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POLYMER COMPOSITE STRUCTURE FOR FUEL CELLS

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A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 2014

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____
(Signature of candidate)

_____ day of _____ (year) 2014

Abstract

Fuel cell was intensively researched in the last several decades with a variety of targeted applications ranging from micro devices to large-scale spacecraft power supplies. For both academics and industries, one of the most challenges in fuel cell design and fabrication is the material to be used in the structure.

Therefore this research is focused on designing and testing carbon black or silver filled thermalset composites with high electrical conductivity, as well as suitable thermal, mechanical and process properties.

In this study, polymer composites were developed with PDMS (polydimethylsiloxane) and two different types of conductive fillers, carbon black and silver. The effect of introducing these fillers in the polymer for varies properties have been investigated. Research was conducted through laboratory experimental setups that include thermal conductivity, thermal stability, electrical conductivity, dynamic mechanical property. The particle size and dispersion was studied with SEM (Scanning Electron Microscopy). The results were presented and discussed. Certain issues still exist before the developed polymer composite can be applied in an industrial fuel cell design and the possible future research work has been suggested.

To my family

爸妈，感谢你们，没有你们的教育和培养，就不会有这篇论文，也就不会有今天的我。妈，这些年你辛苦了，爸，你一直想让我好好读书，我也努力的把研究生读完了，你一定也会为我感到高兴的，我爱你们

感谢全家人对我关怀，支持。还有我伟大的奶奶，让我能够成为一个正直的人。

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List of symbols

CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
CH3OH	Methanol
e^-	Electron
G'	Storage modulus
H_2	Hydrogen
H^+	Proton
H_2O	Water
Jm^{-1}	Impact strength
k	Thermal conductivity
K_2CