane;
- Low permeability to reactants;
- Chemical and electrochemical stability;
- Mechanical properties such as strength, flexibility and process ability;
- Production costs compatible with intended applications.

2.5 NAFION MEMBRANE

Nafion has acquired tremendous importance and attention as a proton conductor and is a widely used commercial PEM fuel cell. It is used in a number of electrochemical applications as a separator as well as a solid electrolyte. It is not only chemically resistant and durable but also highly selective in the absorption and transfer of cations.

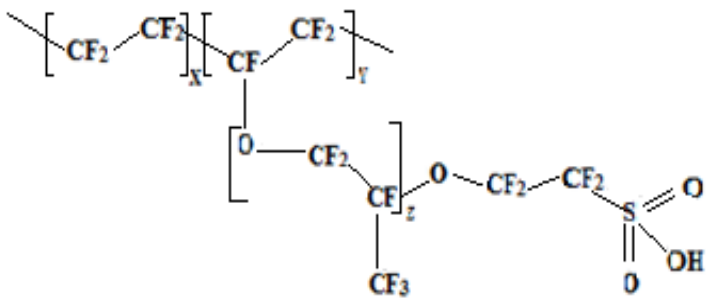


Figure 2.4: Chemical structure of Nafion (Sahu et al., 2009)

Nafion belongs to a new class of polymers called ionomers exhibiting unique ionic properties resulting from the incorporation of perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone as shown in Figure 2.4.

According to DuPont, Nafion has the following properties due to the influence of teflon and sulfonic acid groups:

- It has high cationic conductivity, chemical resistance, excellent mechanical and thermal resistance due to the hydrophobic fluorocarbon back-bone and hydrophilic sulfonic side chains.
- The sulfonic acid groups act as strong proton donor due to stabilizing effect of the polymer matrix (teflon backbone) attached to it.
- It is also selectively and highly permeable to water, as sulfonic acid groups have a high water of hydration due to which they can effectively absorb water which will also help in forming interconnections for proton transfer.
- Protons on the sulfonic acid groups hop from one acid site to another allowing the movement of cations across the membrane channels.

2.5.1 Nafion Modifications

Although Nafion is commercially successful, its proton conduction is highly dependent on the temperature and humidity of the fuel cell. The fuel cell performance reduces drastically at above $100^{o}C$ resulting in dehydration of the membrane (PEMFCs); and high methanol crossover (DMFCs) results in fuel wastage which limits the efficiency of fuel cell. Additionally, the platinum intolerance towards carbon monoxide and high manufacturing cost involving complex methods of synthesis makes Nafion difficult to commercialize at a large scale (Hickner et al., 2004; Zawodzinski et al., 1995; Laberty-Robert et al., 2011 and Ralph, 1997).

Initial attempts to modify Nafion with materials that can retain water at high temperatures were explored and studied as hydration is an essential factor for proton conduction. For example, Nafion membranes with hydrophilic ceramic inorganic fillers such as SiO_2 were

prepared to have more water absorption for enhancing the proton conduction at elevated temperatures.

M. Amjadi et al prepared Nafion/SiO_2 hybrid membrane for high temperature PEMFC with commercially available Nafion 117 doped with different loading levels of SiO_2 particles (2,5,7,10 and 12 wt%). The membrane results showed increased glass transition temperature (T_g) with high water retention and reduced hydrogen crossover. However, there was a reduction in proton conduction at ambient temperature and relative humidity (Amjadi et al., 2012).

Extensive research on several new classes of clay materials is proven to reduce the fuel wastage and increase water retention. Use of Montmorillonite (MMT) in Nafion belonging to a new class of clay family, showed decreased diffusion of gases and fuel crossover (Felice et al., 2010). Layered Double Hydroxides (LDH) with metal cations (Mg^{2+}/Al^{3+}) and different countervailing anions (CO_3^{2-}, ClO_4^-, NO_3^-) is another material of clay family having unique physicochemical properties. The LDH/Nafion composite membrane with Mg^{2+} and Al^{2+} ions at different ratios containing carbonate as interlayer was prepared by Lee et al. (2005) Increase in water uptake was observed while the cation exchange capacity decreased, which was attributed to the neutralization of negative sulfonic acid groups by positive LDH particles (Lee et al., 2005 and Angjeli et al., 2015).

In the last two decades, the evolution of carbon nano technology has helped in developing advanced materials, using carbonaceous materials. Carbon nanotubes (CNTs) became interesting candidates in the making of composite fuel cell membranes due to the excellent results obtained by improving the membrane properties. Wang et al. (2012) prepared SiO_2-MWCNT/Nafion membranes with 4% wt of SiO_2-MWCNT loading in Nafion membrane. The results showed improved dimensional stability and water retention that can help the membrane to maintain reasonable proton conduction.

A variety of materials like TiO_2, ZrO_2, zeolites (Shao et al., 2002); Phosphoric Acid (Yan et al., 2007 and Aili et al., 2011); imidazole moieties (Xu et al., 2015 and Iwan et al., 2015); activated carbon (Chien et al., 2013); cross linking Polyvinyl alcohol (Shao et al., 2002) and various other materials were also explored in modifying the Nafion membrane. Among these, Nafion with carbonaceous nano materials appear to be most favourable and effective for improving the performance and durability of fuel cells.

Despite these changes, there are several drawbacks to the above mentioned modifications which include non-homogenous matrix formation, sedimentation of heavier ceramic particles, leaching effect and; designing issues such as synthesis conditions, compatibility and scale up, and insufficient proton conduction.

2.6 POLYSTYRENE-BUTADIENE RUBBER (PSBR)

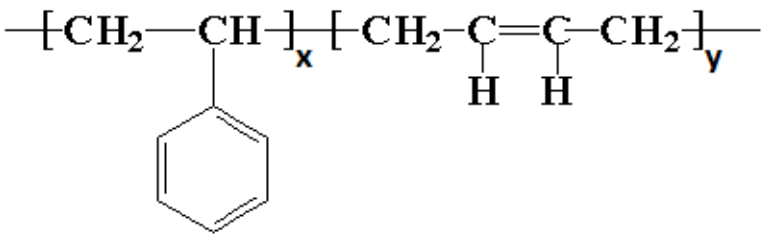


Figure 2.5: Structure of Styrene butadiene rubber (Nyemba, 2010)

Efforts have been made to eliminate and replace Nafion membrane (fluorinated) with non fluorinated materials in order to synthesize a cost effective and better performing membrane than the fluorinated ones. Ballard Advanced Materials (BAM) Corporation introduced, a semi commercial sulfonated trifluorostyrene based membranes which performed better than Nafion 117. Polystyrene butadiene rubber (PSBR), a co-polymer of butadiene and styrene (Figure 2.5) which is available in abundance is selected for polymer electrolyte as they are inexpensive, exhibit excellent mechanical properties and can be synthesized easily. As the proton conduction is not sufficient, several strategies were probed to induce proton conduction in PSBR membranes.

Abdulkareem et al. (2011) explored different methods to sulfonate PSBR with various sulfonating agents such as cholorosulfonic acid (CSA), sulfuric acid and acetyl sulphate.

According to their studies, the sulfonation via cholorosulfonic acid was found to be better than others and the sulfonated membrane via this route showed best electrochemical

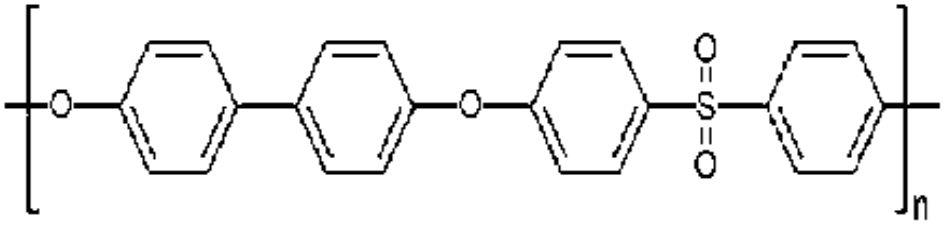
performance. The present research in reference to this work uses CSA for sulfonating the selected polymer.

Chuayjuljit and Luecha (2011) prepared rubber blends of carboxylated styrene butadiene rubber (XSBR) and natural rubber (NR) filled with polystyrene-encapsulated nanosilica (PS-nSiO_2) to investigate the tensile strength, dynamic mechanical properties, thermal behavior and morphology. The incorporation of nano filler-encapsulated with PS into rubber blends improved dispersion of SiO_2 in the rubber blend matrix resulting in an increased tensile strength, elongation at break and thermal stability.

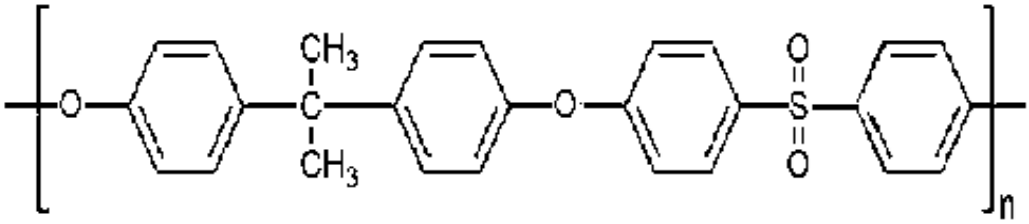
Nyemba (2010) synthesized a sulfonated synthetic rubber with carbon nano balls for ion exchange membranes. The carbon nano balls were prepared by Non Catalytic Chemical Vapour Deposition (NCCVD) method with the sulfonation of styrene butadiene via cholorosulfonation. The addition of low concentration of carbon nanoballs in the sulfonated PSBR resulted in increased degree of reinforcement and dispersion with enhanced mechanical properties. This work has been a valuable reference for the present research work for preparing the composite membrane using polyphenyl sulfone membranes and carbon nano balls.

2.7 POLYPHENYL SULFONE AS ION EXCHANGE MEMBRANE

The main focus during last couple of years was on the applications of aromatic hydrocarbons such as Poly (arylene ether sulfone) (PAES**)** in fuel cell technology (Di Vona et al., 2010 and Dyck et al., 2002)



(a)



(b)

Figure 2.6 (a) Structure of Polyphenylsulfone (Chao and Kelsey, 1986) and (b) Structure of Polysulfone (Zieren, 2011)

Poly (arylene ether sulfone) (PAES**)** are fully aromatic high performance amorphous materials with high thermal and chemical stability due to the bulky and inflexible aromatic groups within the polymer chain. The bond strength of C-H bonds in PEAS benzene rings also contribute to the high chemical stability of these materials (De - Bonis, 2009). According to Iojoiu et al. (2005), the evaluation and comparision of the electrochemical studies of model molecules mimicking several PEAS based materials such as polysulfone (PSU), polyphenylsulfone (PPSU), polyether ether ketone (PEEK) and polyphelylenesulphide (PPS) using sulfolane as solvent showed that the PSU and PPSU exhibited widest electrochemical stability window which make them desirable for fuel cell studies and applications. They also have good redox and thermal stability, high glass transition temperature of 220 C, toughness, low cost, and feasibility of processing which are increasing the interests among the fuel cell research communities (Naim et al., 2004).

As the main objective of fuel cell membrane is to conduct protons at higher rates and as the proton conductivity of PPSU is limited, the aromatic rings in PPSU offer the possibility of

chemical modification through electrophilic and/or nucleophilic substitutions using sulfonation or any other method in order to improve the proton conductivity (Kim et al., 2015).

2.7.1 Polyphenylsulfone Structure

The membrane structure is very crucial for the selection of various reactant materials and modification methods as the synthesized membrane morphology and its properties are directly linked to the structural features of the pure polymer membrane. PPSU is composed of alternating bisphenol and diphenyl sulfone fragments as shown in the Figure 2.6 (a). The aromatic hydrogens in the ortho position have acidic character due to a strong electron withdrawing effect of the sulfonic units in the aromatic ring due to which the carbons at these sites can be metalized using a strong base. Besides this, the phenylene rings of the bisphenol segments can be activated for electrophilic substitutions due to the electron donating nature of the ether linkages. Therefore, the PPSU can be functionalized in several ways as its chemical structure makes it feasible to undergo electrophilic as well as nucleophilic modifications (De - Bonis, 2009).

2.7.2 Modifications of Sulfonated Polyphenylsulfone for Polymer Electrolyte Fuel Cell Applications

Many sulfonated polymers including polyphenylsulfone were expected to enhance proton conductivity with increase in DS maintaining chemical and mechanical stability at long run, but it was proved that DS of polymer beyond 80 percent (%) is found to be water soluble, decreasing their mechanical stability and IEC (Maier and Meier-Haack, 2008). In case of DMFCs, the swelling leads to high methanol permeability resulting in fuel loss. Therefore, the membrane to be synthesized for FC applications should overcome these problems for its commercial success.

Zieren (2011), investigated on SPEEK/amino-benzimidazole-tethered Psf (SPEEK/Psf-ABIm) and SPEEK with benzotriazo tethered polysulfone (SPEEK/Psf-Btraz) membranes. Both the blend membranes exhibited better strength and showed suppressed methanol

crossover than Nafion. They understood that the properties were depending on the crosslinking variables like degree of carboxylation on Psf, casting solvent and amount of PSf-COOH in SPEEK used.

Acid-base cross linked membranes of sulfonated polyphenylsulfone/polybenzimidazole (SPPSU/PBI) membranes were synthesized by Xing and Kerres (2006). PBI (basic polymer) when mixed with an acidic polymer like SPPSU is reported to produce a membrane with excellent mechanical and thermal properties due to the formation of ionic crosslinkage between them (Kerres and Cui, 2001 and Kerres et al., 2000). The SPPSU/PBI membranes showed better mechanical and thermal stability and suitable proton conductivity than their parent membranes. The main disadvantage is that the increase in DS deteriorates the mechanical properties due to excess swelling (Xing and Kerres, 2006). Several other crosslinked membranes of acid-base polymers such as PBI/H_3PO_4 membranes and SPSU/PBI/H_3PO_4 were also produced in recent times (Kerres and Cui, 2001; Kerres et al., 2000; Hasiotis et al., 2001 and Kerres, 2001).

Karlsson and Jannasch (2005) synthesized sulfophenylated PSU using a different method of metalating the polymer using BuLi as metalating agent (lithiation) via one pot synthesis. The thermal stability was good enough with degradation of membrane starting at 300^oC and constant water absorption till 120^oC. The proton conductivity was high, maintaining a constant level at temperatures between 90-120^oC. However, Nafion 117 showed better conductivity under similar conditions.

Membranes with nano additives in SPPSU were synthesized by Hartmann-Thompson et al., (2008) to manage hydration and thermal issues. Functionalisedd nano polydedral oligosilsesquioxane fillers in SPPSU showed good conductivity but did not possess required water retention capacity resulting in dissolution of membrane in water. Lee et al. (2012) developed a multilayer-structured SPPSU-impregnated nano SiO_2 mixed ceramic layer followed by another SPPSU layer upon that. The dimensional change was effectively suppressed and proton conductivity was high which is attributed to the close packed mechanical framework of the nano SiO_2 ceramic layer.

In spite of these and many other modifications, there is lack of an appropriate membrane with ideal proton conduction having minimum or zero humidity working at or above 100^oC. As

synthesis of SPPSU-CNB is not reported till now, the present work is expected to give promising results for the fuel cell applications.

2.8 REQUIRED PROPERTIES OF A SOLID POLYMER FOR FUEL CELL APPLICATIONS

The literature studies indicate that the properties owing to the solid membranes should meet the requirements of a fuel cell for real time applications with durability and lifetime for maximum number of years. Therefore, the PEM functionality is directly dependent on the chemical and mechanical stabilities of membrane (Maier and Meier-Haack, 2008 and Gubler and Scherer, 2008).

The criteria for a polymer to be used in fuel cell applications include: high ionic conductivity, low electronic conductivity, oxidative and hydrolytic stability, good mechanical properties both in dry and hydrated conditions, cost and capability of fabrication into MEA (membrane electrode assembly).

A host of electrochemical reactions such as transportation of protons from anode to cathode, providing reactants to the catalyst and ensuring the electronic conductivity through a connection outside the cell, removing products from catalyst etc., are dependent directly or indirectly on the type of the polymer used for the fuel cell. The effects of these working conditions such as fuel start up/shut down, operation under aggravated temperature, low/high hydration states and transient electrical load (high voltage/energy bursts) will determine the overall stability of the polymer membrane. Therefore, the selection of material and optimization are important for the success of the fuel cell.

2.8.1 Ion exchange capacity (IEC)

The ion exchange capacity is generally used to characterize proton conducting polymer as a measure to transport protons from anode to cathode. It can be defined as the total number of chemical equivalents (IEC groups) available for ion exchange per unit weight or unit volume of the resin. For example, a PEM with more number of sulfonic acid (SO_3H) groups is said to

have high proton conductivity in presence of water and thus the degree of sulfonation (DS) in the polymer backbone depicts the IEC of the fuel cell membrane. ^{1}H NMR and/or acid-base titration are the general methods used to calculate IEC of the fuel cells.

The overall efficiency of fuel cell is dependent on ionic conductivity which in turn depends on temperature and humidity of the operating fuel cell. At higher temperatures, the polymer undergoes structural reorganisation to promote flexibility favouring faster ionic migration. If the operating temperature exceeds membranes dew point, the water vapour is lost resulting in loss of ionic conductivity especially in case of sulfonated perfluorinated membranes (Kumar and Nahm, 2011).

2.8.2 Water Sorption

Water sorption is the measure of the capacity of water uptake. This parameter highly influences the physico-chemical properties such as conductivity, permeability and mechanical strength of the membrane (Zawodzinski et al., 1993). For the fuel (methanol) in DMFCs, water is essential for the initiation of the reaction at anode. In PEMFCs, the dissociation of acidic groups to produce protons and their transportation via narrow channels (*Grotthus mechanism*) is possible only in presence of water. The relative humidity has a significant role in lowering the viscosity and increasing the ionic mobility of the polymers, (Li et al., 2006) however, the limiting factor for water management is the loss of water molecules on reaching the boiling point of water.

The sulfonated aromatic polymers such as SPPSU may uptake excess water resulting in the membrane swelling and mechanical degradation and in contrast low water uptake may decrease the conductivity (Di Vona et al., 2011). Thus, the effect of carbon nanoball filler in SPPSU polymer may help in mitigating this problem and help in optimizing the water uptake capacity of the fuel cell.

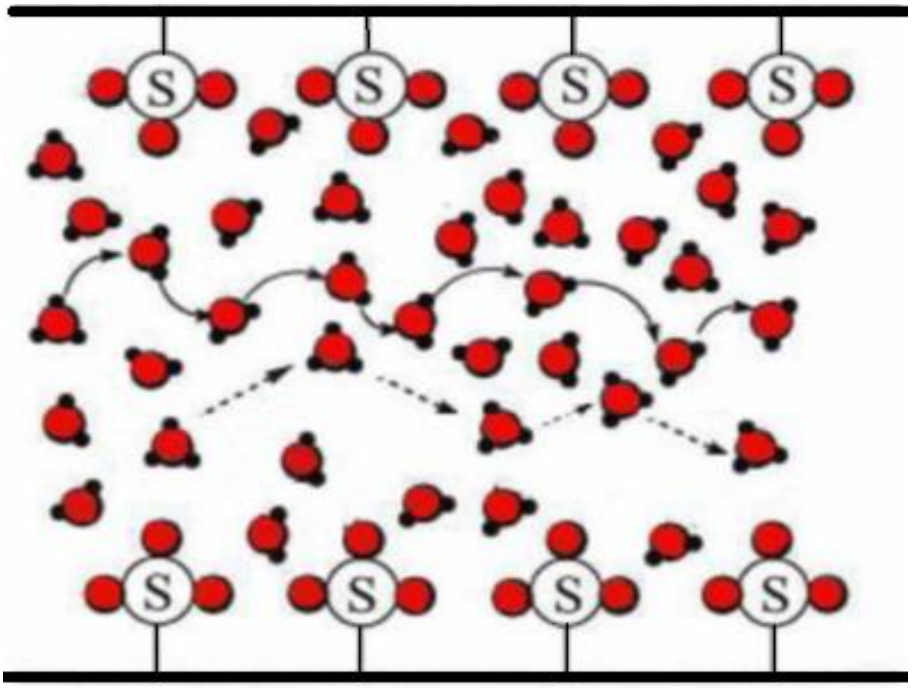


Figure 2.7: Scheme of proton transfer in Nafion with solid lines indicating Grotthus mechanism and dotted lines indicating vehicle mechanism (De - Bonis, 2009)

Figure 2.7 shows two kinds of proton transfer mechanisms and the selection of method depends on the level of hydration. In vehicle mechanism, the water molecule acts as vehicle to diffuse the proton with counter diffusion of unprotonated water allowing the net transport of the protons. Therefore, the proton conductivity depends on the rate of diffusion of water in the membrane. In Grotthus mechanism or proton hopping, the water molecules reside on their sites where the proton moves from one water molecule to the other via hydrogen bonds (Kim et al., 2015).

2.8.3 Durability (Lifetime)

The oxidation and reduction cycles to produce electricity create harsh mechanical and electrochemical environments that demand tough materials to withstand such conditions. Hence, there is a need for the fuel cell to function with acceptable efficiency for maximum number of years as there is a possibility of mechanical and chemical degradation after a certain period of time. The factors such as chemical reactions, sudden/quick start-stop cycles

and constantly changing power levels affect the membrane durability. Therefore, the mechanical and chemical integrity of the membrane and its components over an anticipated period of time is significant for the success of the fuel cell (Li et al., 2006).

2.8.4 Chemical Resistance

Chemical stability is one of the main factors that contribute to the long life of the fuel cell. The operating fuel cell membrane is exposed to a variety of chemical reagents and intermediate products which may affect the cell functioning. The interaction of different radicals with electrodes leads to reduced potential, unnecessary side reactions (result in chain scissions), loss of important functional groups, and fuel crossover (DMFC). The chemical resistance may be tested by exposing the membrane to different chemicals of oxidising, reducing and acidic hydrolysing conditions (Li et al., 2006) for a set period of time. The preferred membrane electrolyte should possess a strong ability to withstand these conditions and be compatible to the catalysts and other cell components without compromising the proton conductivity.

2.8.5 Mechanical Strength

Membrane stability is greatly affected due to constant changes in temperature, humidity and electrochemical reactions taking place in the operating fuel cells. The limiting factors like swelling and dehydration at elevated temperatures result in the loss of active sites or in the breakage of bonds causing chain deterioration.

The membrane materials should meet the extremely demanding requirements and there are various methods of testing the mechanical stability. The stability upon hydrolysis, tensile strength, percentage (%) resilience, elastic modulus, yield strength, elongation at break values and resistance to crack formations are generally calculated to measure the membrane strength. Thus, the fuel cell membranes are tested in the imitating environments of fuel cells subjecting them to variant temperatures, hydration levels and chemicals in order to check the

capability of the membrane to withstand severe operating conditions of the fuel cell (Maier and Meier-Haack, 2008; Gubler and Scherer, 2008 and Kumar and Nahm, 2011).

2.8.6 Thermal Stability

Most of the commercially available membranes operate excellently at low temperatures, but tend to lose stability resulting in reduced or zero conduction after reaching 100^{o}C. Typically, above 100^{o}C, the membranes become brittle due to the loss of water which is not ideal. The CO interference leading to the platinum poisoning is generally observed in low temperature fuel cells. This undesirable CO adsorption onto Pt electrode is thermally reversible, thus faster desorption of CO than the adsorption is required which can be achieved at elevated temperatures. Therefore, the fuel cells with high operating temperatures are desirable to tolerate the contaminants like CO, and other radical species without the loss of performance (Iojoiu et al., 2005).

2.8.7 Cost

In addition to the above discussed factors, the cost is a major limiting factor for the commercialization of PEMs. Apart from Nafion, there are other fuel cells and their derivatives such as Flemion (Asahi Glass, Japan), Aciplex (Asahi Kasei, Japan), Gore-Select (W.L. Gore, USA) which are commercially successful but the manufacturing becomes a costly affair due to the highly complex methods and use of expensive catalyst Platinum. Owing to the high cost, only few countries and companies are able to afford fuel cells, therefore, it is highly desirable to develop cost effective fuel cell that can reach out to a large number of consumers without cost being a hindrance (Laberty-Robert et al., 2011).

2.9 USE OF NANOMATERIALS IN FUEL CELLS

Nanotechnology is the most popular area in current research and development of fuel cells which can deliver environmental benefits and reduce the impact of energy production, storage and use (Paul and Robeson, 2008). The reduction of micro particles to nano size results in increased surface area and aspect ratio capable of creating large power and energy densities, a long shelf life and ease of manufacture. The fuel cells, with the incorporation of nano materials are reported to be reliable and cost effective over conventional membranes (Thiam et al., 2011).

Nanotechnology can be defined as the creation of materials through controlled manipulation of size and shape on atomic, molecular and supramacromolecular scales where quantum mechanical and surface boundary effects become relevant, conferring properties on materials that are not observable on larger and macroscopic length scales (Pitkethly, 2004). Design and synthesis of these materials with desired properties using such technologies is of great benefit to the scientific world.

Since, the proton conduction is a water assisted mechanism; relative humidity at high temperatures is a critical issue in developing advanced materials with improved hydration above 100^{o}C. These issues were addressed by incorporating hydrophilic inorganic fillers into the polymer membranes like Nafion (Uchida et al., 2003) and hydro carbons (Kim et al., 2006) to improve the water retention properties. Many studies on the use of nano particles in PEMs have proved to be effective in achieving the required hydration, thermal and mechanical stability with enhanced proton conductivity. The enhanced properties were due to the improved polymer/nano interfacial properties (Marani et al., 2009). To compensate proton conduction and reduce methanol crossover, nano clay materials like Montmorillonite (MMT), and other composite membranes were explored in the past (Xing and Kerres, 2006; Gubler and Scherer, 2008; Kang et al., 2003 and Xu, 2005). Though some of the composites were capable of reducing the fuel crossover, they had a negative effect on proton transport.

Also, the self-agglomeration and non-homogenous dispersion in the polymer matrix resulted in poor electrochemical performance limiting the use of such fillers. Addressing these issues will not only help in utilizing the latest nanotechnology but will also develop fuel cell performance (Thiam et al., 2011).

2.10 CARBON IN FUEL CELL APPLICATIONS

Carbon is diverse, abundant in nature and can bond in variety of ways to give a wide range of carbonaceous structures with considerably different properties. The structural diversity, texture and surface chemistry of carbon has attracted big research devoted to carbon production, characterization, surface modification and application in various fields (Mhlanga, 2009; Nieto-Marquez et al., 2007 and Pol et al., 2004).

There has been a long history of using carbon in various forms (graphite, carbon black etc.) in the construction of fuel cells either as a part of the fuel cell structure or as a support, owing to the unique electrical and structural properties, chemical stability and low cost (Zhong et al., 2000). The uses of carbon in fuel cell systems decribed by Dicks (2006) is as follows:

a) As a part of the structure of the fuel cell and stack (e.g., bipolar plate or as gas diffusion layer in PEMFC)

b) As a reacting species in Hydrocarbon-fuelled systems

c) As a potential means of storing Hydrogen

d) As a fuel in its own right, in the Direct Carbon Fuel Cell (DCFC)

The present paper does not describe the above parameters in detail as the main objective is to focus on using nano carbon materials as a part of the fuel cell membrane system.

2.10.1 Carbon Nanoballs

The discovery of carbon nanostructures such as nanotubes and fullerenes has resulted in carbon nanotechnology becoming the building block of the entire field of nanotechnology (Mhlanga, 2009 and Nieto-Marquez et al., 2007). New carbon based nano structures such as nanofibers, capsules, nanohorns, nanorods, onions, calabashes, flasks and nanospheres etc have also been discovered during various synthetic techniques of nanomaterials (Xu et al., 2010 and Deshmukh et al., 2010). Though CNBs have a long history of study, the main research focus till recent times was on the studies related to production and properties of CNTs and fullerenes but the accidental discovery of carbon nano spheres as a by-product

during the synthesis of CNTs (by CVD method) has brought back the focus on the Carbon Spheres (CSs) or CNBs. Even, the accessibility of the advanced microscopic techniques has resulted in more research focusing on the spherical carbon forms (Zhang et al., 1998; Nyemba, 2010 and Mhlanga, 2009).

CNBs are more or less spherical with the size ranging from about 50nm-1mm (Dicks, 2006 and Zhong et al., 2000). They have attracted great attention as potential materials in various synthesis and applications because of their interesting morphologies and properties such as excellent mechanical strength, high thermal resistance, low cost and light weight etc., (Mhlanga, 2009; Xu et al., 2010; Deshmukh et al., 2010; Yoshimura et al., 2009; Afolabi et al., 2007 and Coville et al., 2011). Their applications according to literature papers are described in applications section of this chapter.

CNBs are emerging as potential materials for designing fuel cells with desired membrane properties because of their interesting morphology and ease of synthesis where the size and structure can be controlled by varying the reaction conditions and carbon source based on the availability (Yoshimura et al., 2009; Afolabi et al., 2007 and Coville et al., 2011). They have not received much interest till recent times, as proper techniques were not available. Invention of new synthetic and analytical techniques in nano technology has increased the focus on other available carbon forms while CNBs are found to have important applications in various fields like batteries, fuel cells, capacitors, cathode support materials, composites etc., (Nyemba, 2010).

The general techniques used to synthesize CNBs are arc discharge, laser ablation, chemical vapour deposition (CVD), catalytic methods and autoclave process. CVD is reported to be the most favoured methods as most of the above processes have issues with mass production, purity and cost while few others needed complicated equipment or rigorous conditions (high vacuum or high pressure) (Afolabi et al., 2007).

2.10.2 Structure and Morphology

Carbon nanoballs (CNBs) as shown in Figure 2.8 (A to C) are circular concentric graphitic layers formed by pairing of pentagonal and heptagonal carbon rings during the growth or

nucleation (synthesis) (Kristianto et al., 2015). The graphite sheets that form CNB structures are generally unclosed shells with wavy flakes that follow the curvature of the sphere, creating many open edges at the surface which create reactive "dangling bonds" to give the spheres a high chemical activity and make them suitable for various applications as mentioned above. The exposed surface of CNBs has prismatic planes with high surface reactivity when compared to the basal planes. The graphitic layers in CNBs have interlayer spacing of about 0.34-0.37nm and their low I_G/I_D (intensity of graphitic C-C bond stretching band/intensity of distorted layer band) ratios from Raman Spectroscopic analysis show that they are less graphitic than the CNTs ((Nieto-Marquez et al., 2007).

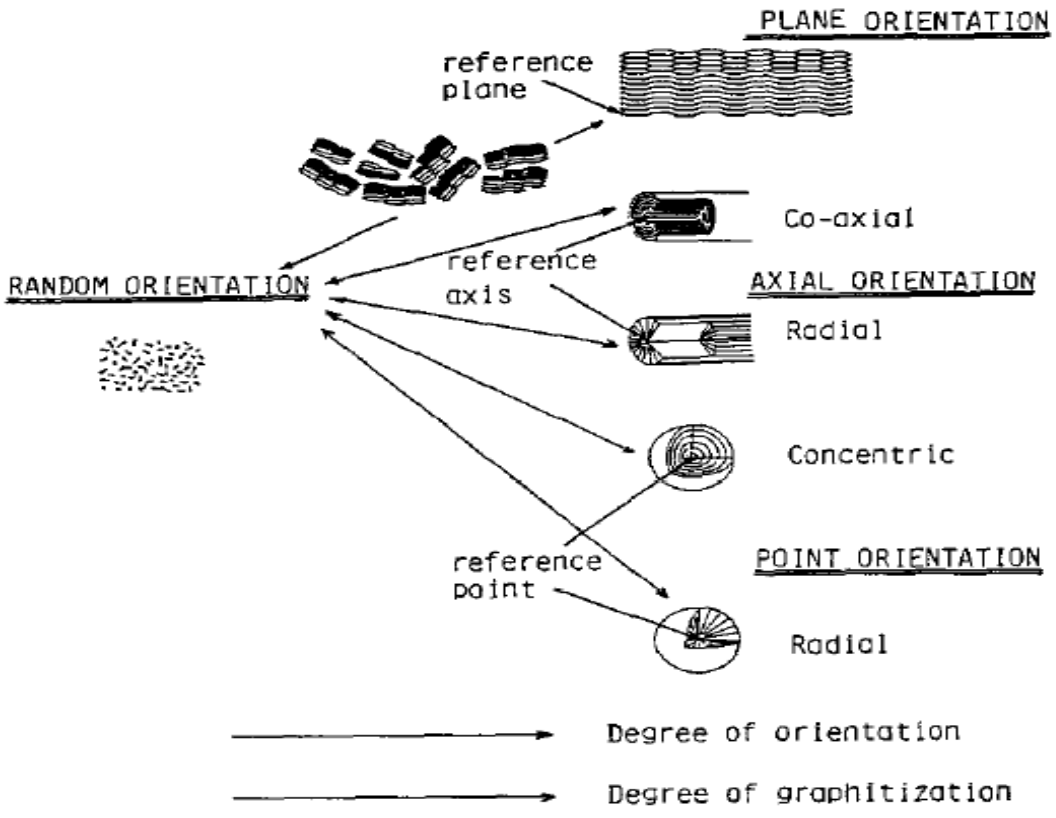


Figure 2.8 (A): Classification of nanometric texture in spherical carbons based on orientation of carbon layers (Inagaki, 1997)

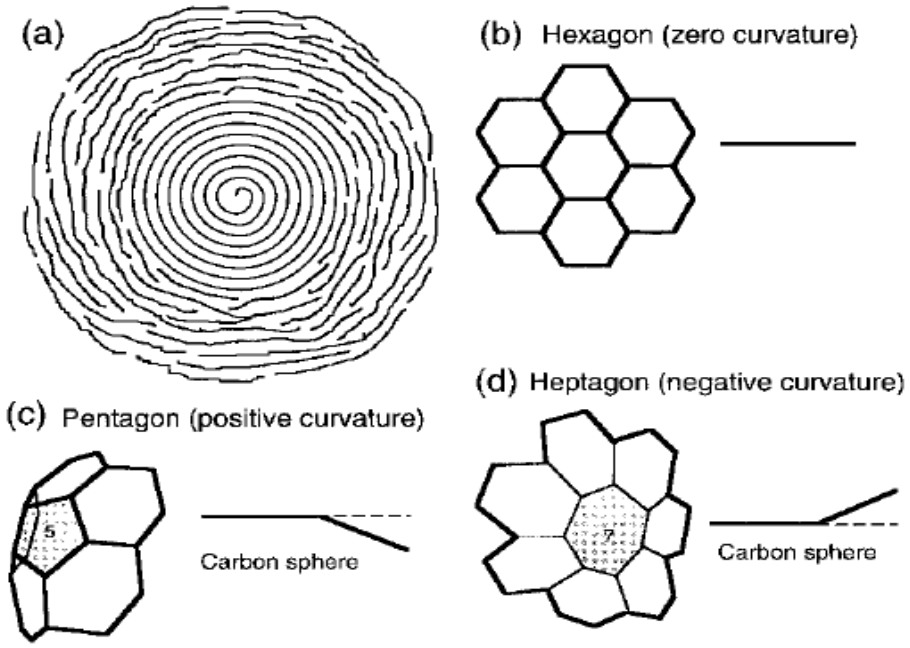


Figure 2.8 (B): (a) Schematic representation of graphitic flakes in carbon spheres, (b) hexagonal (c) pentagonal (d) heptagonal carbon rings (Kang and Wang, 1996)



Figure 2.8 (C): Orientation of carbon spheres (a) random (b) concentric (c) radial carbon layers (Deshmukh et al., 2010)

2.10.3 Types of Carbon Nanoballs

Several techniques used in the synthesis of CNBs produced CNBs with various sizes and textural properties. The spherical CNBs have been classified by several scientists in the past. Based on the texture of CNB, Inagaki (1997) has classified them into concentric, radial or randomly oriented carbon layers. He claims that the structure of spheres depends on the precursors used and the heating treatment conditions of the synthetic methods (Pol et al., 2004). According to his theory, a solid/liquid interface results in concentric growth, liquid/liquid interface gives radial spheres and solid/gas yields random texture. This indicates that during thermal decomposition, the interface between caron and its surroundings plays an important role in the formation of the spherical structure. Serp et al, categorized CNBs into fullerens, carbon onions, CNB and Carbon beads based on their diameter sizes ranging from 2nm, 2-20nm, 50-1mm and 1-several microns respectively (Nieto-Marquez et al., 2007). While most of the synthetic methods produced solid carbon nanospheres, hollow carbon spheres were isolated during the synthesis methods of shoch compression of graphite, pyrolysis of methane, ethane/acetylene and styrene (Nieto-Marquez et al., 2009).

2.10.4 Applications

CNBs have been found to have wide range of applications due to their unique physicochemical properties. The available literature on their applications is vast therefore; the following list shows few important applications of CNBs (Nieto-Marquez et al., 2007; Pol et al., 2004; Deshmukh et al., 2010; Nieto-Marquez et al., 2009 and Joula and Farbod, 2015).

- Adsorption
- Energy storage
- Electronic applications such as electrodes and superconductors
- Lithium batteries
- Material reinforcement
- Templates for hallow structures
- Capsules for magnetic nanoparticles
- Refinement of aqueous solutions

- Catalyst support
- Drug delivery
- Encapsulation of active transition metals and dyes
- Lubricants
- Removal/extraction of contaminants from water
- Enzyme and protein protection
- Magnetic data storage
- Modification of electronic properties of insulating materials
- Polymer additives
- Nanodevices
- Separation technology
- Elastomers and plastics

2.10.5 Synthesis of Carbon Nanoballs

The production of CNBs with high purity, uniform size distribution and good yield is desired for CNBs production. The strategies used in CNB synthesis have a major effect on the physicochemical properties of CNBs as different methods use different precursors, apparatus and reaction conditions (Deshmukh et al., 2010). A number of methods have been developed to synthesize CNBs with each technique having its own advantages and disadvantages (Joula and Farbod, 2015). The techniques include: chemical vapour deposition, arc plasma technique, oxide-catalytic carbonization, catalyzed reduction, hydrothermal synthesis and autoclave method to name some (Kang et al., 2003; Xu et al., 2010; Deshmukh et al., 2010 and Joula and Farbod, 2015). All the synthetic techniques do not give required results and may result in low yields and may produce toxic compounds (Joula and Farbod, 2015). The present synthesis of CNB is non catalytic method as most catalytic methods are not economical, involves complicated equipment or rigorous conditions such as high vacuum or high pressure (Xu et al., 2010).

2.11 CHEMICAL VAPOUR DEPOSITION (CVD)

2.11.1 Definition of CVD

Chemical Vapour Deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapour phase. It belongs to the class of vapour-transfer processes where the deposition species are atoms or molecules or combination of both (Pierson, 1999).

2.11.2 Advantages of CVD

According to Pierson (1999), CVD is one of the most preferred processes because of the following reasons:

- The rate of deposition is high and the products can be readily obtained.
- The process is competitive and economical
- It is flexible and can be adapted to many variations

CVD is a versatile and widely used and most suitable process involving in the conversion of a volatile carbon source into a solid non-volatile carbon product. The decomposition of carbon source in the gas phase uses high temperature furnace as energy source is used to crack the carbon molecule into reactive atomic carbon. The process is simple, highly reliable, industrially scalable, and cost effective leading to a large scale production of nano particles under optimized reaction conditions (Mhlanga, 2009).

CVD methods are classified into several processes depending on different factors which include the initiated chemical (activation) reaction, type of reactor used and the process conditions etc. (i)Based on the pressure conditions, CVD can be categorized into-the atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD), ultra-high vacuum CVD (UHCVD) and high pressure autoclave CVD (HPACVD). (ii)The difference in physical characteristics of the injected vapour into the reactor classifies the CVD into: Gas Phase CVD (GPCVD) - processed gas directly added to the reactor, Sublimation CVD (SCVD) - a solid

converted directly into a gas is added to the reactor, and The Direct Liquid injection CVD (LICVD) - liquid precursors added to CVD reactor.

Above processes can be carried out in either a horizontal or a vertical reactor in the presence (Catalytic CVD) or absence (Non Catalytic CVD) of catalysts with the pyrolysis of carbon source taking place in a quartz reactor at temperatures ranging from 600-1100^{o}C in an electronically operated furnace (Nyemba, 2010).

2.11.3 CNB synthesis by Swirled Floating Chemical Vapour Deposition Method (SFCVD)

CNB synthesis in present paper is a non catalytic SFCVD method using a vertical reactor where Acetylene (C_2H_2) and inert argon gas were used as carbon and carrier gas sources (Nyemba, 2010). It is advantageous over other methods because: it does not involve in purification step as there is no use of catalyst; the collection of carbon product is simple; the product is reported to be free from impurities and 99% pure; the reaction times are short and there is no occurrence of secondary reactions that involve in undesirable annealing and growth of CNBs (Nyemba, 2010 and Mhlanga, 2009).

The size, shape, quality and yield of CNBs depend on the factors such as temperature, flow rate of carbon and carrier gas, and the time spent by CNBs in the reactor during the CVD process. The effect of these parameters on CNB production was investigated elsewhere and proved that this method with Acetylene and argon as carbon and carrier source allowed for a controlled and continuous production of CNBs with high yields. It was also reported that pure argon gas favour carbon sphere growth (Nyemba, 2010 and Qian et al., 2004). Hence, the present research utilized the results from Nyemba (2010) and used the optimized conditions to synthesize CNBs.

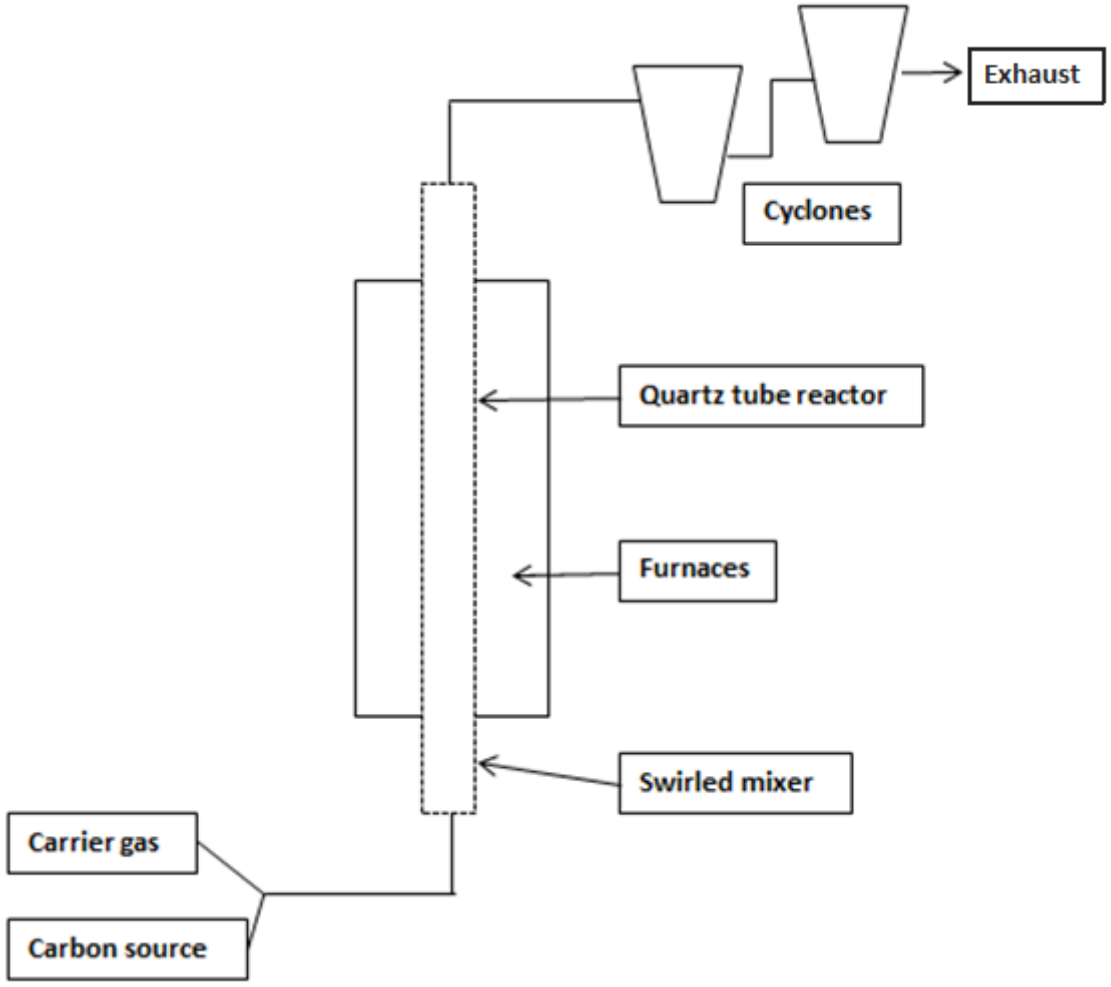


Figure 2.9: Schematic presentation of CVD Reactor for carbon nanoballs synthesis (Mhlanga, 2010)

2.12 SULFONATION

Table 2.2: Comparing the advantages and disadvantages of different methods for the sulfonation of polysulfones (Iojoiu et al., 2005 and Kerres, 2001)

Sulfonating Agent	**Concentrated Sulfuric Acid/ Fuming Sulfuric Acid**	**Sulphur Trioxide (SO_3)**	**SO_3-triethyl Phosphate Complex (TEP)**	**CSA ($ClSO_3H$)**	**BuLi**	**$(CH_3)_3SiSO_3Cl$**
Advantages	Inexpensive	Very reactive, not expensive	Sulfonation may be too high with high TEP content	Not expensive	Only method for sulfonation of e^- deficient rings	Homogenous reaction with better control
Disadvantages	Production of water with agent dilution during reaction Weakening the reactivity	Side reactions with crosslinking are possible Heterogenous	Minimization of crosslinking	Chain cleaveg/ branching, crosslinking reactions are	Expensive	Reltively expensive

		reaction		possible; Heterogenous reaction (affect reproducibility)		
Sulfonated Aromatic Ring	e^- rich	e^- rich	e^- rich	e^- rich	e^- deficient	e^- rich

The ion exchange membranes have garnered significant importance as suitable materials for fuel cell applications. The ionic conductivity is proportional to the concentration and mobility of protons, which are inturn dependent on the attached ionic moiety of the polymer backbone. Phosphonation (phosphoric acid), carboxylation (carboxylic acid) and sulfonation (sulfonic acid) are the general methods of functionalization but the sulfonation method is proved to be effective due to these reasons: a) sulfonic acid groups are easy to introduce into the polymer, b) they readily dissociate than any other acid (carboxylic acid) resulting in increased production of charged carriers and c) they do not easily form anhydrides on dehydration (Phosphoric acid) resulting in easy and quick rehydration of polymers.

2.12.1 Sulfonation Methods

The sulfonation technique was first published in the US Patent 3,709,841 by Quentin and Rhone - Poulenc (1973) that led to many studies on various sulfonating processes and sulfonating reagents in order to improve the technique and quality of the polymer product (Naim et al., 2004).

Post sulfonation and direct copolymerization are the two main approaches for sulfonation of polymers that have been investigated so far which can either be homogenous or heterogeneous in nature. The heterogeneous sulfonation involves in a reaction where the phase of sulfonating agent is different from the phase of polymer solution whereas in homogenous reaction, both are in the same phase (liquid/gas/solid) (Maier and Meier-Haack, 2008; Iojoiu et al., 2005; Kang et al., 2003).

- **Post-sulfonation method**

This is widely used method involving in the sulfonation of already prepared polymer membrane using sulfonating agents such as concentrated sulfuric acid/fuming sulfuric acid, cholorosulfonic acid, sulphur trioxide (SO_3), trimethylsilylchlorosulfonic acid or SO_3-triethyl phosphate complex. Generally, post-sulfonation method leads to electrophilic (sulfonic acid) substitution reaction of the aromatic ring, and the substitution is restricted to ortho position of the activated aromatic polymer, which is believed to cleave the ether linkage affecting the

chemical stability of the polymer. The use of strong acids for sulfonation leads to harsh chemical treatment resulting in undesirable side reactions, chain cleavage and sometimes cross-linking. It is also very difficult to control the sulfonation process which often leads to high DS. Although high DS is beneficial for proton conduction, the polymer at or more than 80% sulfonation is reported to dissolve in water therefore limiting the IEC and mechanical strength. Moreover, the post sulfonation via strong sulfonating agents is a reversible reaction often leading to the desulfonation of the membrane resulting in the degradation of the membrane. Hence, selection of an appropriate sulfonating agent and the optimization of process conditions such as temperature, time and concentration are important to prepare a sulfonated polymer with desired degree of the sulfonate groups in the polymer.

- **Direct copolymerization**

This is a different and alternative approach through which copolymerization of sulfonated and or non-sulfonated monomers occur via aromatic nucleophilic substitution reaction. On adjusting the ratios of the monomers prior to polymerization, the DS can be controlled to provide a good opportunity for improving the performance of the polymer.

- **Lithiation**

Sulfonation can be also be achieved through metalation route with the substitution of lithium on the deprotonated (ortho position) carbon of the phenyl ring, adjacent to the SO_2 group. The reaction of this lithiated polymer with SO_2 yields a sulfinated polymer, and a final oxidation with an oxidizing agent ($KMnO_4$, or H_2O_2) yields the sulfonated polymer. This approach of lithiation was demonstrated by Beihoffer and Glass (1986). In their study, the aromatic hydrocarbons in suitable anhydrous solvents like THF and/or diethyl ether were reacted with n-butyl lithium to obtain lithiated intermediates and a reaction with electrophilic reagent (SO_3, CO_2) gives desired functionalized polymer. Guiver et al., (1989) explained the mechanism of this particular method. The method is advantageous because the main chain of the polymer can be activated easily for the reactions with various commercially available electrophilic reagents and the product obtained will be in high yields (Maier and Meier-Haack, 2008 and Guiver et al., 1989).

Among the above mentioned methods, post sulfonation method will be employed in the present research paper as it is widely used and considered to be the best with proper selection and optimization of reaction conditions.

2.13 SULFONATING REAGENTS FOR PPSU

The sulfonation of a polymer can be performed by using the following reagents as described by Iojoiu et al. (2005).

2.13.1 Concentrated Sulfuric Acid

Post sulfonation of polymers using conc.H_2SO_4 is reported to be attractive as there is no requirement of organic solvents because the acid itself acts as both solvent and sulfonating reagent but the degradation of the membrane by chain breakings occur rapidly via this route.

2.13.2 Cholorosulfonic Acid

It also acts both as solvent and sulfonating reagent; however, the sulfonated polymer is found to precipitate out of the solution leading to non-homogenous and uncontrolled DS.

2.13.3 Sulfur Trioxide or SO_3/Triethylphosphate Complex

It has been reported that this route can be more reliable and can minimize side reactions while the toxicity, high reactivity of SO_3 and the highly exothermic reaction with triethylphosphate makes it difficult to work with.

2.13.4 Trimethylsilyl Chlorosufonic Acid

This route is advantageous when used with chlorinated solvents as homogeneity of the polymer is not lost even at higher DS and the possibility of chain breakage and side reaction is less.

2.14 DEGREE OF SULFONATION

Degree of sulfonation was calculated using the spectral data obtained from ^{1}H NMR. The DS was estimated using a method similar to the one reported by Dyck et al. (2002).

$$DS = (12-4A_{abc}/A_{de})/(2+A_{abc}/A_{de}) \quad (2.1)$$

Where A_{abc} and A_{de} are the sums of the areas of peaks due to a, b, c protons and d, e protons respectively.

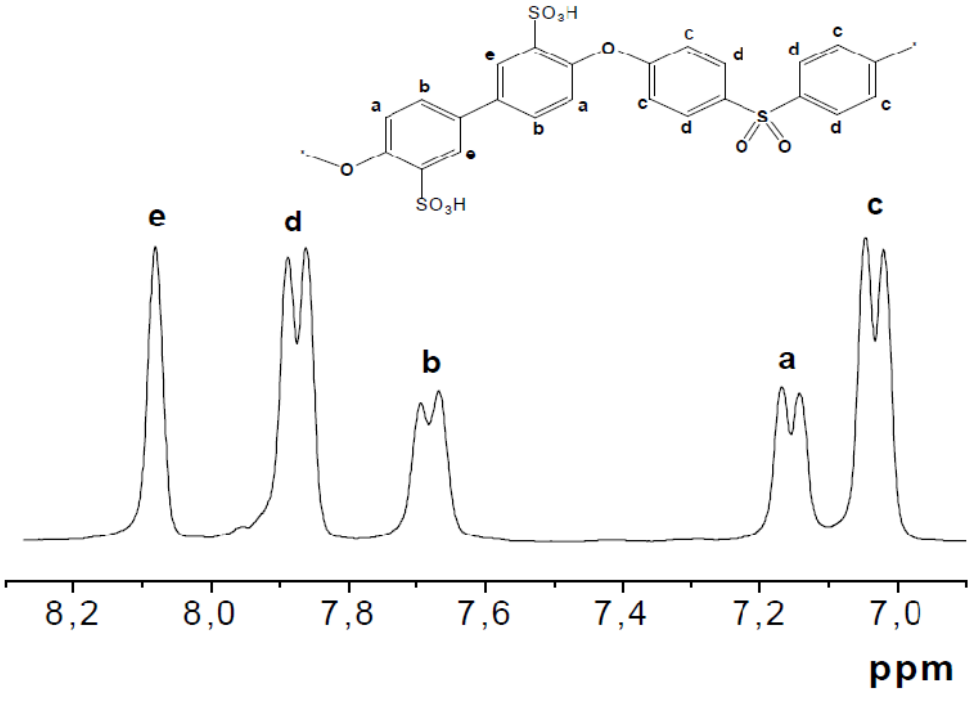


Figure 2.10: ^{1}H NMR spectra of SPPSU (Dyck et al., 2002)

2.15 ION EXCHANGE CAPACITY

IEC is a measure of the number of counter ions exchangeable in SPPSU. It provides an idea of amount of acidic groups present in the polymer for the proton conduction. It can be calculated by using the the following formula as used by Unnikrishnan et al. (2010).

$$IEC=1000 \times DS/[436+81 \times DS] \quad (2.2)$$

Where, 436=molecular weight of PPSU and 81=molecular weight of $–SO_3H$

2.16 WATER UPTAKE

Water uptake of plain sulfonated membrane and CNBs blended membranes was determined by drying the membranes overnight at 100^{o}C under vacuum prior to immersing them in water at room temperature for 1 hour. The wet membranes were removed after 1 hour and excess water droplets were removed with a blotting paper. The dry and wet weights of the membrane samples were recorded and the WU was calculated using the formula:

$$WU\ (\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (2.3)$$

CHAPTER 3: EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES

3.1 MATERIALS USED

Materials

Polyphenyl sulfone (Radel R-5000) was kindly provided by Solvay Polymers and Chemicals (Pretoria, South Africa) for free of charge. Other solvents and reagents of analytical grade were purchased from Sigma-Aldrich (South Africa) and were used as received. PPSU were dried overnight in vacuum oven at 50^{o}C prior to use.

3.2 METHODS

Below are the steps followed in the preparation of SPPSU-CNB composite membranes:

- Synthesis of sulfonated polyphenylsulfone membranes, their functionalizations and the characterizations;
- Synthesis of carbon nanoballs and their characterization;
- Blending and casting processes for preparing nanocomposite ion exchange membrane, and their characterizations;
- Testing the morphology and mechanical properties of synthesized membranes.

3.3 SYNTHESIS OF SULFONATED POLYPHENYLSULFONE (SPPSU)

3.3.1 Experimental Procedure for Sulfonation of PPSU

The post sulfonation method was selected for Sulfonation of polyphenylsulfone using a method similar to the one used by Tang et al., (2014).

20 g of dried Polyphenylsulfone (PPSU) was dissolved in 200 ml of dichloromethane (DCM) in a 500 ml three neck flask with constant stirring at room temperature until a clear solution was formed. Freshly prepared solution of 40 ml of chlorosulfonic acid (CSA) in 100 ml ice cold DCM was added dropwise to the above PPSU solution under stirring for 30 minutes and

the reaction was carried out for another 30 minutes at 0^{o}C. The reaction was stopped and the polymer solution was transferred into a beaker containing crushed ice and stirred. The obtained product was then filtered and washed with deionized water until a pH of 6-7 was reached. The obtained sample was then dried in a vacuum oven at 60^{o}C for 48 hours.

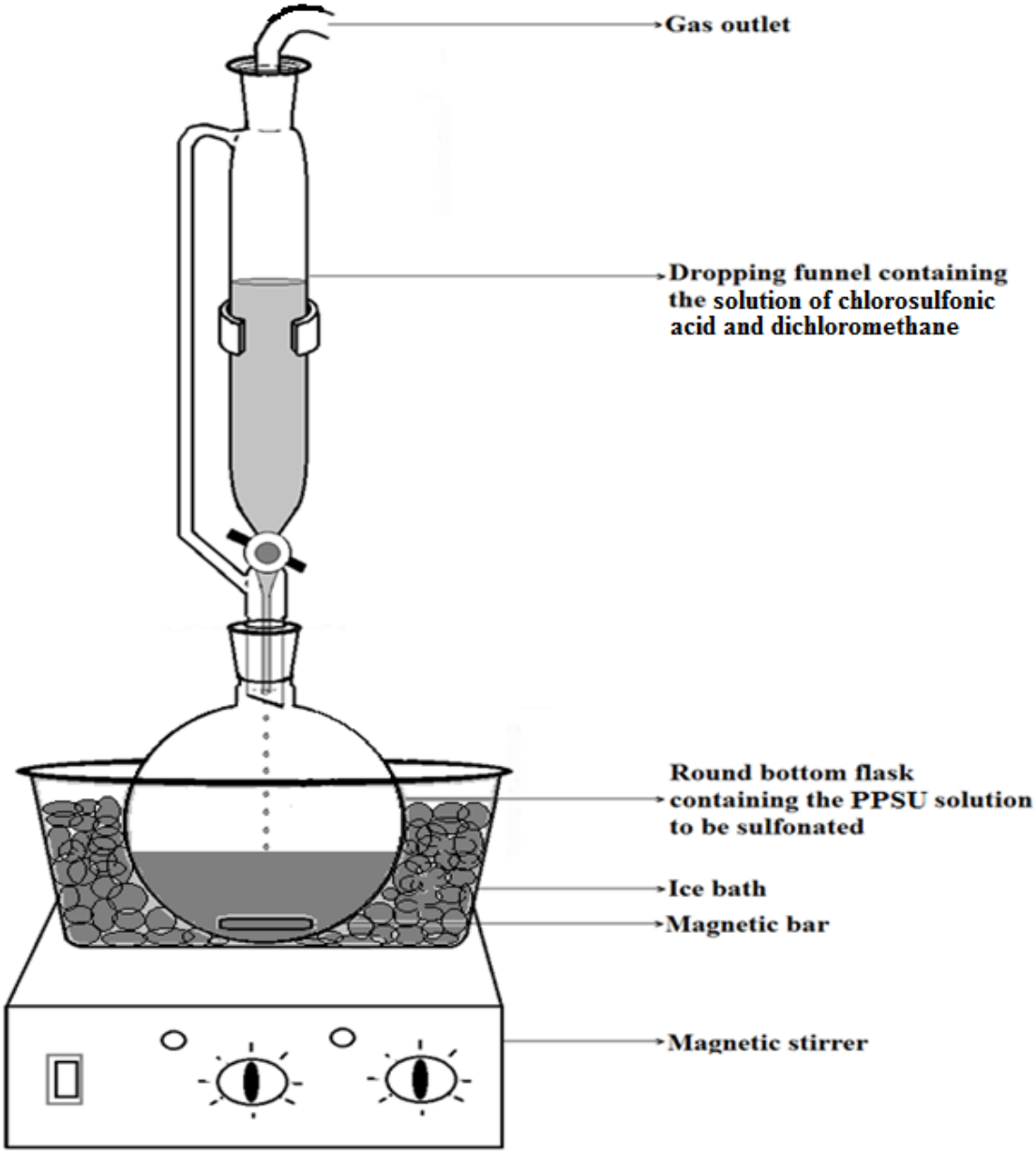


Figure 3.1: Sulfonation set-up for polyphenylsulfone synthesis

3.3.2 Characterization of Sulfonated Polyphenylsulfone (SPPSU)

The produced sulfonated polyphenylsulfone was characterized by Hydrogen-1 Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) for structural analysis and thermo gravimetric analysis (TGA) for thermal behaviour.

- **Hydrogen-1 Nuclear Magnetic Resonance Spectroscopy (1H NMR)**

^{1}H NMR spectra of unsulfonated and sulfonated PPSU were obtained using a Bruker 300-MHz spectrometer after polymer dissolution in deuterated dimethyl sulfoxide (DMSO). The chemical shifts (expressed in parts per million-ppm) are recorded with tetramethylsilane (TMS) as reference. The peaks and peak areas from the spectra were used to calculate the degree of sulfonation of SPPSU.

- **Thermo gravimetric analysis (TGA)**

The thermal stability of plain PPSU and sulfonated PPSU were investigated using a TGA Perkin Elmer Pyris analyser in nitrogen atmosphere at a flowrate of 60ml/min. The temperature range was fixed between 25 to 800°C with a heating rate of 20°C/min.

3.4 MEMBRANE PREPARATION

3.4.1 Choice of Solvent for Casting

N,N-dimethylacetamide (DMAc), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO) are the common solvents used to prepare the polymer solutions. The boiling points of NMP, DMSO, DMF and DMAc are 202, 189, 153 and 166^{o}C respectively, which show that NMP and DMSO have high boiling points than DMF and DMAc. As a result, the membranes prepared from casting solutions of NMP and DMSO take very long to dry and sometimes it is difficult to form a membrane from such

solutions. The other two amide based solvents DMAc and DMF can form hydrogen bonds with sulfonic acid groups of the polymer which might reduce the conductivity due to reduced mobility of protons in the membrane. Therefore DMAc was used in membrane casting as it has relatively low boiling point and can form hydrogen bonds only above 140^{o}C (De - Bonis, 2009).

3.4.2 SPPSU Membrane Preparation

10 wt% SPPSU membranes were prepared using solution casting method. The SPPSU was dissolved in DMAc under stirring at room temperature until a homogenous solution was formed. The solution was then cast onto a rectangular glass plate and spread thoroughly using a casting machine. The membranes were dried by slow evaporation till all the solvent was removed. The dried membranes of about 100-120 μm thickness were peeled off carefully and dried at 70-80°C overnight.

3.5 SYNTHESIS OF CARBON NANOBALLS USING NON CATALYTIC CHEMICAL VAPOUR DEPOSITION (NCCVD) METHOD

Non Catalytic Chemical Vapour Deposition (NCCVD) Equipment method was used to produce the carbon nanoballs as described by Nyemba (2005). The experimental set up consists of a vertical quartz tube reactor immersed in a furnace with a temperature regulator. The flow of reactant gas (acetylene) and carrier gas (argon) into the reactor were controlled by a set of rotameters, valves and pressure controllers which are connected to the quartz tube reactor as shown in the Figure 3.2. The CNBs produced were collected continuously using a delivery cyclone which is connected at the upper part of the reactor.

3.5.1 Synthesis of CNBs

Initially, argon gas was fed into the reactor for about 30min to achieve non-oxidative environment in the reactor. Then, the furnace was heated up to 1000^{o}C at a heating rate of 20^{o}C/min under argon atmosphere. Acetylene and argon were fed in to the NCCVD system as

the carbon source and carrier gas respectively as described by Nyemba (2010) and Afolabi et al. (2007). The flowrates of acetylene and argon were 456 and 100 ml/ min, respectively with a heating rate of 20^{o}C/min. A black product from the reactor was collected into the cyclone, and characterized.

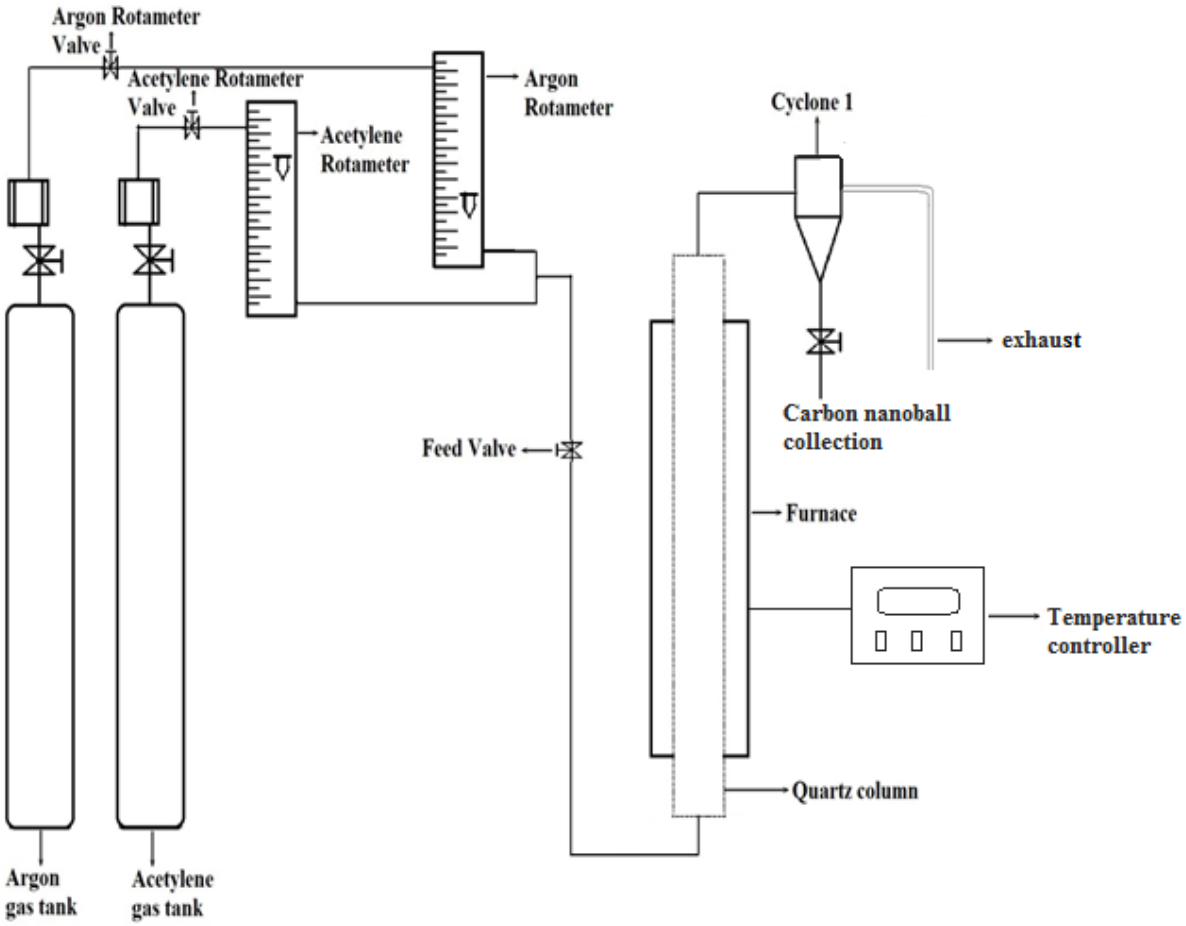


Figure 3.2: Schematic presentation of NCCVD Reactor for carbon nanoballs synthesis (updated from Nyemba, 2010)

3.5.2 Characterization of CNBs

The collected samples were analyzed with Transmission Electron Microscope (TEM) (JEOL 100S Electron Microscope), Thermo gravimetric Analyser (TGA) (Perkin Elmer Pyris 1 TGA Analyzer), BET surface area analyser (Micrometrics TriStar Surface Area and Porosity

Analyzer) and Raman spectroscopy for morphology, thermal stability, surface area and conductivity, respectively.

- **Transmission Electron Microscope (TEM) (JEOL 100S Electron Microscope)**

The morphology of the produced CNBs was analysed using TEM microscope. The samples for analysis were prepared by mixing a small amount of CNB powder in methanol by using ultrasonication. CNB particles were evenly distributed in the solvent. A small drop of this suspension was applied onto a 300 mesh carbon grid with lacy carbon film and allowed to dry. The grid was then introduced into the TEM instrument to analyse and save the images of interest in the sample at different magnifications.

- **Bruner-Emmett-Teller (BET) surface area analysis**

The surface areas of the prepared CNBs were measured using BET analyser. Surface area is the measure of the exposed surface of a solid on a molecular scale. It helps in predicting how the materials burn, dissolve, adsorb or react with other materials (Pol et al., 2004). A sample of 0.2 g CNB was analysed using a Micrometrics Tristar Surface Area Analyser for surface area measurements.

- **Thermo gravimetric analysis (TGA)**

The thermal stability of CNB sample was investigated using a TGA Perkin Elmer Pyris analyser in N_2 atmosphere (flowrate of 60ml/min). The temperature range was fixed between 25 to 1100°C with a heating rate of 20°C/min.

- **Raman Spectroscopy**

Raman spectroscopy is essential to check for the presence of carbon nano particles and determine whether the nanoparticles produced are single/multiwalled CNTs, nanofibers or nanoballs (Nyemba, 2010). Measurements were made with 514.5 nm line of an argon ion laser. The laser power at the sample was about 0.4mW.

3.6 PRODUCTION OF SPPSU-CNB COMPOSITE MEMBRANES

The polymer solution of 10% (w/v) of polymer in solvent was prepared by similar method described in section 3.4.2. Different amounts of the nano material were added to the polymeric solution and mixed using a probe Ultrasonicator at three different amplitudes of sonication and at full cycle for 1 hour. The casting was done using a simple evaporative technique.

3.6.1 Preparation of SPPSU-DMAc Solution

30 g of synthesized SPPSU was dissolved in DMAc to get 10% (w/v) of polymer solution. The clear homogenous mixture was divided accordingly to prepare the blends. One sample was left aside to represent the plain sulfonated membrane with 0% filler addition.

3.6.2 Preparation of CNB-DMAc Solution for Blending

Carbon nano balls solutions of different wt% of 0.25, 0.5, 0.75, 1, 1.75, 2.5 and 4% of CNB in DMAc were prepared by using ultrasonication for 1 hour, keeping the solvent volume constant for each preparation. Three sets of CNB solutions were prepared with each set containing the above wt% of CNB in the solution. Each set represents the amplitude (20, 60 or 75%) at which they are being ultrasonicated to prepare the CNB solutions and Blend membranes (Nyemba, 2010).

3.6.3 Blending and Casting of SPPSU and CNB Nanofiller Solutions

The blend membranes were prepared by adding the polymer solution into the CNB solution and ultrasonicating for 2 hours at specified amplitude at constant frequency until a homogenous mixture was obtained. The blended polymers were then casted onto a glass plate

using a similar method mentioned in 3.4.2. The casted membranes after drying were peeled off from the plate.

3.7 CHARACTERIZATION OF SPPSU-CNB BLEND MEMBRANES

The morphology and properties such as thermal stability, % resilience were analysed with Scanning Electron Microscope (SEM), Thermogravimetric Analyzer, texture analyser model TA-XT plus, respectively.

3.7.1 Scanning Electron Microscope (SEM) Analysis

The morphology of the nanocomposite membranes were analysed by FEI Quanta 200 SEM instrument. The SPPSU membrane samples were mounted onto spuds using a double sided tape and were coated with gold palladium to make the membrane surface conductive. The coated samples were then observed under the microscope to get the morphological images.

3.7.2 Tensile Strength Analysis

The plain SPPSU and nanocomposite membranes were tested for tensile strength properties using a texture analyser model TA.XT plus at 25^{o}C at a strain rate of 5mm/min. All the casted membranes had a uniform thickness of 0.2 mm and the samples for analysis were cut from their respective membranes with a 30mm length and 4mm width respectively. Three test results were obtained for each membrane sample to get an average value.

The samples were tested for % resilience. Before fixing the sample to the analyzer, the system was calibrated using texture analyser software and all gains were reset to 10. The dimensions of the sample and its identity were recorded and saved onto the machine for documentation and analysis and then set into a large displacement mode (maximum extension of 150mm) with a maximum operating load of 10.624 mN. The displacement/strain rate was set to 5mm/min for all samples.

The sample was now loaded onto the upper gripper of the analyser and tightly fixed using a torque wrench set to 20lb.inch (figure 3.3). The mass of the sample was measured and saved

in the software after which the sample was lowered and fixed into the bottom gripper with appropriate alignment. The sample was then tested and the values are saved for analysis.

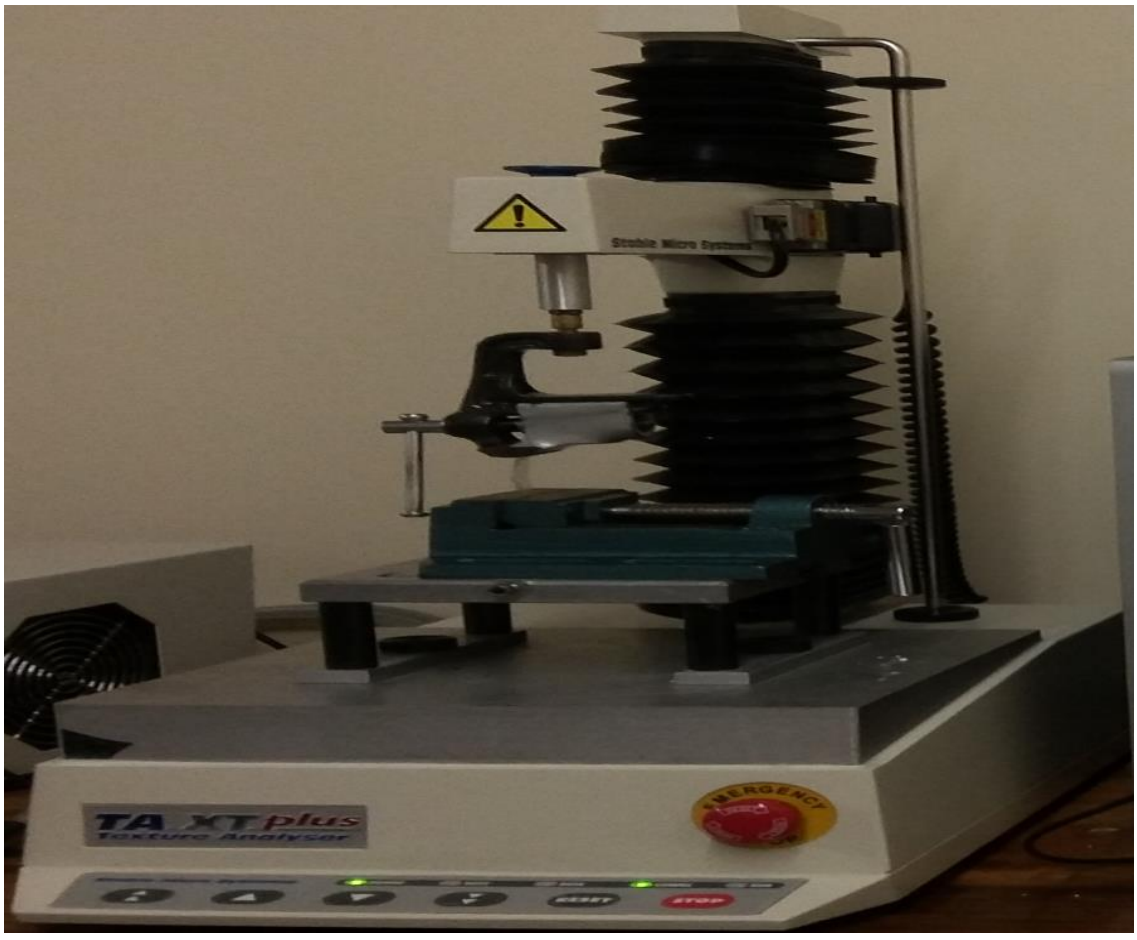


Figure 3.3: Tensile strength analyzer

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 SYNTHESIS OF CARBON NANOBALLS

Carbon nanoballs were synthesized according to the procedure described by Nyemba (2010). Generally, CNB with diameters below 100nm is preferred as above 100nm would be considered microscopic and the particles in micro range would have significant differences in their properties when compared to nano particles. Nano materials are homogeneously dispersed with larger surface area for a given volume compared to the micro particles. Non-catalytic chemical vapour deposition equipment was used to produce uniform CNBs of around 50nm diameter using 16mm diameter reactor. The NCCVD apparatus consists of a 16mm x 300 mm length reactor where 456 ml/min and 100ml/min flow rates of acetylene and argon gases, respectively are fed into the reactor at a temperature of 1000^{o}C with a heating rate of 20^{o}C/min. The produced CNBs were collected and analysed for morphology and other properties.

4.1.1 TEM analysis of CNBs

The morphology of CNBs was analysed using Transmission electron microscope. The images taken at X200 and X500 magnifications show that the CNBs are graphitic, round and solid but most of the images show accretion.

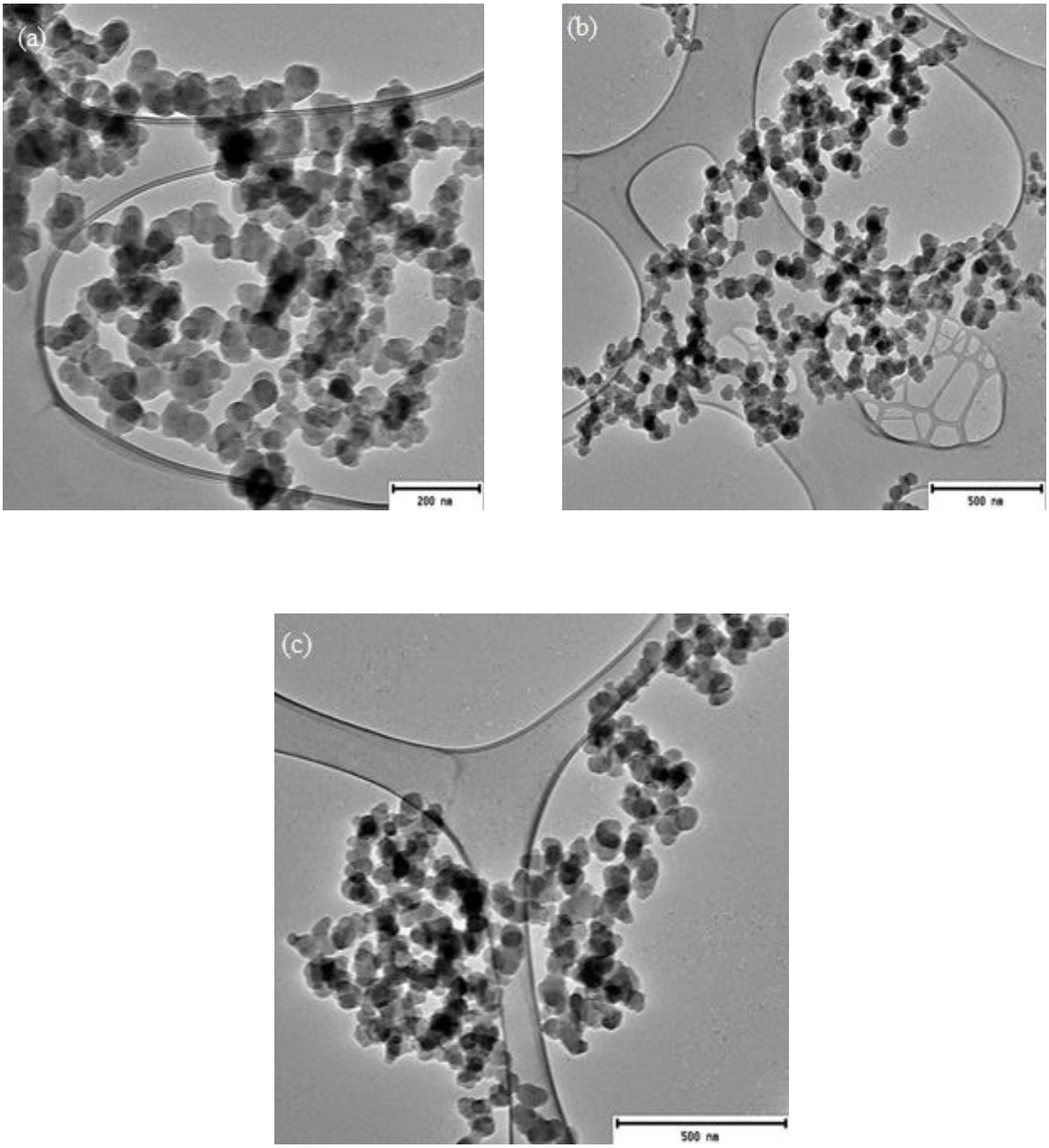


Figure 4.1: TEM images of (a) pure CNB and (b) uniformly distributed CNB

(c) CNBs produced by NCCVD method

TEM images of Figure 4.1 (a) (b) and (c) show that the NCCVD method resulted in production of pure CNBs that are spherical as no impurities can be seen. The morphology of the produced CNBs was evaluated using images taken at X200 and X500 magnifications. The CNBs were almost uniform in size as shown in Figure 4.1 (b) and were ranged between 40 to 60nm diameter. There is a clear indication of the CNBs forming chain like structure (forming

a necklace), a phenomenon called accretion which can be shown in Figures 4.1 (a) and (b). The images also show the agglomeration of CNBs which can be attributed to the strong attractive forces present among themselves (Kang and Wang, 1996).

4.1.2 BET Analysis of CNBs

The Brunauer–Emmett–Teller (BET) analysis of the synthesized CNBs show that CNBs are non-porous structures as indicated by the low BET surface areas of 7.5960 m^2/g, which is in the surface area range of the CNBs produced by Tetana (2013), and quite higher to the non purified CNBs produced by Phadi (2012). This result shows that the CNBs produced have less impurities (oily material), which could block the pores. The pore volume and pore diameter measurements were 0.0316 cm^3/g and 16.743 nm, respectively. TEM results as seen in Figure 4.1 support the BET results as less impurity can be seen on the TEM image.

4.1.3 Thermal Stability of CNBs

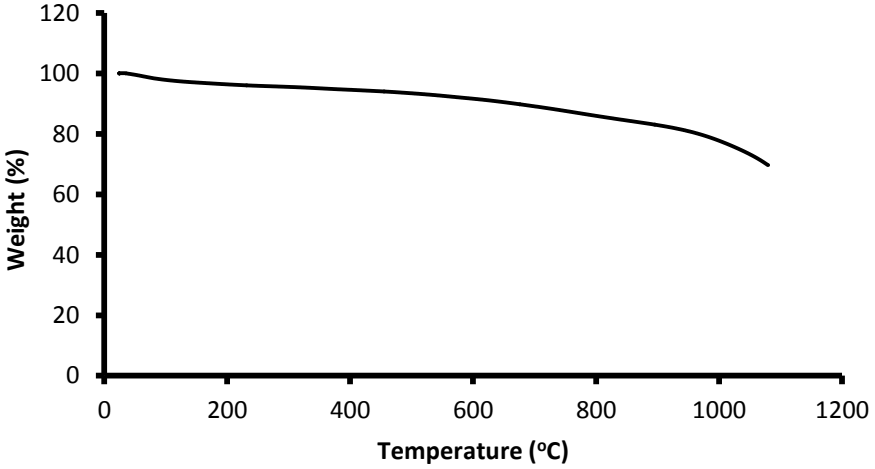


Figure 4.2: TGA graph showing thermal behaviour of produced CNBs

The thermal behaviour of the CNBs was studied by heating around 11.02 mg of the CNB material in an Aluminium crucible. The temperature range for heating CNB was selected from

25-1100^{o}C in the presence of N_2 with a flowrate of 60ml/min using a Thermogravimetric analyzer. The graphitic CNBs were found to be stable under the inert atmosphere maintaining the wt% of upto 95 till 360^{o}C. The weight loss was very low throughout the TGA run with 70 wt% at the end. This proves that using CNBs as nanofiller in polymer membrane will be advantageous as it will help in maintaining thermal stability of the nanocomposite membrane even at higher operating temperatures.

4.1.4 Raman Analysis of CNBs

Raman spectra of CNBs were recorded with 514.5nm argon ion laser with 0.4 mW power. The two main bands G and D of the spectra are crucial to measure the I_G/I_D (intensity of graphitic C-C bond stretching band/intensity of distorted layer band) value to indicate graphitic nature of the material and to know if the sample is conductive or non-conductive (Nieto-Marquez et al., 2007). The spectra shown in the Figure 4.3 has a strong peak of G band at 1588.6 cm^{-1} and a weak peak of I band at 1350.8 cm^{-1}. If I_G/I_D value more than 2, then the material is electron conductor otherwise it is an electron insulator. CNBs should be non-conductive when used in composite membranes in order to avoid unnecessary short circuits in the fuel cells. The If I_G/I_D value of CNBs is 1.18 indicating CNB as electron insulator (Nyemba, 2010).

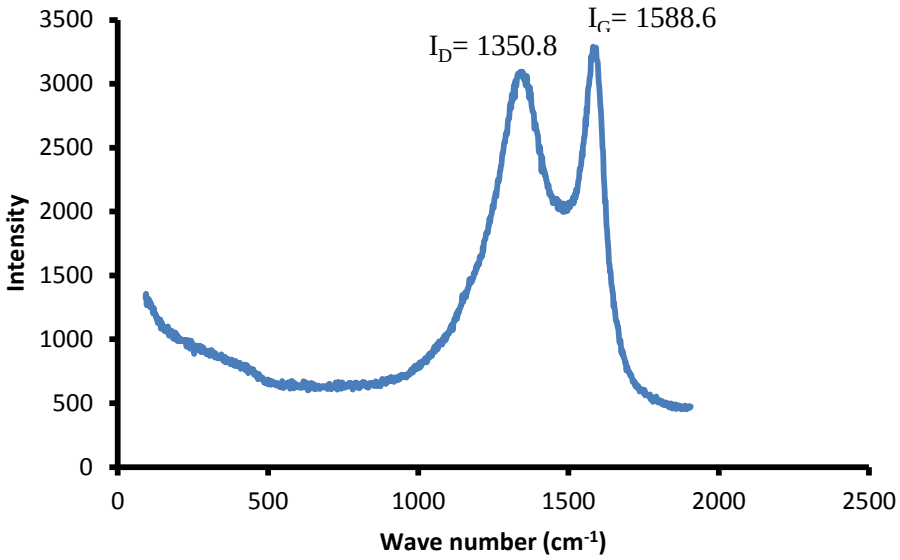


Figure 4.3: Raman Spectroscopy of CNB

4.2 SULFONATION OF PPSU POLYMER

With respect to other available polysulfone membranes, polyphenylsulfone has high thermal stability and strength for which it has been selected for producing sulfonated membranes. PPSU was sulfonated using Chlorosulfonic acid (CSA) as sulfonating agent (SA). CSA was preferred because it gives a high degree of sulfonation with minimal requirements of time and effort and it is more affordable than the other available sulfonating agents. The advantages and disadvantages of different sulfonating agents are discussed in section 2.13. Several sulfonations were performed using different parameters such as varying reaction times, concentration of SA and temperatures to optimize the suitable operating conditions for producing strong SPPSU membranes with good mechanical stability.

A high degree of sulfonation is required for the membrane because the ion exchange capacity is directly proportional to the degree of sulfonation. CSA is advantageous over other reagents because it results in production of highly sulfonated products. However, challenges such as non-homogeneity of the sulfonation mixture and gelation of the reaction solution in N_2 atmosphere were observed. This has resulted in performing different sets of sulfonation experiments to study the effect of concentration of sulfonating agent, reaction time and

temperature. The polymer once sulfonated becomes insoluble in the medium and precipitates out of reaction solution which leads to non-homogeneity of the sulfonation mixture.

4.2.1 Effect of Chlorosulfonic Acid on Sulfonation

All the experiments were performed with varying volumes of CSA varied from 0.25ml to 3.5ml against 1 gram of PPSU. DS was calculated using equation 2.1 from section 2.14.

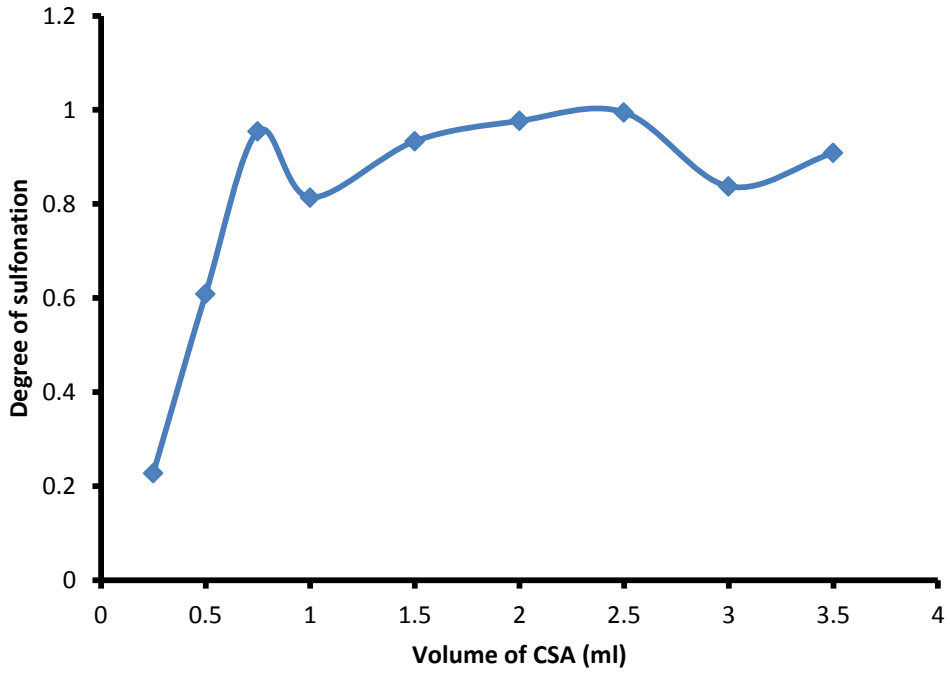


Figure 4.4: Graph showing the effect of CSA volume (concentration) on DS of PPSU

Figure 4.4 shows that with increase in the volume of CSA, the degree of sulfonation also increases, reaches a maximum sulfonation of 99% (DS=0.99) and then decreases again. The highest volume of CSA (3.5ml) did not give the expected DS as it shows a value higher than the previous one, which should not be the case.

4.2.2 Effect of Reaction time on Degree of Sulfonation

The procedures for the sulfonation reactions were similar to the one described by Tang et al. (2014). As the experiments were conducted to investigate the effect of reaction time on DS, the sulfonation reactions were carried using 1 g PPSU against 2.5ml CSA (gave maximum DS evaluated from effect of volume of CSA) and with varying sulfonation reaction times.

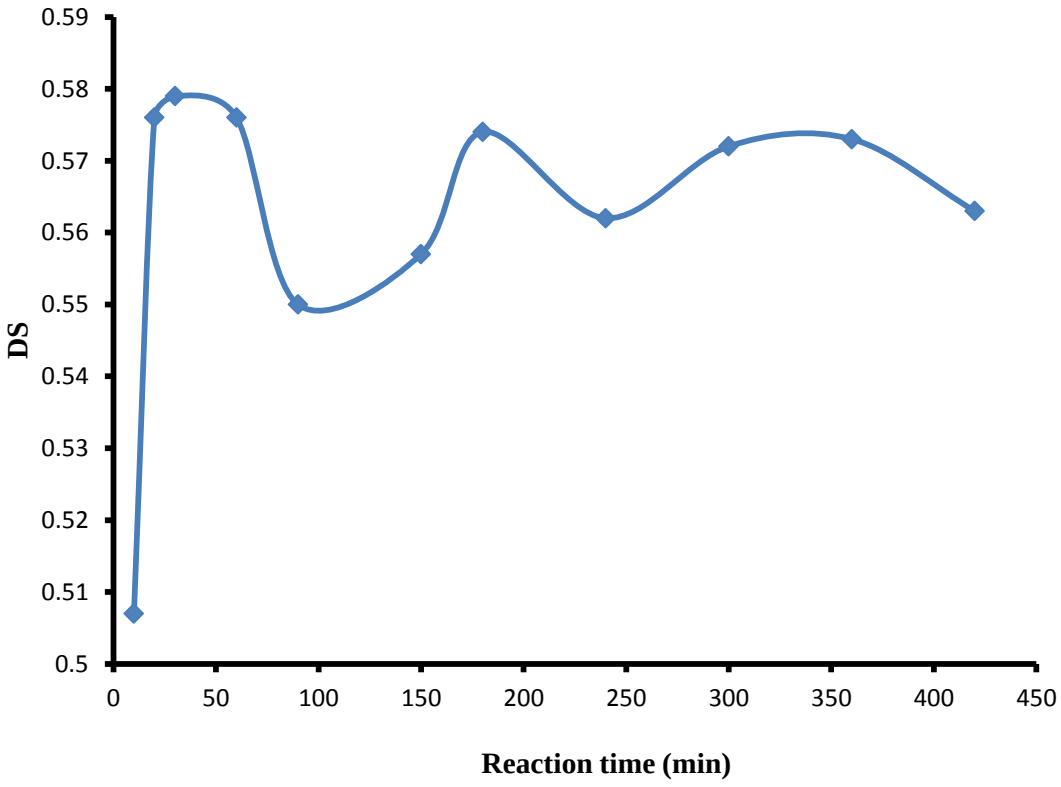


Figure 4.5: Graph showing the effect of reaction time on degree of sulfonation of PPSU

Figure 4.5 shows the sulfonation behaviour of PPSU with time. It can be seen that when the process reach its maximum DS, the polymer started to precipitate resulting in non-homogeneity of the reaction mixture. The highest DS (DS = ± 0.58) was obtained between 20 to 30 minutes.

4.2.3 Effect of Temperature on DS

The procedures followed were similar to the one described by Tang et al. (2014) but with variations in reaction temperatures.

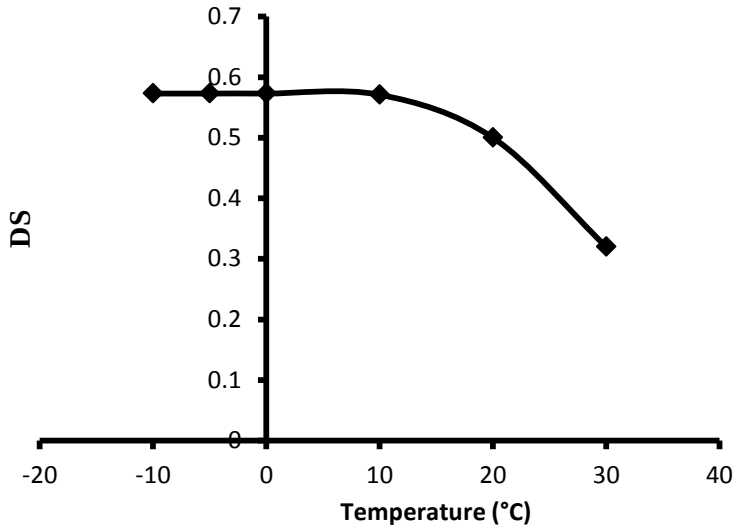


Figure 4.6: Effect of Temperature on DS

The results (Table 4.3 and Figure 4.6) show that the sulfonation is not favorable at higher temperatures. It was observed that the solvent tends to evaporate or solvate with the precipitate medium when reaction temperature was raised. It is also mentioned elsewhere that if the reaction temperature or time goes beyond threshold, chain scission may happen in postsulfonation (Hartmann-Thompson et al., 2008).

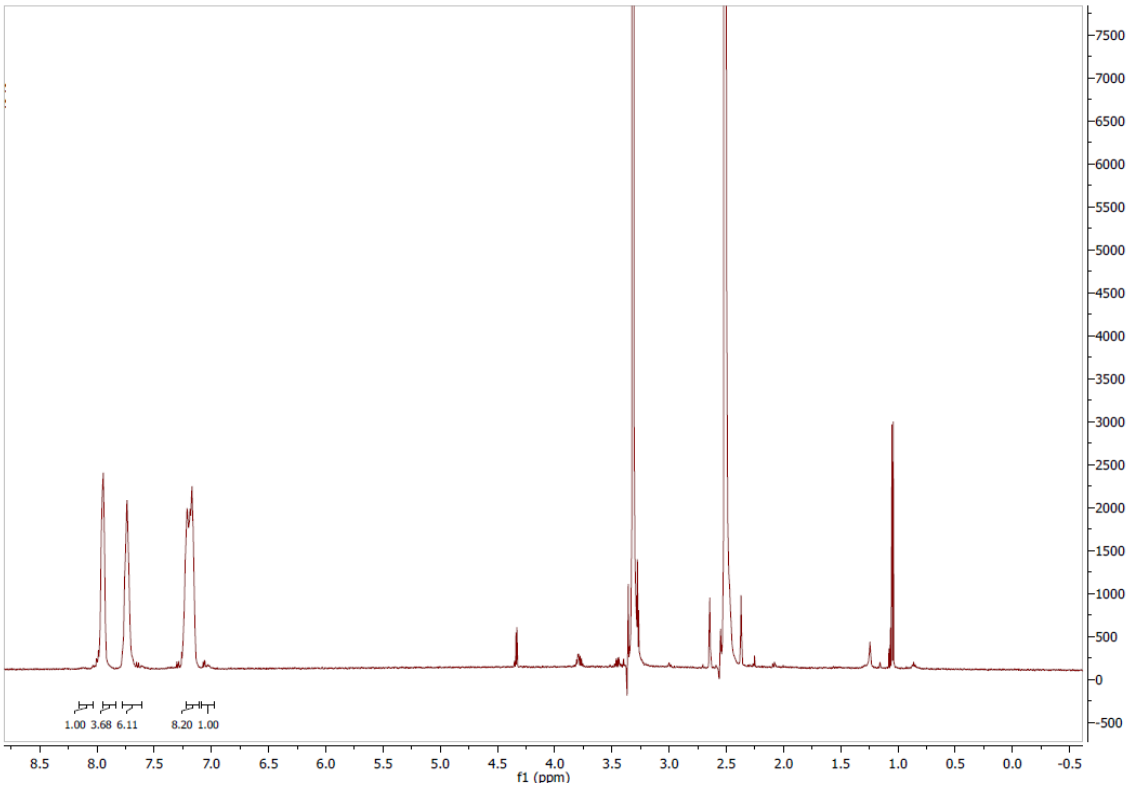
PPSU was perfectly soluble in the DCM solvent because of the presence of strong nucleophilic agent Cl^- in DCM (DCM has poor solvating capacity, so Cl^- might be responsible for inducing substitutions on the aromatic ring) but the ionomer precipitates as soon as CSA is added and the sulfonation degree is uncontrolled. It is understood that the formation of the arylsulfonic acid groups modify the solubility parameters of the polymer and results in ionomer precipitation resulting in non-homogeneity of the mixture. It is also indicated that the

partial precipitation during the sulfonation reaction may result in formation of the longest polymer chain in the precipitate and the shortest as soluble portions in the remaining solution. The reaction rate of the precipitate is slowed down resulting in the formation of unpredictable degree of sulfonation for different reactions. However, according to the kinetics, the rate of reaction with CSA is more when compared to Trimethylsillyl cholorosulfonic acid (TMSCSA) which can be assumed that the electrophilicity of CSA is much higher than TMSCSA (Iojoiu et al., 2005).

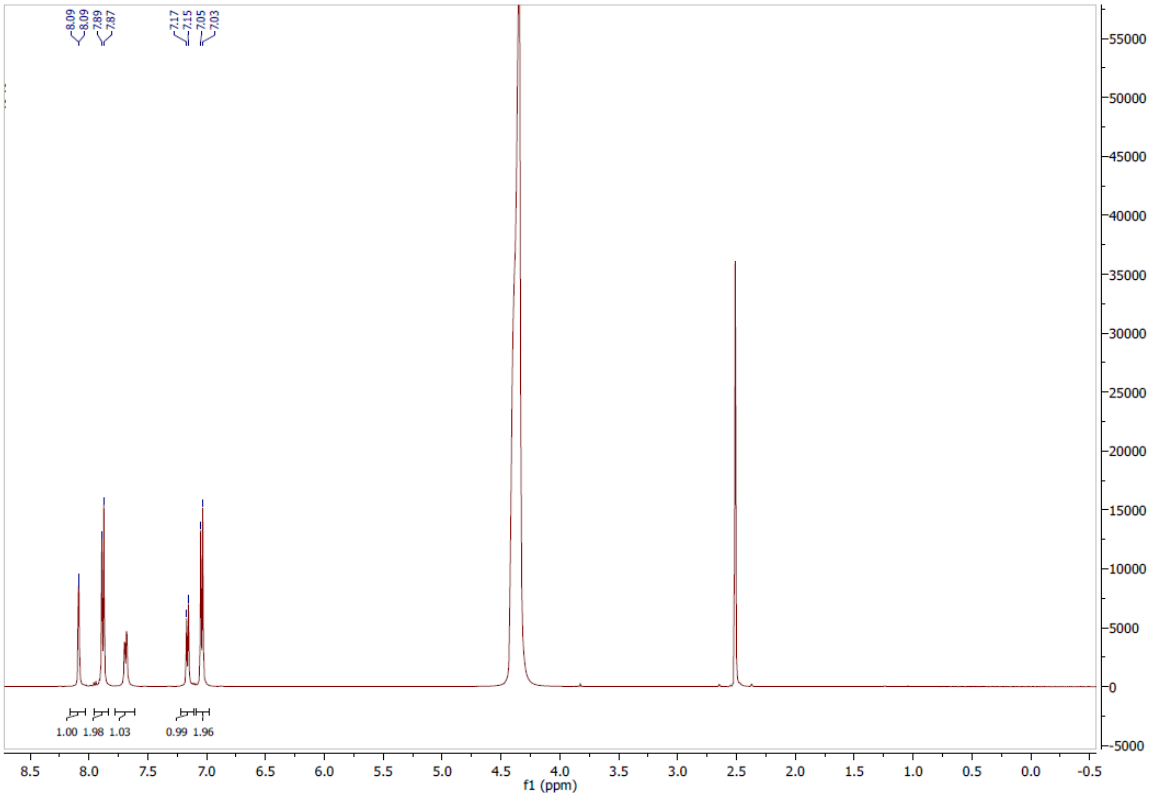
Despite the challenges, some of them gave satisfactory results and also the observations made during the reactions resulted in obtaining highly sulfonated product with only 30min reaction time. The inert atmosphere was also avoided which saved cost and time during the process. However, some preventive methods have be taken during sulfonations and encouraging more research into PPSU sulfonations might significantly reduce undesirable degradations and non-homogeneity of the sulfonation mixture ultimately resulting in high DS.

4.2.4 ^{1}H NMR Interpretation for Degree of Sulfonation

Sulfonated polyphenylsulfone polymers have been synthesized by post sulfonation method using chlorosulfonic acid and characterized by ^{1}H NMR which was used to confirm successful introduction of sulfonic acid groups into PPSU.



(a)



(b)

Figure 4.7 (a) ^{1}H NMR peaks of pure PPSU and (b) sulfonated PPSU

^{1}H NMR confirmed the sulfonation of PPSU and the spectral data was used as a quantitative technique to determine the degree of sulfonation of the sulfonated polymer. The NMR spectra show a peak critical to the sulfone group at 8.09 ppm for all the sulfonated membranes indicating the successful sulfonation. This peak is absent for the unsulfonated polymer. Though the membranes were sulfonated with different concentrations of CSA, the graphs with varying parameters show a nonlinear relationship between the concentration, reaction times, and temperatures with DS. This can be attributed to the fact that the reaction solutions were non homogenous and that they affected the sulfonations. According to the literature, the non homogeneity of the reaction mixture results in highly sulfonated product being dissolved in solution and the less sulfonated polymer in form of precipitate in the mixture (Iojoiu et al., 2005).

4.2.5 Water Uptake

The water uptake (WU) analysis is an essential parameter, which may improve conductivity of the membrane. In this report, the effect of sulfonation degree on WU was not investigated because it is known from the literature that the water uptake capacity will increase for increasing level of sulfonation as reported by Lufrano et al. (2000) and Isaacs-Sodeye (2008). This behavior was attributed to greater densities of HSO_3^- water clusters and distance between the clusters.

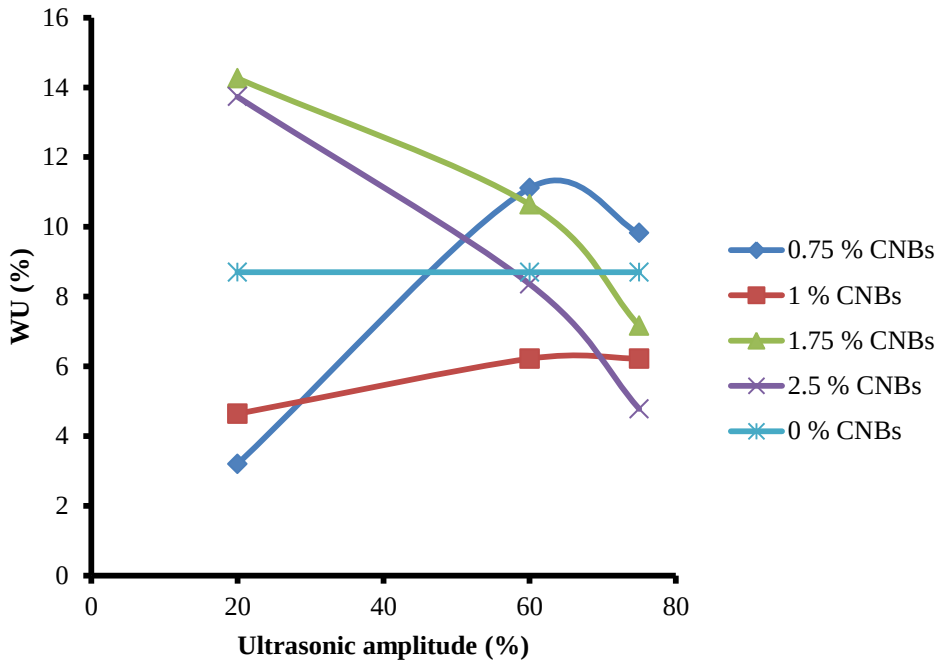


Figure 4.8: Effect of Ultrasonication amplitude and CNB addition on percentage water uptake of composite membranes

As mentioned in chapter 2, CNBs contribute in optimizing the water uptake capacity of the SPPSU fuel cell membrane to avoid membrane swelling and mechanical degradation, which may decrease membrane conductivity (Di Vona et al., 2011). As seen in Figure 4.8, 1.75 wt% CNBs gave higher ability to uptake water compared to the other CNB loading. Low CNB loading (0.75 wt% CNB) shows better WU capacity at higher blending ultrasonic amplitude.

The WU result shows that the blending ultrasonic amplitude has an effect on the ability to absorb water, and this ability decrease with an increase in ultrasonic amplitude for more than 1 wt% CNB; and increase with ultrasonic amplitude for low CNB loading. This observation reveals that swelling of the SPPSU is constrained by the nano-fillers, which is inferred to their mechanical reinforcement contribution.

4.2.6 Optimum sulfonation of Polyphenylsulfone

The optimum reaction conditions were chosen according to the results obtained from 4.2.1. The volume of 2.5 ml CSA gave higher and hence 2.5 ml CSA was considered to perform sulfonations at varying reaction times and temperatures. The volume of CSA, time and temperature at which higher DS was achieved were selected to prepare the SPPSU that was used to prepare SPPSU-CNB blend membranes. Therefore, 1 g PPSU was sulfonated using 2.5 ml chlorosulfonic acid at a temperature of 0^{o}C with reaction time of 30 minutes after addition of CSA. The degree of sulfonation is found to be 99% (DS=0.99) which was used for blending and producing nanocomposite membranes.

4.3 PRODUCTION OF SPPSU-CNB COMPOSITE MEMBRANES

Blending technique is one of the crucial steps in the production of the homogenous nanocomposite membranes. The challenging task while using nanomaterials in polymers is to avoid formation of uneven membranes due to agglomeration of nanoparticles and improve the distribution of nanoparticles in the polymer matrix. Therefore, the dispersion of CNBs in solvent and blending it with polymer solution was achieved by using ultrasonication technique. Ultrasoniction helped in uniform distribution or dispersion of the nanomaterial into the polymer solution which resulted in appropriate casting of the blend solution to produce even surfaced or homogenous membranes.

The nanocomposites membranes were produced using three different sonication amplitudes percentages i.e., 20%, 60% and 75%. The membranes produced at 20% amplitude could not disperse nanoparticles uniformly in the solution which led to the agglomeration giving rise to uneven surfaced composites. This is attributed to the low interaction of polymer and nanoparticles and the uneven surfaces might result in instability of the membranes in the long run. Thus higher amplitudes which induced polymer fragmentation resulted in increased interactions between CNB and Polymer fragments resulting in homogenous membranes.

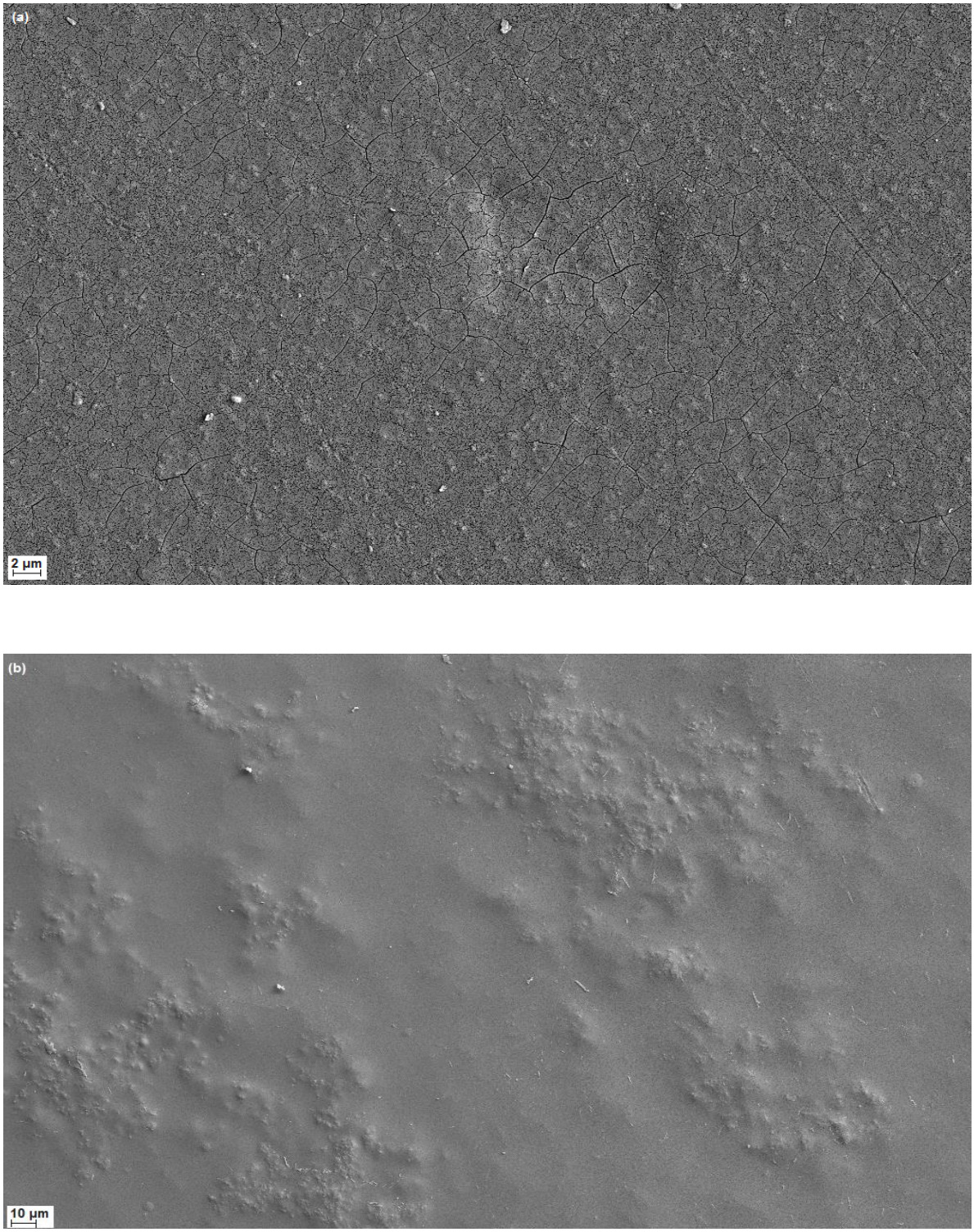


Figure 4.9 A: SEM images (a) 0. 5 wt% CNB loaded IEM at 20% sonication amplitude (b) 2.5 wt% CNB loaded IEM at 20% sonication amplitude

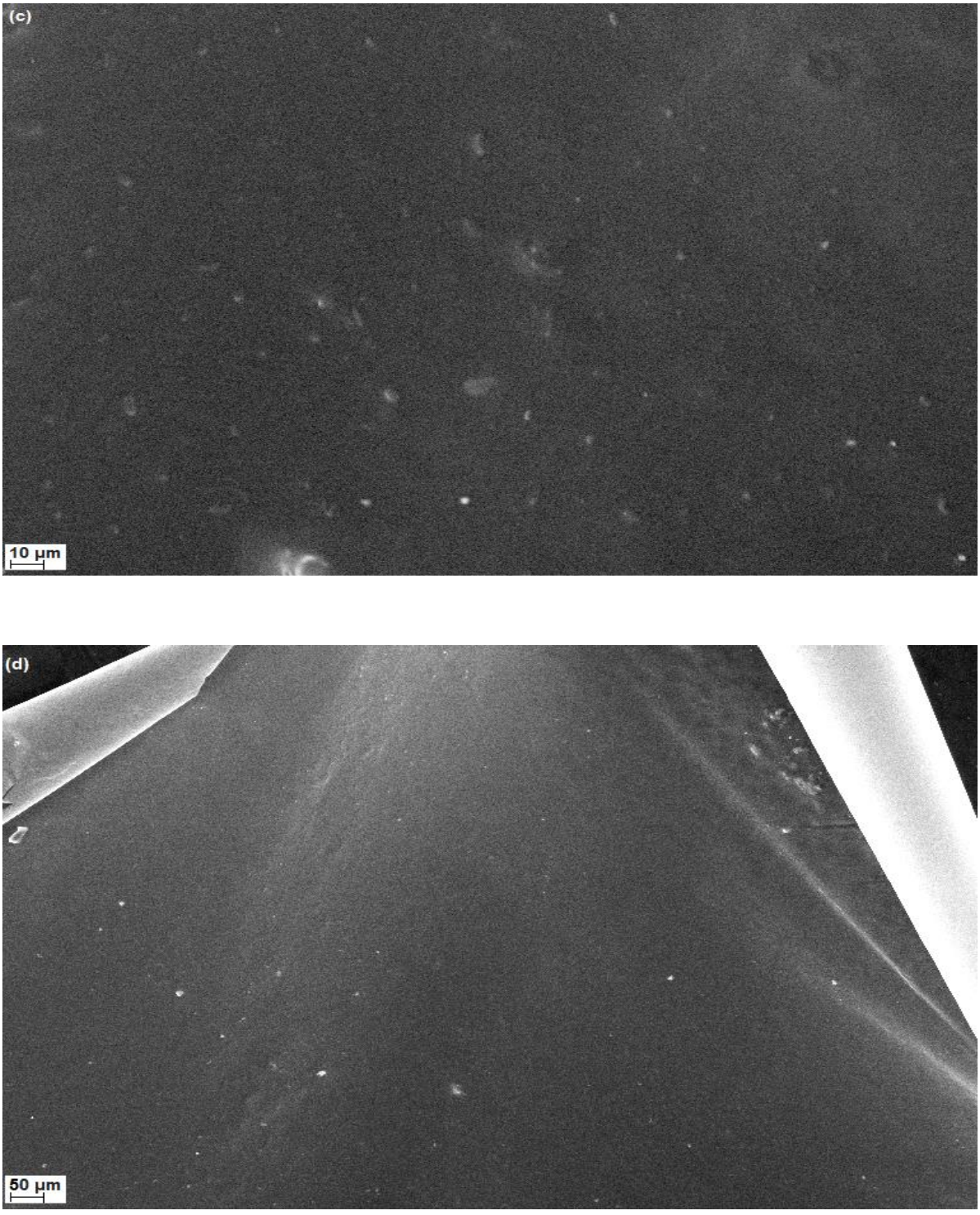


Figure 4.9 B: SEM images (c) 1.75 wt% CNB loaded IEM at 60% sonication amplitude (d) 1.75 wt% CNB loaded IEM at 60% sonication amplitude

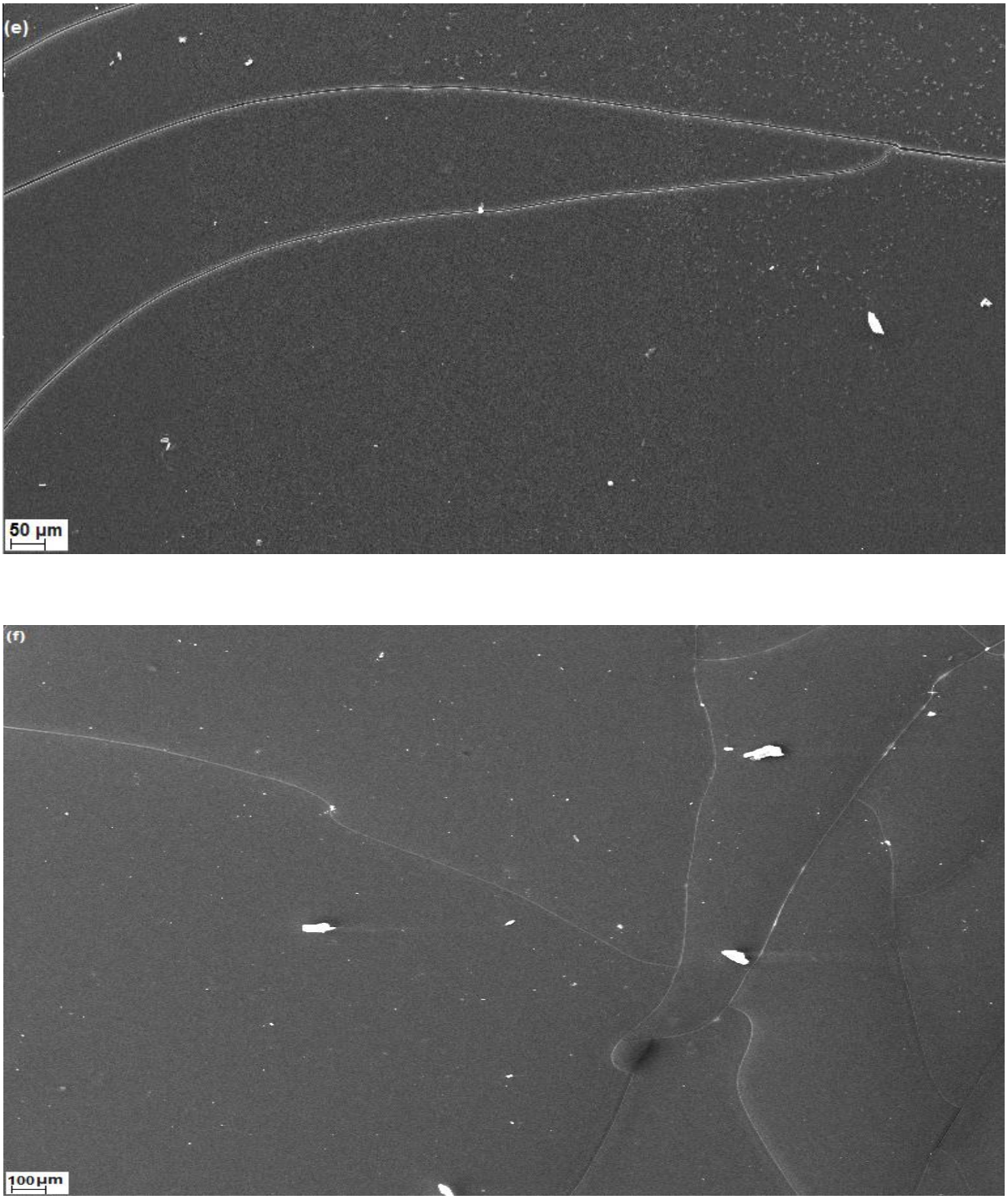


Figure 4.9 C: SEM images (e) 1 wt% CNB loaded IEM at 75% sonication amplitude

(f) 4 wt% CNB loaded IEM at 75% sonication amplitude

SEM images in Figure 4.9 A, B and C show nanocomposite membranes of varying CNB loading at different sonication amplitudes. As previously discussed, the images show that the membranes formed with 20% amplitude (Figure 4.9 A (a) and (b)) resulted in uneven membrane surfaces and the ones at higher amplitudes gave homogenous membranes (Figure 4.9 C (e) and (f)). For a fixed amplitude, higher CNB concentration results in clear uniform image. CNBs are well distributed compared to the lower CNB concentration (Figure 4.9 A (a)) where fissures could be observed. This shows that the concentration of CNB and the ultrasonic amplitude had an effect on the morphology of the blended membrane using same solvent.

4.3.1 Thermal Stability of Nanocomposite Membrane

The thermogravimetric analysis in Figure 4.10 shows that the plain SPPSU membrane decomposing rapidly with 20 % weight loss at 80^{o}C temperature. 50% weight loss occurs at 100°C and a major loss happens at around 138^{o}C temperature.

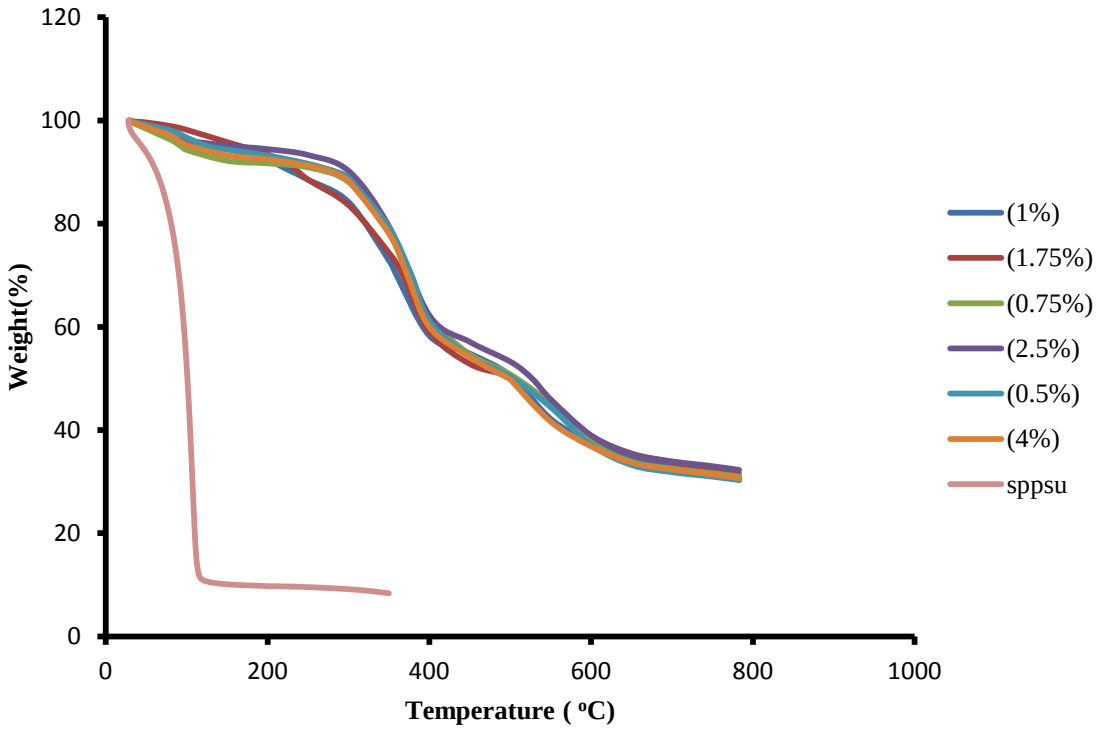
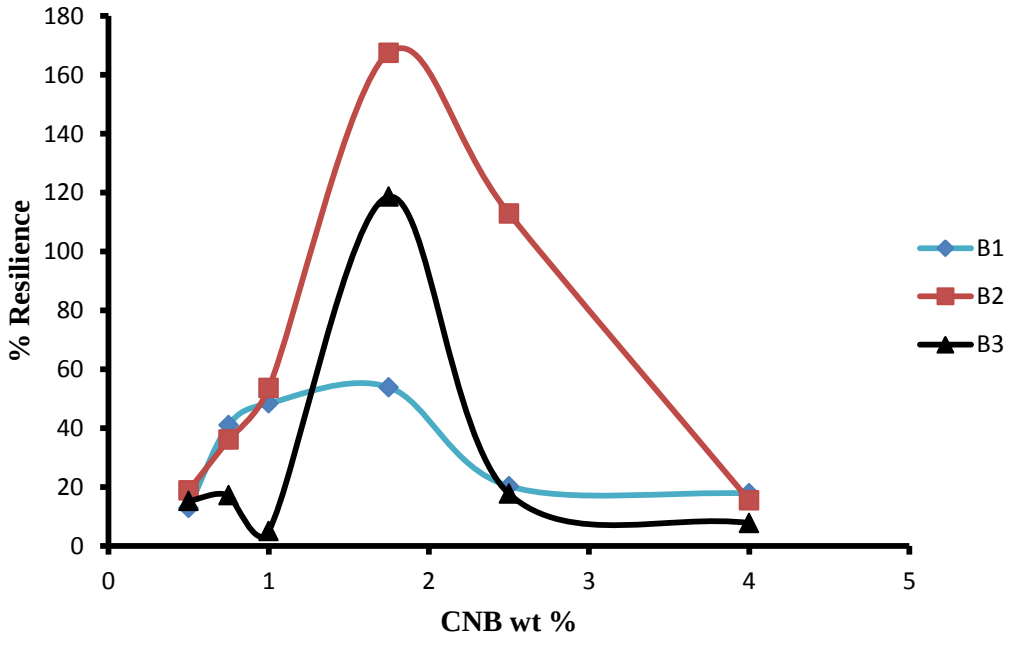


Figure 4.10: Thermal stability of nanocomposite membrane

The addition of CNB fillers into the SPPSU matrix has significantly improved the thermal stability of the composite membranes owing to the high thermal stability of CNBs. All the composite membranes showed similar thermal behaviour profile. The weight loss was very low with first decomposition occurring at around 280^{o}C with 10% followed by a 40% rapid weight loss at 450^{o}C. Major decomposition occurred at 650^{o}C with 70% weight loss. Therefore the addition of nanofillers in PPSU membrane successfully enhanced the thermal behavior of the composites that can have better performance above 100^{o}C and long life span.

4.3.2 Mechanical Test of Composite Membrane

Figure 4.12 shows the resilience test results of the three batches of composite membranes prepared at different amplitudes (20, 60 and 75%).



B1 (Batch 1) = composites prepared at 20 % sonication amplitude

B2 (Batch 2) = composites prepared at 60 % sonication amplitude

B3 (Batch 3) = composites prepared at 75 % sonication amplitude

Figure 4.11: % Resilience of Composite membrane

The three batches, as seen in Figure 4.11 showed similar resilience profile with 1.75% CNB loaded composites showing high % resilience for all the three batches. The % resilience of composites prepared at 60% amplitude (Batch 2) shows high resilience followed by 75% amplitude (Batch 3). The membranes prepared at 20% amplitude (Batch 1) showed least resilience because of uneven distribution of CNBs in the polymer membrane. The fragmentation of polymer chains in B2 composites due to high amplitude may have resulted in decreased mechanical strength.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Different degrees of sulfonated polyphenylsulfone membranes and hybrid membranes of sulfonated polyphenylsulfone embedded with carbon nanoballs were successfully prepared and tested for various membrane properties. The sulfonation was achieved by using chloro sulfonic acid as a sulfonating agent through post sulfonation of the polymer. Proton NMR spectral analysis confirmed the successful sulfonation of the polymer and the spectral data was used to calculate degree of sulfonation and ion exchange capacity. Several sulfonation experiments were conducted by varying volume of chlorosulfonic acid, reaction time and temperature in order to optimize the sulfonation reaction conditions. However, the results obtained from these experiments were uncertain due to the non homogeneity of the reaction solutions which affected the optimization of the sulfonation reactions. Though, the sulfonations did not produce expected results, the aim of producing carbon nanoballs within the nano range and the production of SPPSU-CNB blend membranes were successfully carried out.

The samples of sulfonated membrane and the nano composite membranes were analysed using various techniques such as proton NMR, TEM, SEM, Raman and BET etc. The synthesis of carbon nanoball fillers with non catalytic CVD method with acetylene as carbon source and argon as carrier gas at 1000^{o}C in a 16mm diameter reactor produced CNBs of 40 to 60nm size with 99% purity and uniformity.

The blending technique with a Probe Ultrasonicator at 20%, 60% and 75% amplitudes with carbon nanoball loading levels of 0.25wt%, 0.5wt %, 0.75wt %, 1wt %, 1.75wt%, 2.5wt% and 4wt% into the sulfonated polyphenylsulfone matrix produced nanocomposite membranes of around 100-120 μm thickness. The casting of polymer blends was achieved using evaporative technique and drying at room temperature. These strategies resulted in production on homogenous and non homogenous membranes where increasing amplitude resulted in increasing dispersion of nano particles in the polymer matrix. As a result, the blend solution prepared at 75% amplitude led to the production of smooth homogenous membranes. However, the composites prepared at 60% sonication amplitude showed better performance while the membranes with 20% amplitude performed least which was attributed to poor

interactions between sulfonated polymer and carbon nanofillers as less energy was induced with 20% amplitude.

Of all the composite membranes (composites prepared at 20, 60 and 75% sonication amplitudes), the membranes with 1.75 wt% carbon nanoball loading showed high thermal stability, % resilience and satisfactory water uptake capacity in all the three batches. However, the (1.75wt% CNB loading) membrane prepared at 60% amplitude had better membrane stability which confirms that the optimum level of CNB loading should be 1.75wt% for 10 % wt of sulfonated polymer solution. As thermal and hydration stabilities are most crucial for the long term performance of fuel cells, the addition of carbon nanoballs has helped achieve exceptional thermal stability of SPPSU-CNB composites than the plain membranes. Despite this achievement, the sulfonations and water uptake experiments could not produce results as expected which provokes further research into these areas.

5.2 RECOMMENDATIONS

One of the remaining problems is the optimization of sulfonation reaction of polyphenyl sulfone with chlorosulfonic acid. Therefore, more research work on sulfonations of PPSU is strongly recommended. Further work should be done to investigate the stability of the sulfonating membrane and the sulfonating agent in the aqueous environment. Lastly, the investigation of the ion exchange capacity of the membrane in fuel cell stack is recommended.

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APPENDICES

APPENDIX 1

Sulfonation of PPSU

Table A1 (a): Effect of CSA volume (concentration) on DS of PPSU

Volume of CSA (ml)	DS	IEC (meq/g)
0.25	0.22	0.50
0.5	0.60	1.25
0.75	0.62	1.27
1	0.81	1.61
1.5	0.93	1.81
2	0.97	1.88
2.5	0.99	1.91
3	0.83	1.64
3.5	0.90	1.76

Where, CSA=Chlorosulfonic Acid

DS=Degree of Sulfonation

IEC=Ion Exchange Capacity

Table A1 (b): Effect of Reaction time on DS

Reaction Time (min)	DS	IEC(meq/g)
10	0.507	1.06
20	0.576	1.19
30	0.579	1.2
60	0.576	1.19
90	0.550	1.14
150	0.557	1.15
180	0.574	1.18
240	0.562	1.16
300	0.572	1.18
360	0.573	1.19
420	0.563	1.17

Table A1 (c): Effect of Temperature on DS

Temperature (°C)	DS	IEC(meq/g)
-10	0.573	1.19
-5	0.573	1.19
0	0.573	1.19
10	0.571	1.18
20	0.5	1.04
30	0.32	0.65

APPENDIX 2

Table A2 (a): Effect of ultrasonication amplitude and CNB addition on percentage water uptake of composite membranes

	Water Uptake				
Sonication Amplitude (%)	**0.75 wt% CNB**	**1 wt% CNB**	**1.75 wt% CNB**	**2.5 wt% CNB**	**0 wt% CNB**
20	3.2	4.64	14.26	13.73	8.7
60	10.64	6.22	10.64	8.36	8.7
75	9.82	6.22	7.16	4.78	8.7

The wt% indicates the amount of CNB addition in SPPSU

0wt%=plain SPPSU membrane

Table A2 (b): % Resilience of composite membranes

B1		**B2**		**B3**	
CNB wt%	**% Resilience**	**CNB wt%**	**% Resilience**	**CNB wt%**	**% Resilience**
0.5	12.9192	0.5	18.8747	0.5	15.3522
0.75	41.0996	0.75	36.1895	0.75	17.2187
1	48.4338	1	53.6254	1	5.0699
1.75	53.9019	1.75	167.5052	1.75	118.63
2.5	20.3394	2.5	112.9086	2.5	17.7564
4	17.8698	4	15.5654	4	7.8151

B1 (Batch 1) = composites prepared at 20 % sonication amplitude

B2 (Batch 2) = composites prepared at 60 % sonication amplitude

B3 (Batch 3) = composites prepared at 75 % sonication amplitude

APPENDIX 3

^{1}H NMR Spectra of SPPSU

A: Spectra of SPPSU at varying volumes of CSA

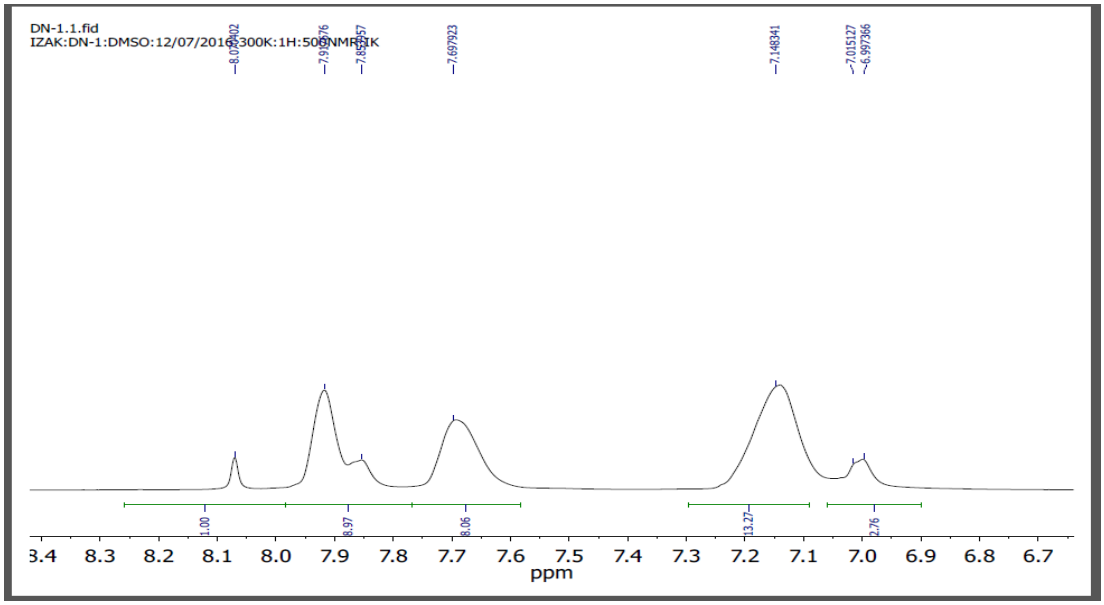


Figure A3 (a): ^{1}H NMR Spectra of SPPSU with 0.25 ml CSA

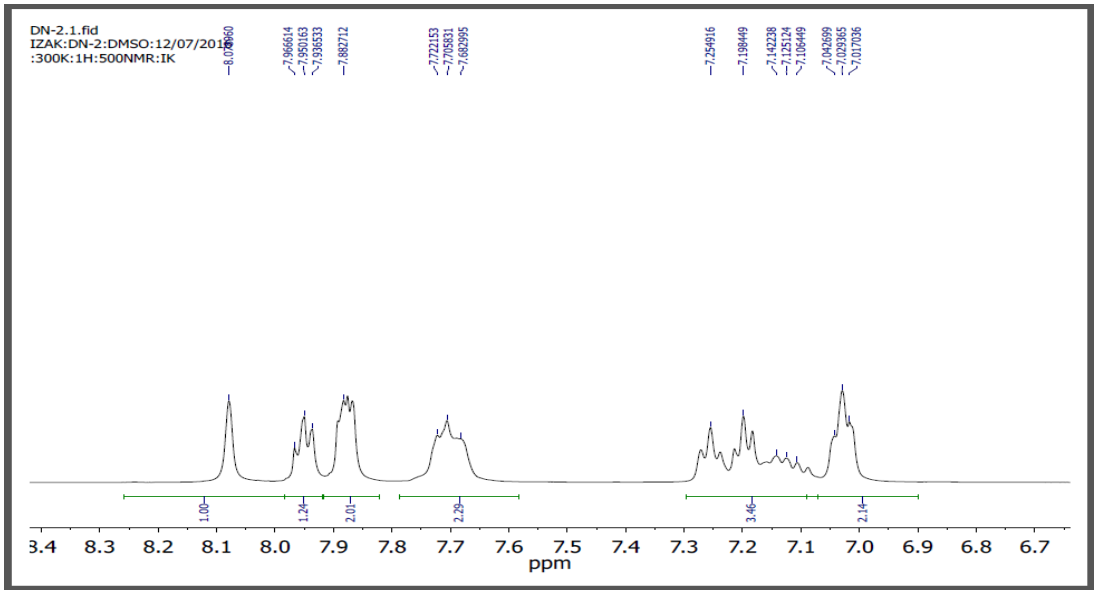


Figure A3 (b): ^{1}H NMR Spectra of SPPSU with 0.5 ml CSA

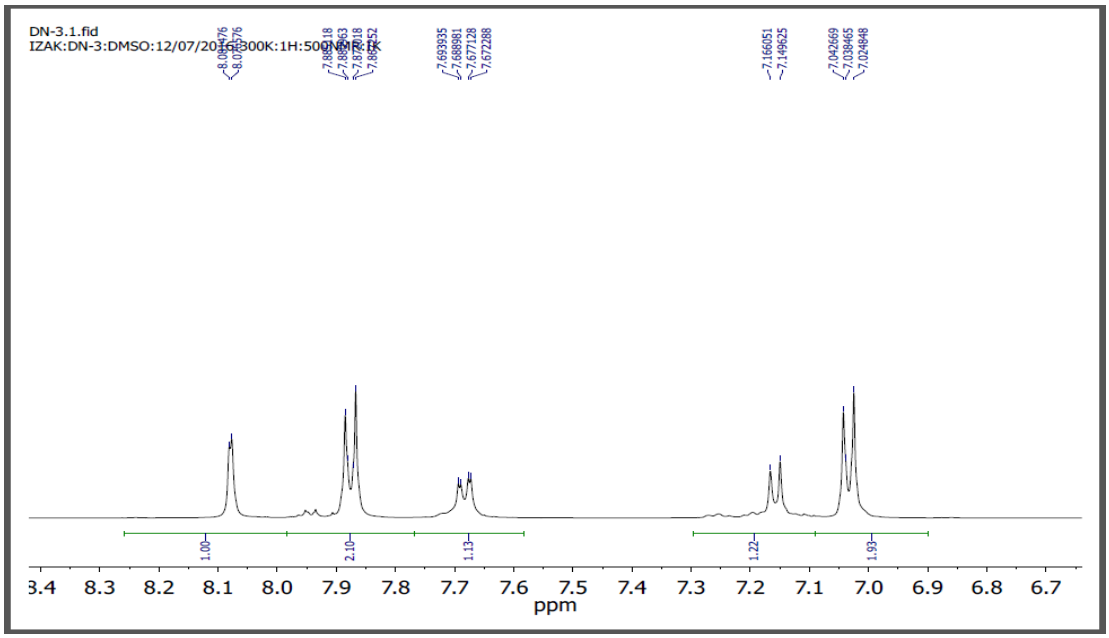


Figure A3 (c): ^{1}H NMR Spectra of SPPSU with 0.75 ml CSA

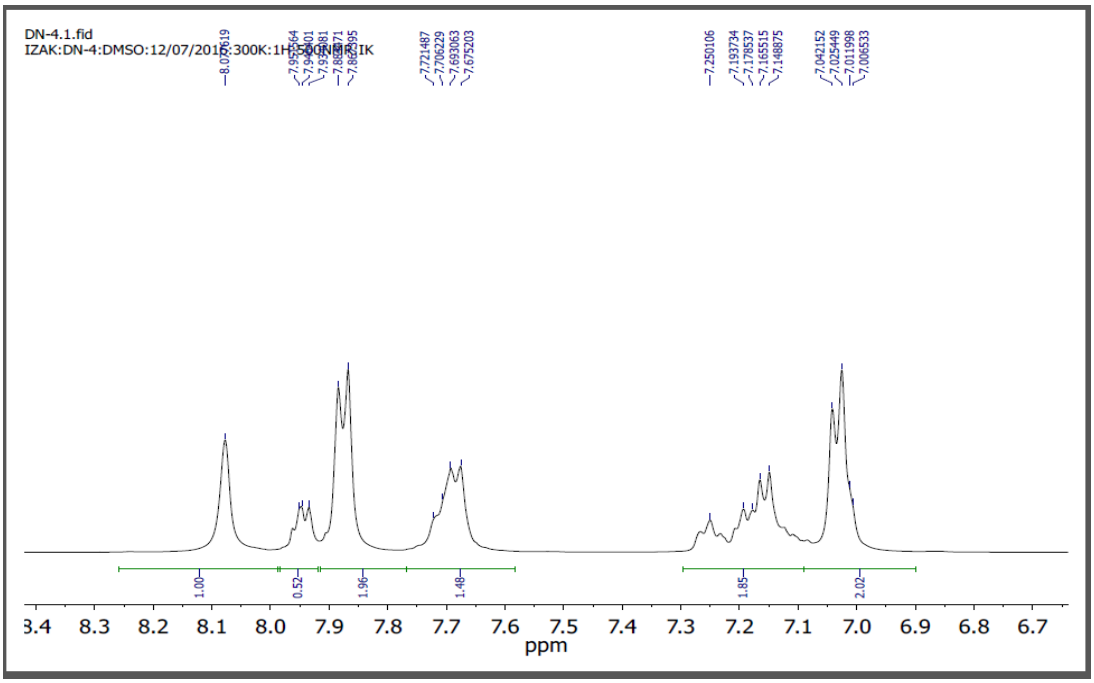


Figure A3 (d): ^{1}H NMR Spectra of SPPSU with 1 ml CSA

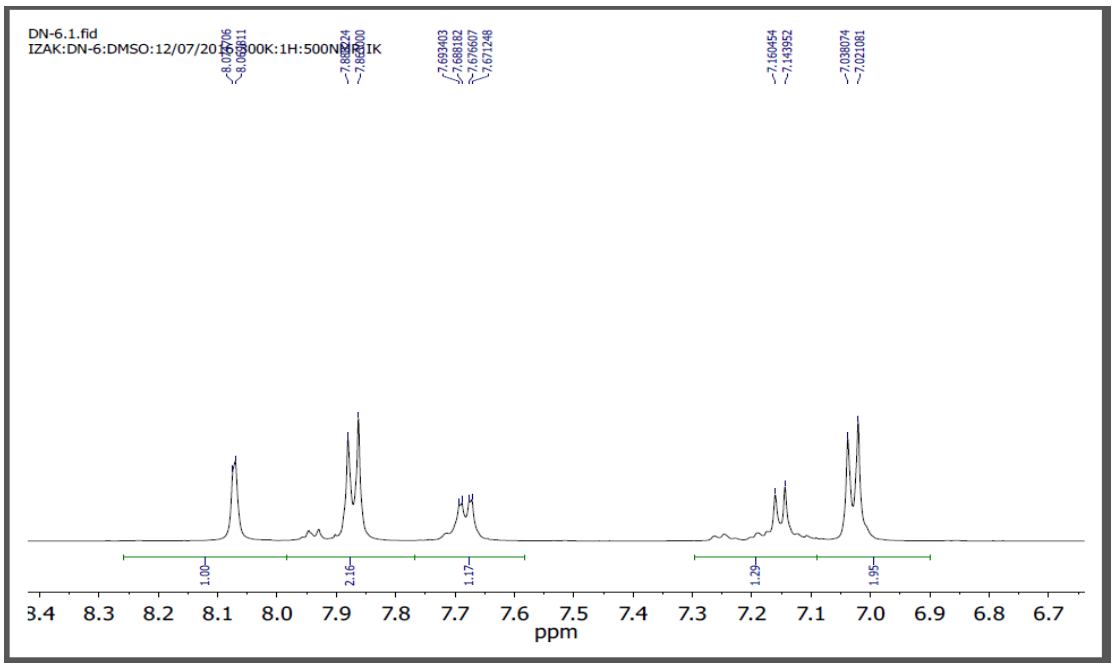


Figure A3 (e): ^{1}H NMR Spectra of SPPSU with 1.5 ml CSA

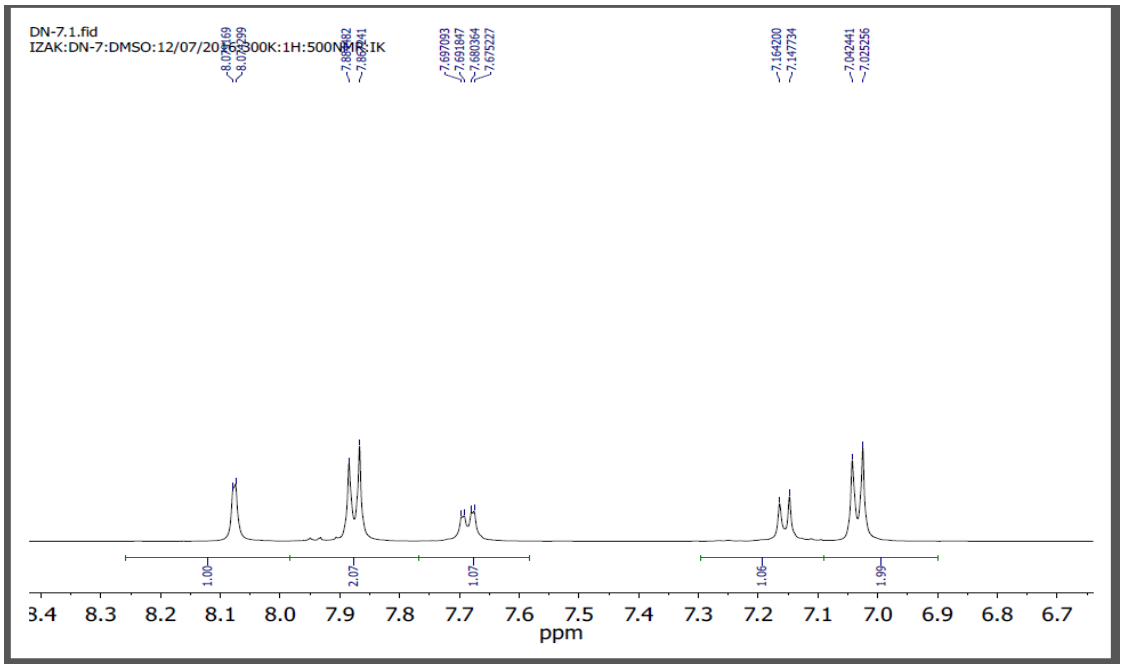


Figure A3 (f): ^{1}H NMR Spectra of SPPSU with 2 ml CSA

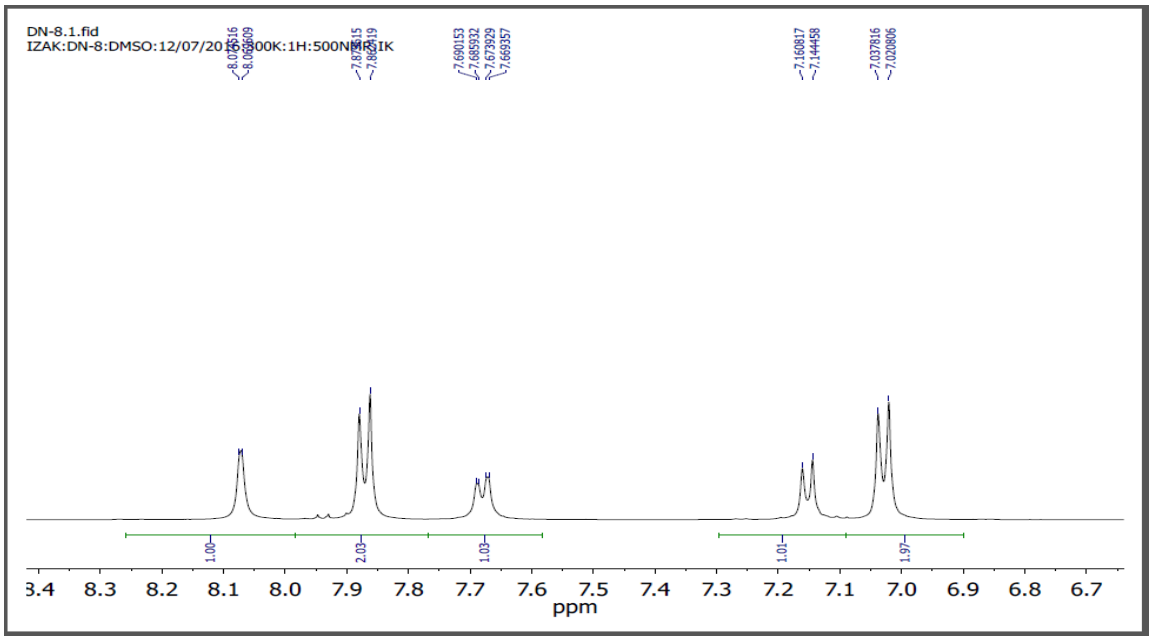


Figure A3 (g): ^{1}H NMR Spectra of SPPSU with 2.5 ml CSA

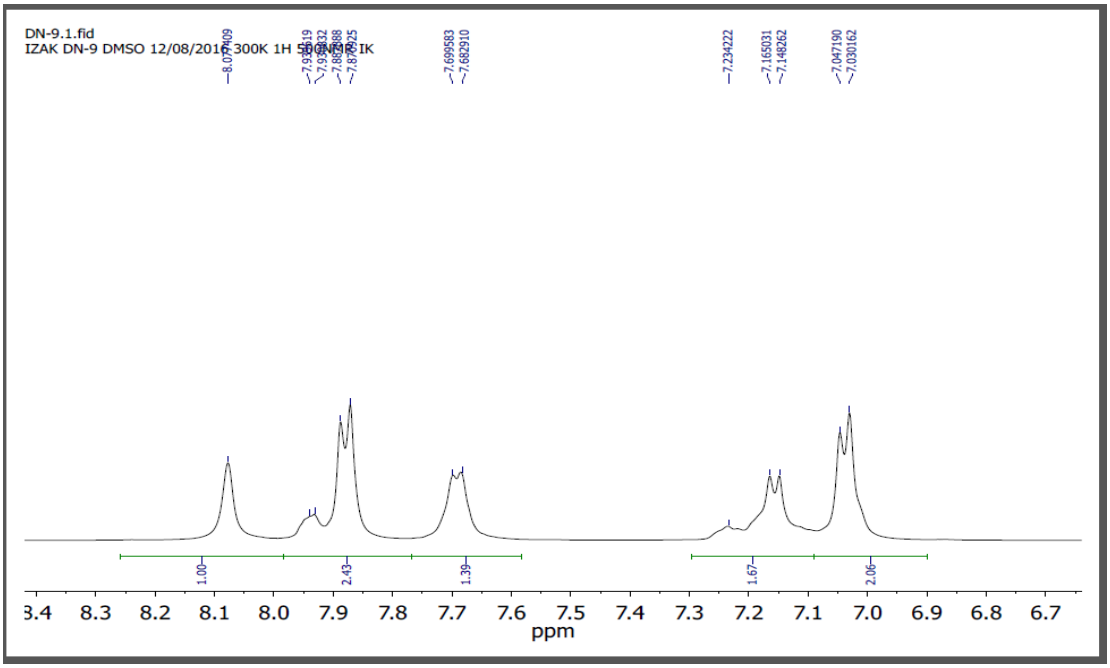


Figure A3 (h): ^{1}H NMR Spectra of SPPSU with 3 ml CSA

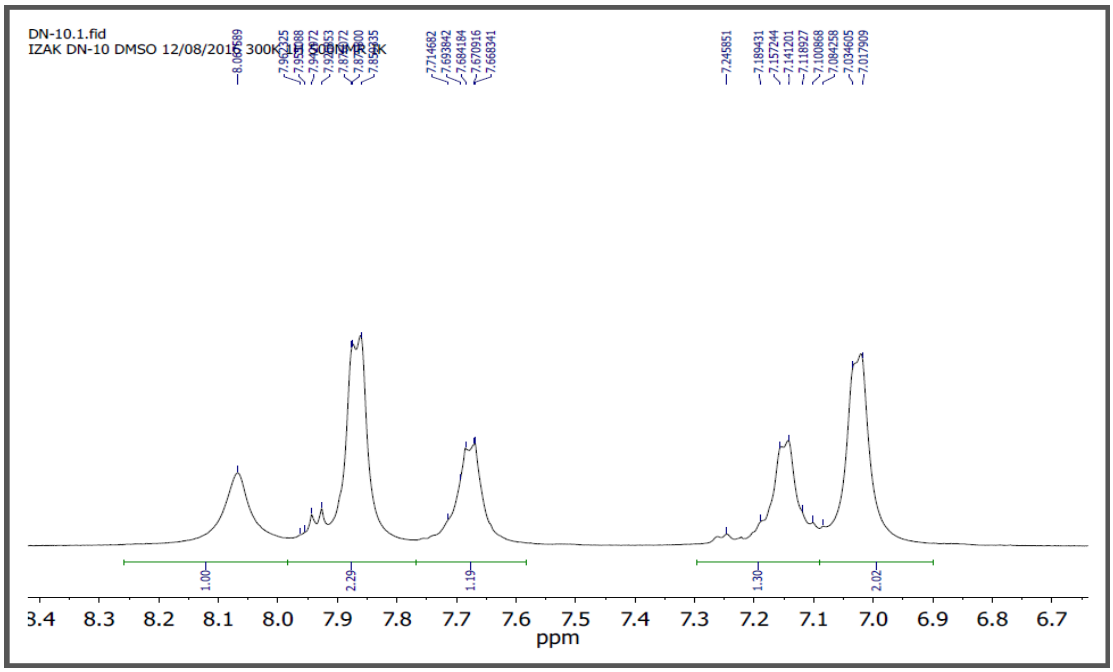


Figure A3 (i): ^{1}H NMR Spectra of SPPSU with 3.5 ml CSA

B: Spectra of SPPSU at varying reaction time

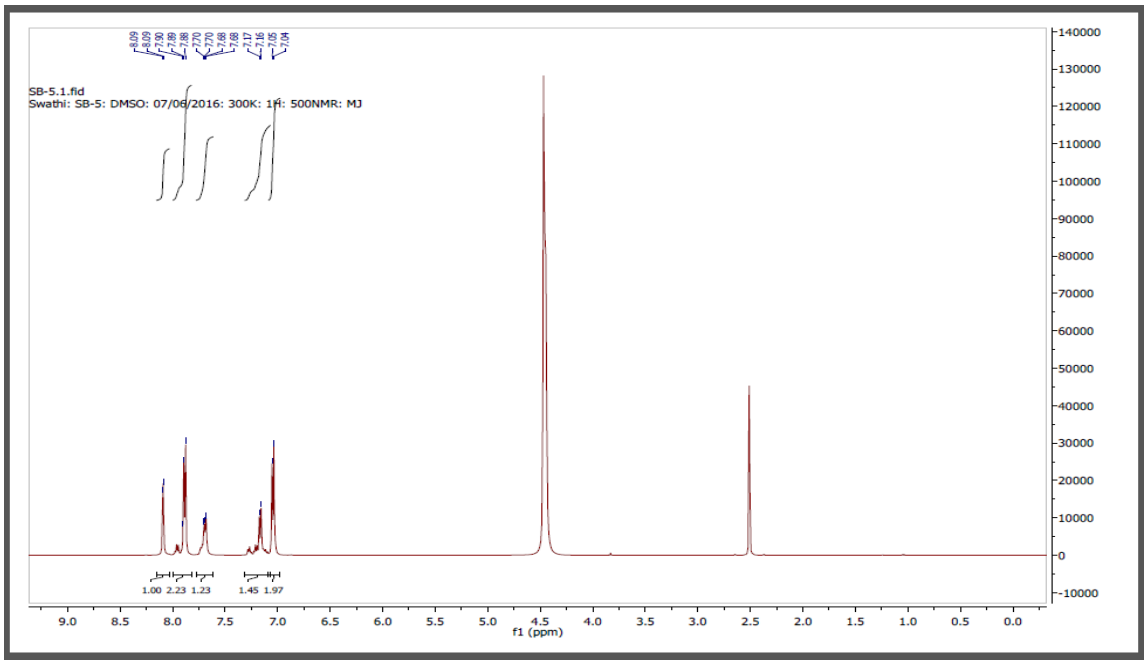


Figure B3 (a): ^{1}H NMR Spectra of SPPSU at 10 min reaction time

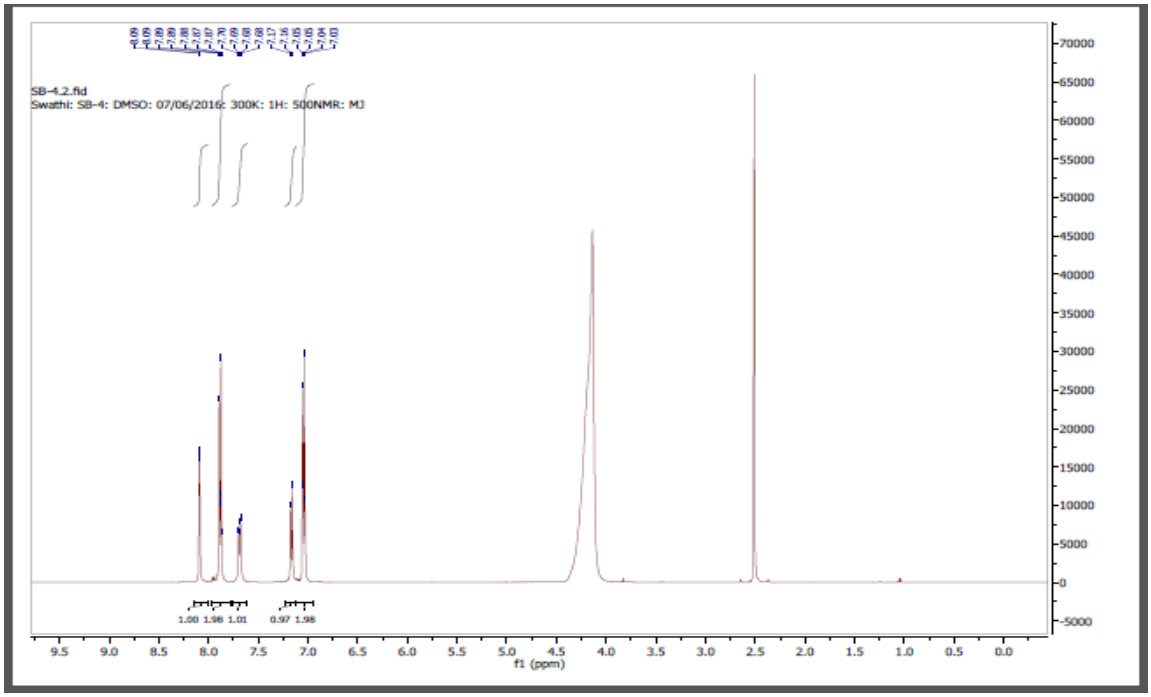


Figure B3 (b): ^{1}H NMR Spectra of SPPSU at 20 min reaction time

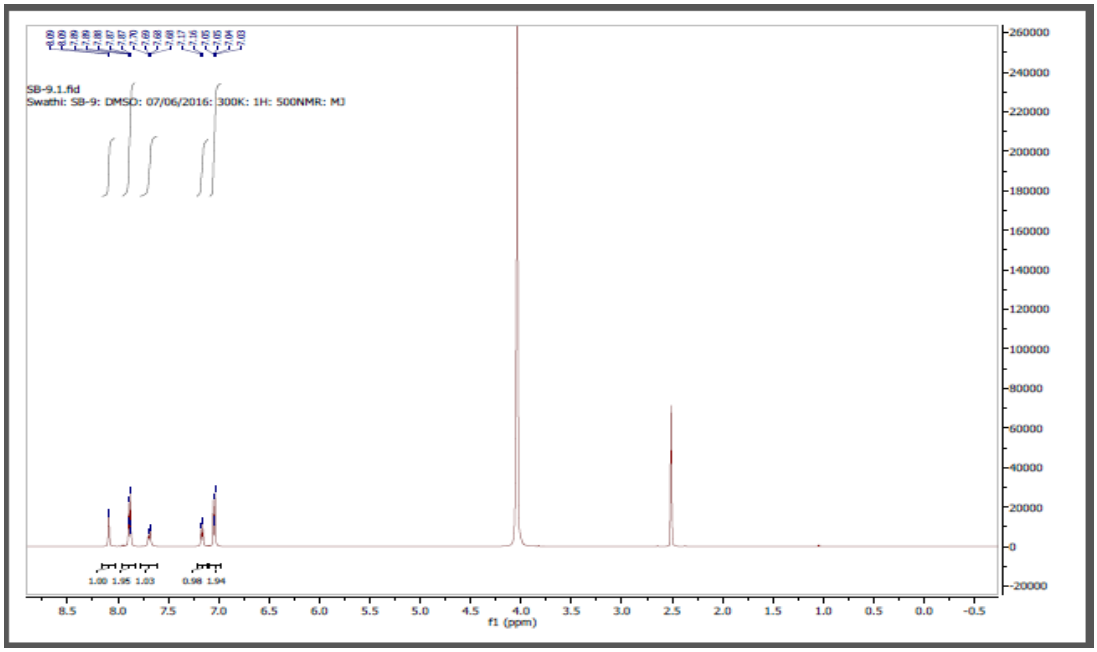


Figure B3 (c): ^{1}H NMR Spectra of SPPSU at 30 min reaction time

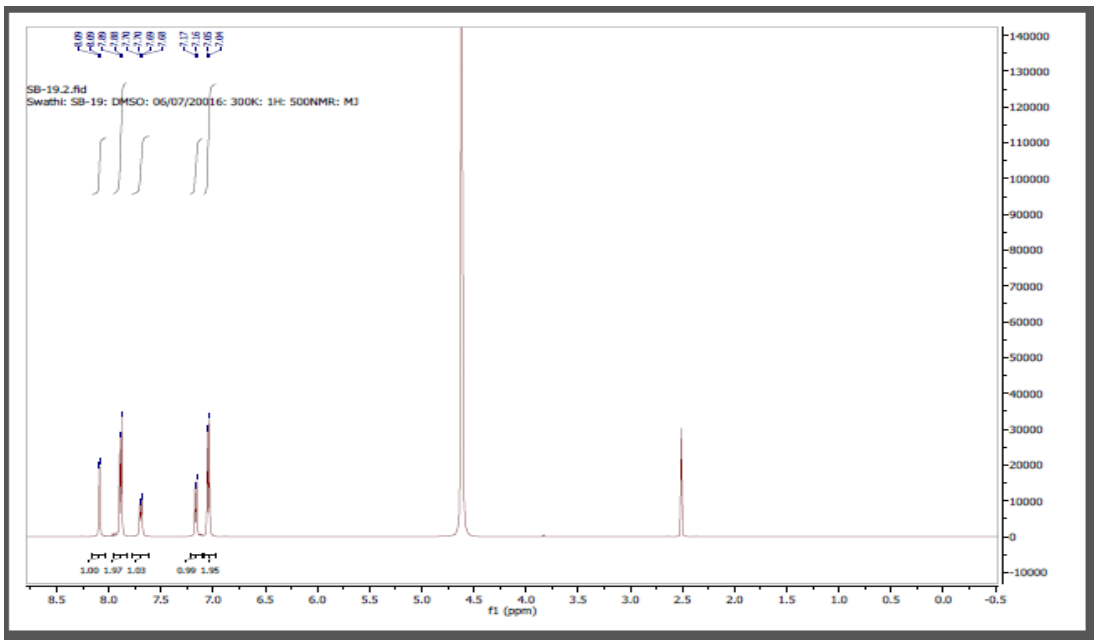


Figure B3 (d): ^{1}H NMR Spectra of SPPSU at 60 min reaction time

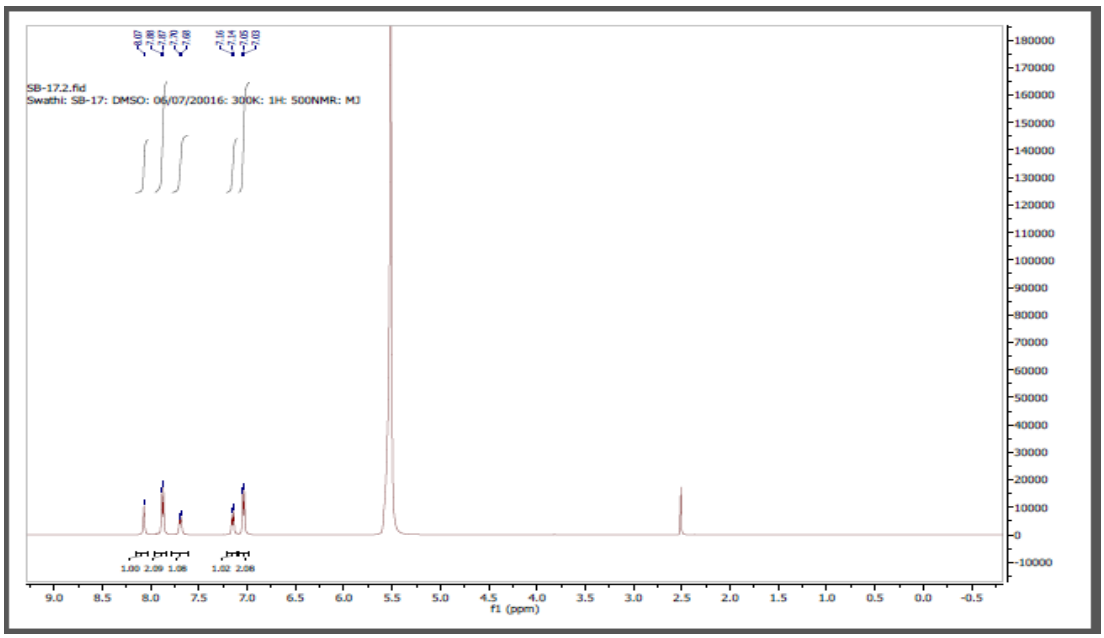


Figure B3 (e): ^{1}H NMR Spectra of SPPSU at 90 min reaction time

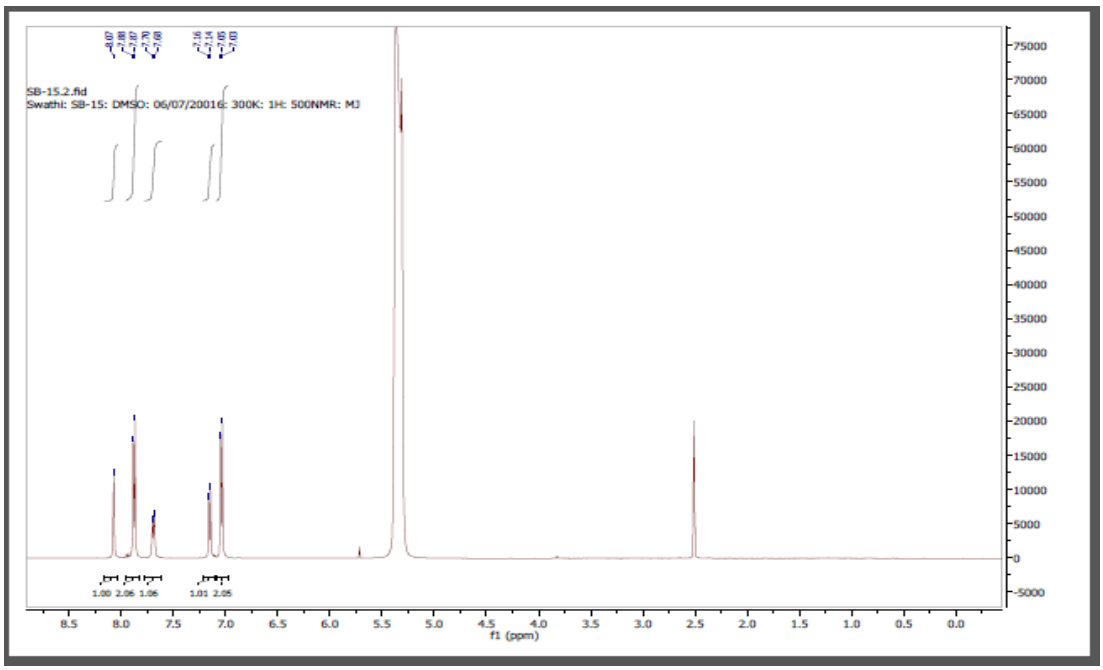


Figure B3 (f): ^{1}H NMR Spectra of SPPSU at 150 min reaction time

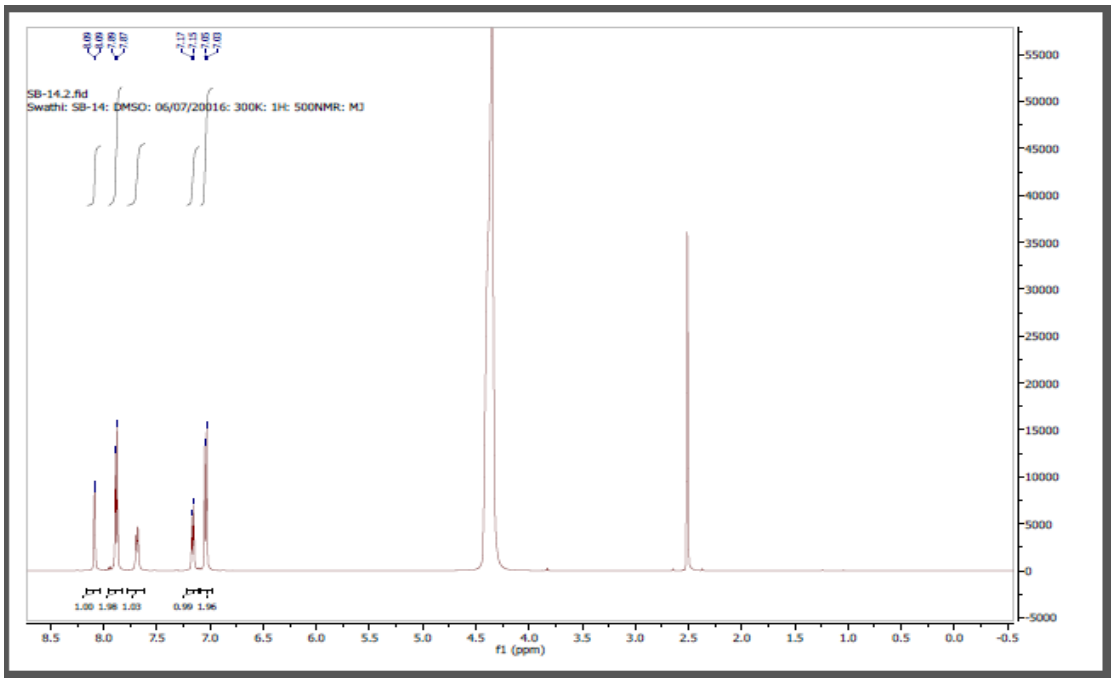


Figure B3 (g): ^{1}H NMR Spectra of SPPSU at 180 min reaction time

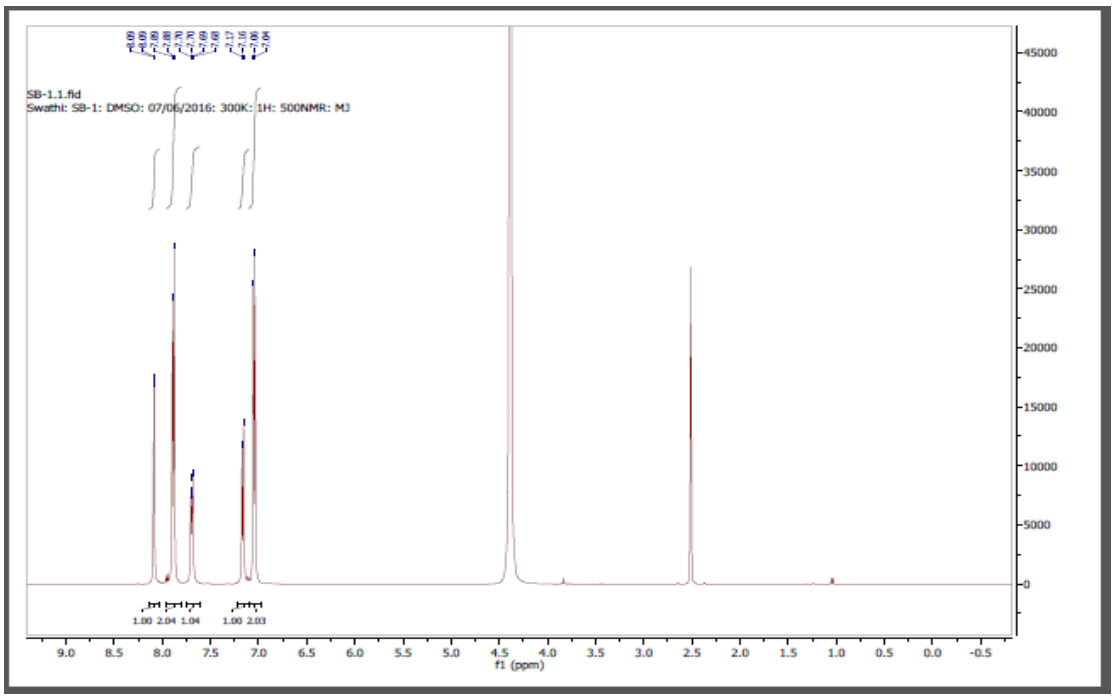


Figure B3 (h): ^{1}H NMR Spectra of SPPSU at 240 min reaction time

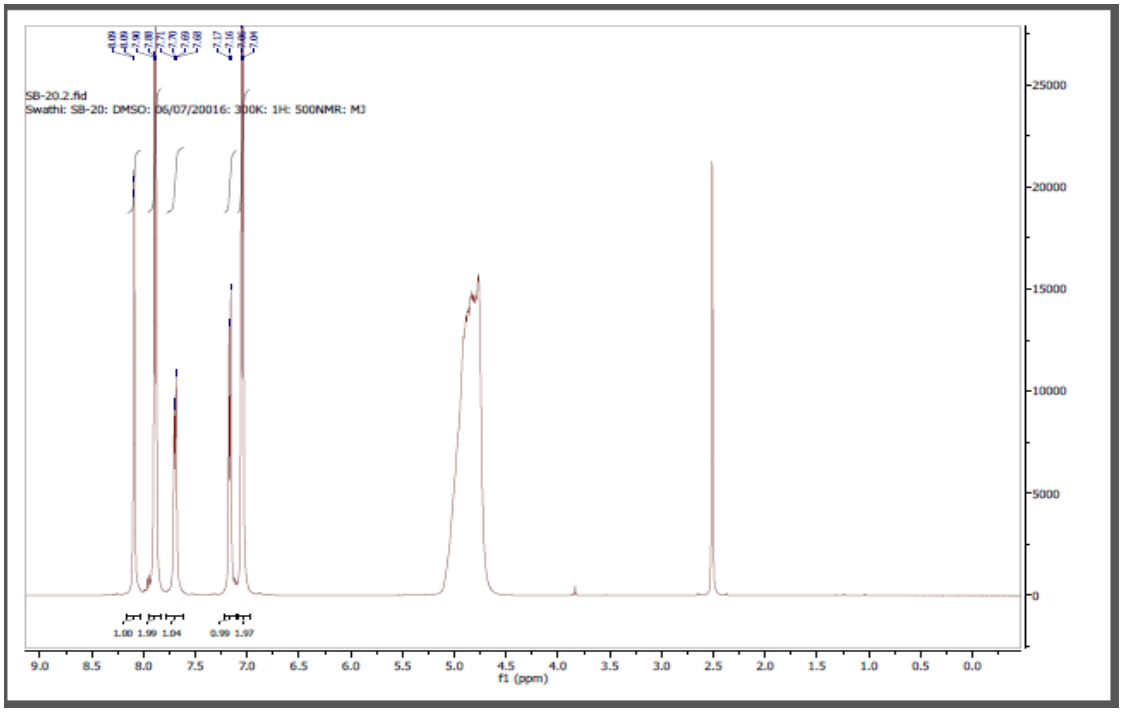


Figure B3 (i): ^{1}H NMR Spectra of SPPSU at 300 min reaction time

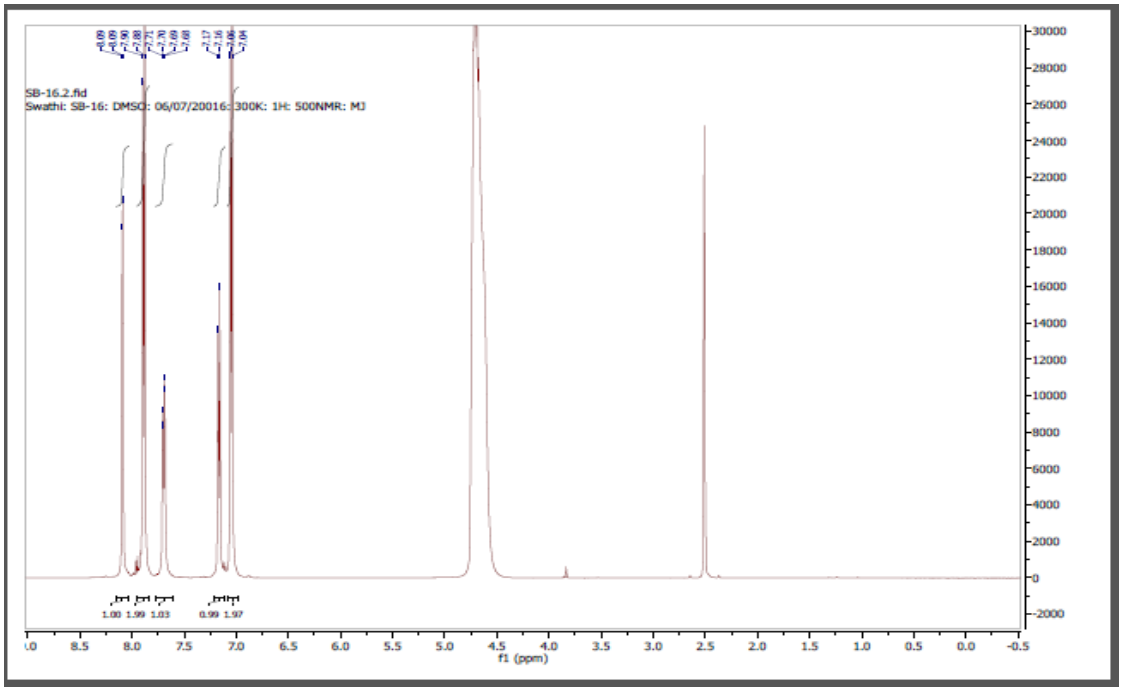


Figure B3 (j): ^{1}H NMR Spectra of SPPSU at 360 min reaction time

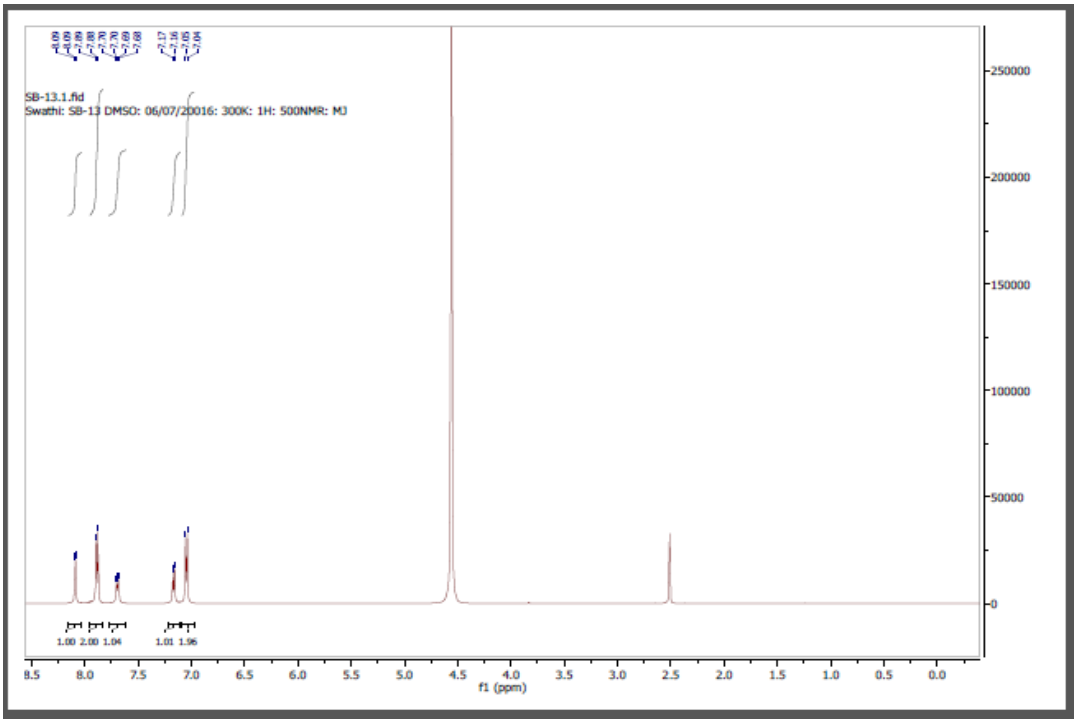


Figure B3 (k): ^{1}H NMR Spectra of SPPSU at 420 min reaction time

C: Spectra of SPPSU at varying reaction temperature

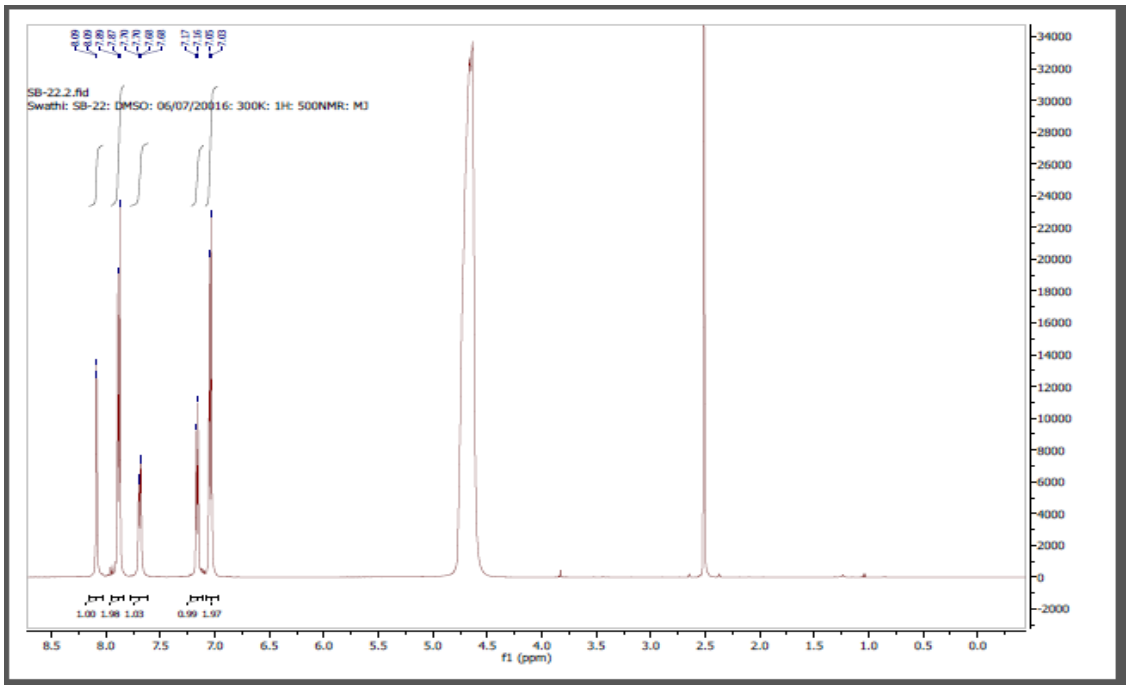


Figure C3 (a): ^{1}H NMR Spectra of SPPSU at -10^{o}C

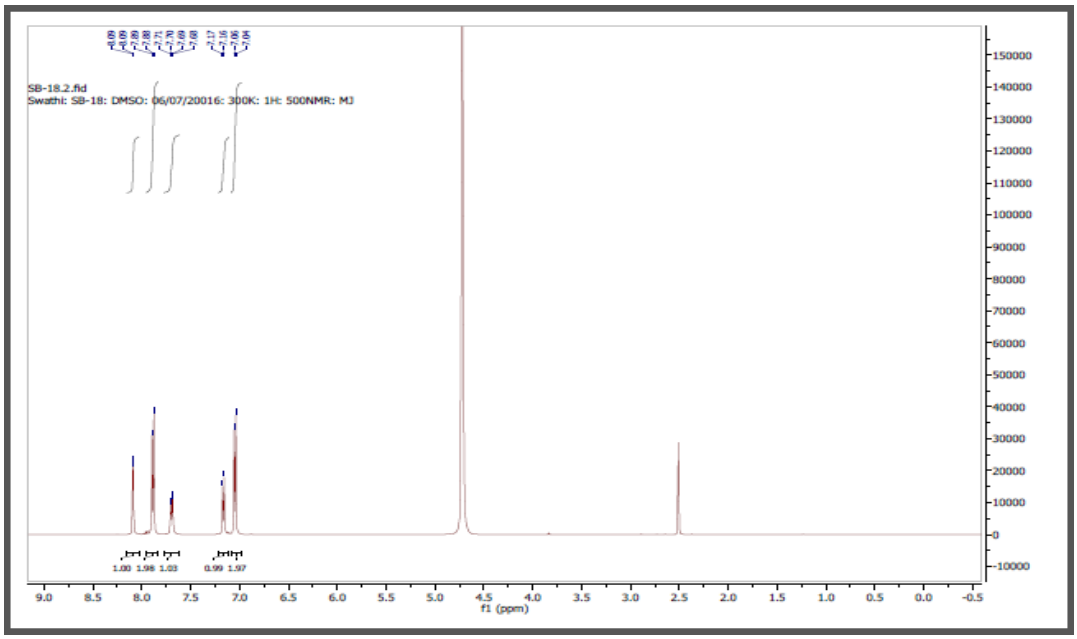


Figure C3 (b): ^{1}H NMR Spectra of SPPSU at -5^{o}C

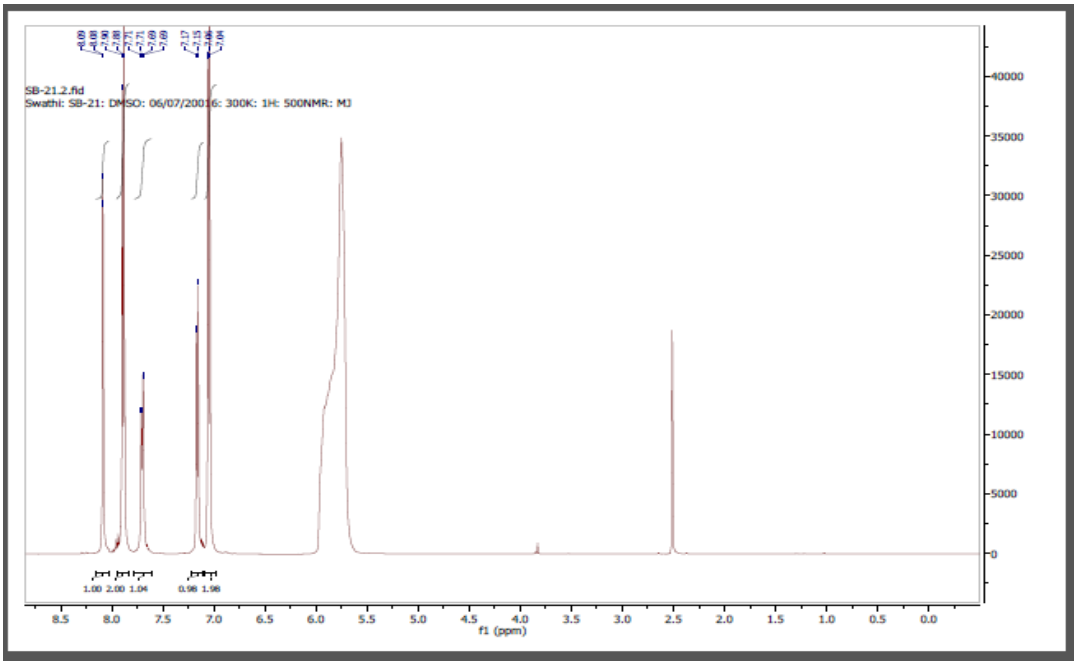


Figure C3 (c): ^{1}H NMR Spectra of SPPSU at 10^{o}C

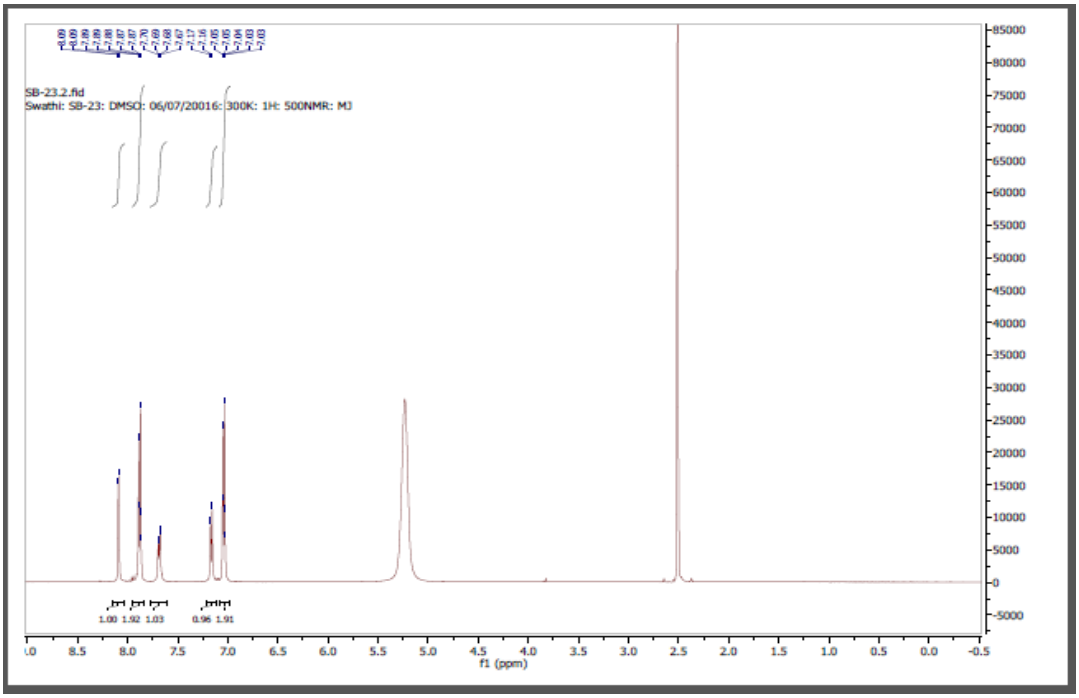


Figure C3 (d): ^{1}H NMR Spectra of SPPSU at 20^{o}C

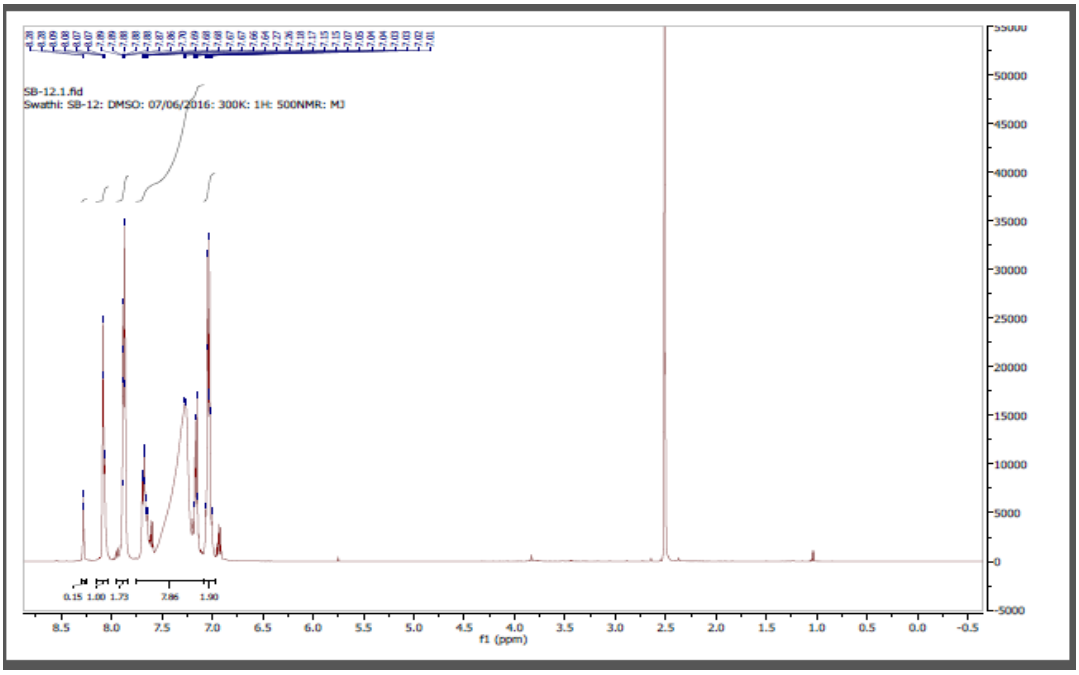


Figure C3 (e): ^{1}H NMR Spectra of SPPSU at 30^{o}C

APPENDIX 4

TEM images of CNBs

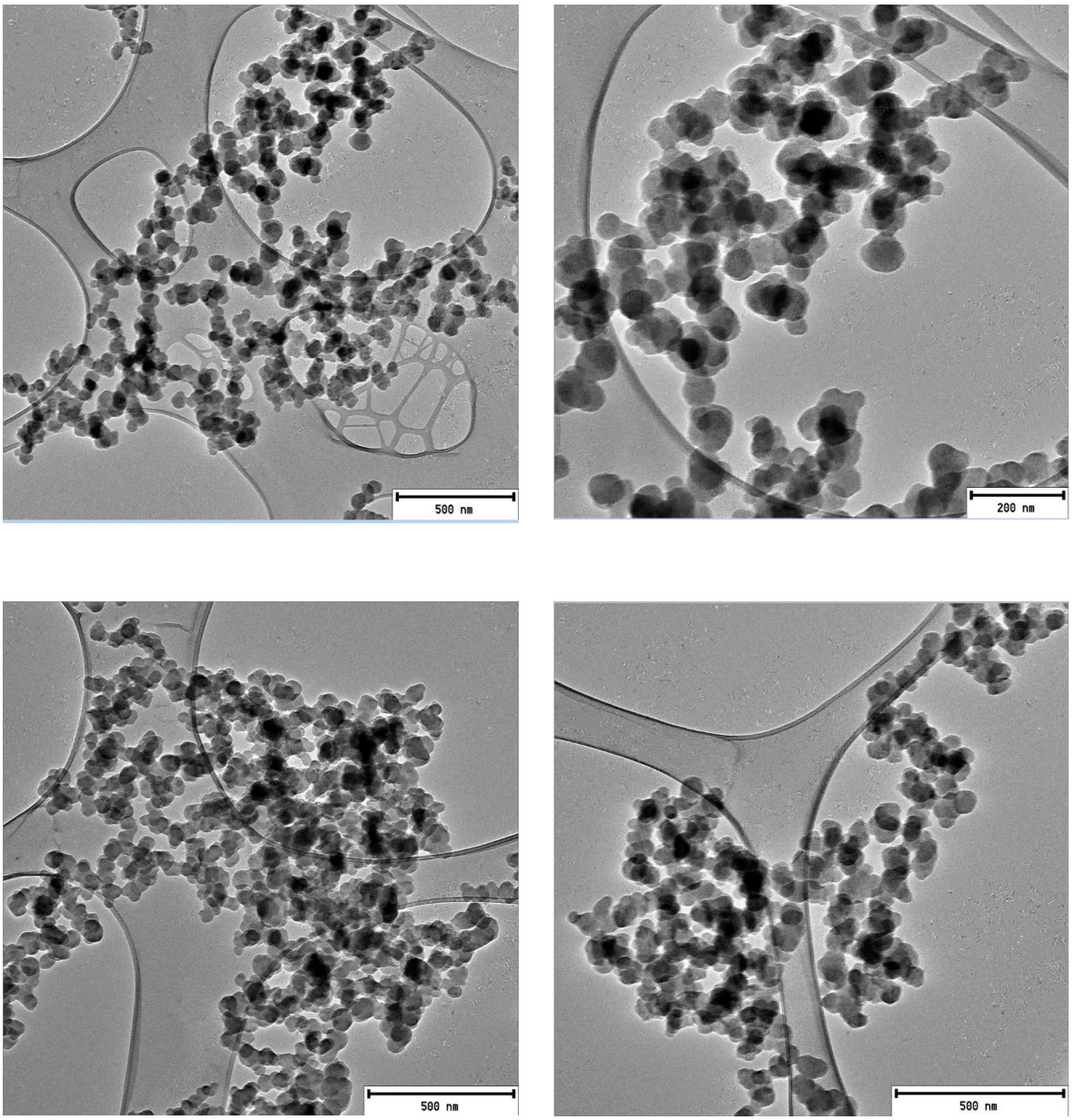


Figure A4: TEM images of CNBs

APPENDIX 5

SEM images of SPPSU-CNBs composite membranes

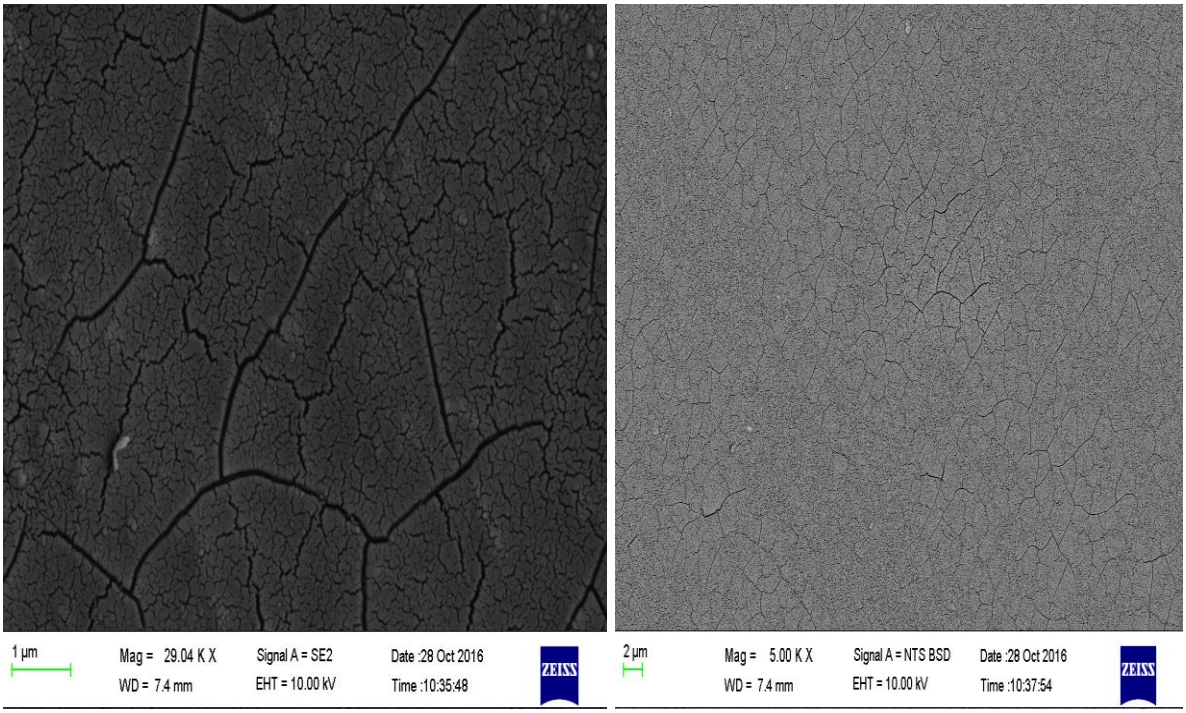


Figure A5 (a): SEM images of SPPSU membranes with 0.5wt% CNBs

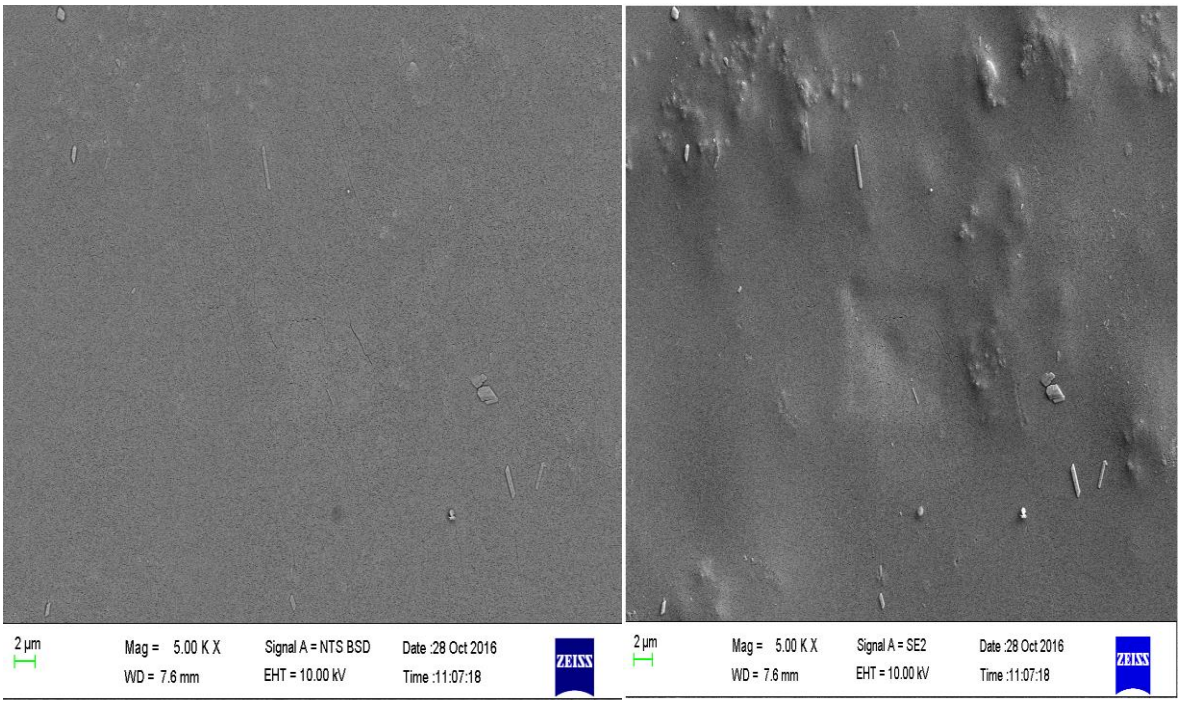


Figure A5 (b): SEM images of SPPSU membranes with 2.5wt% CNBs

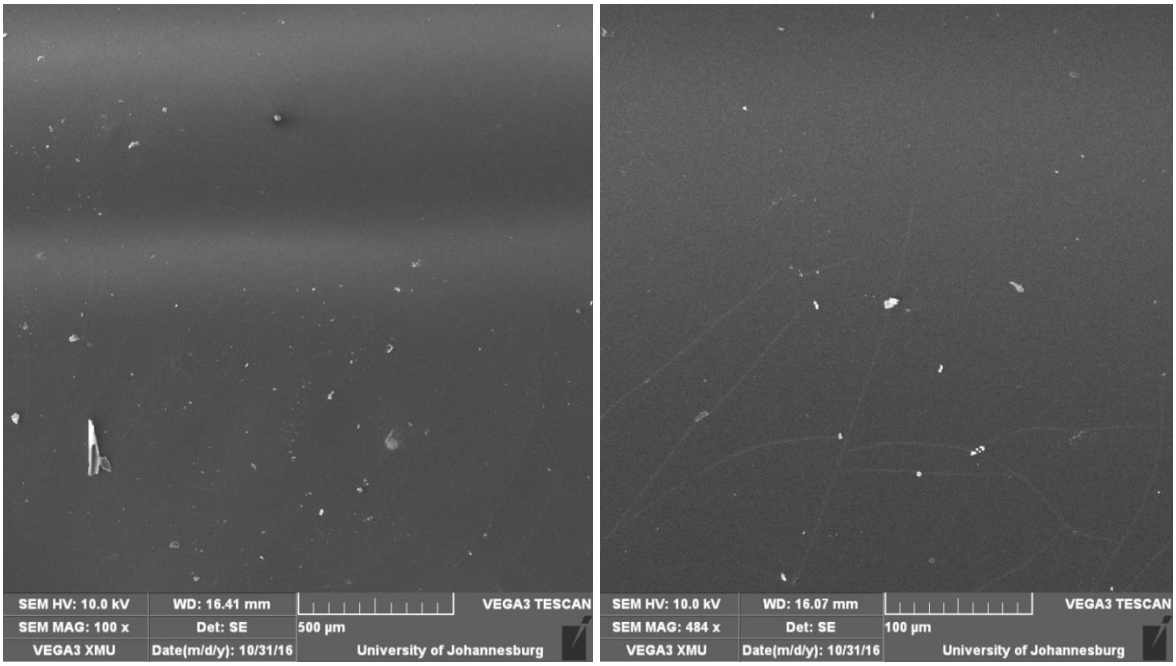


Figure A5 (c): SEM images of SPPSU membranes with 1wt% CNBs

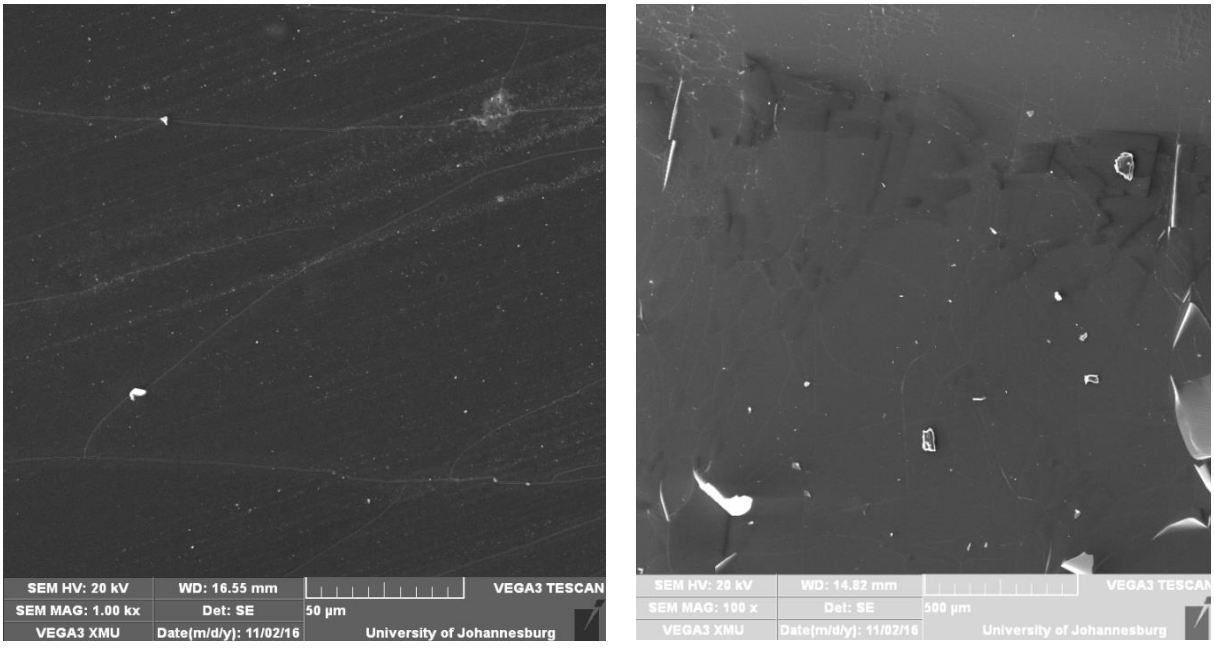


Figure A5 (d): SEM images of SPPSU membranes with 4wt% CNBs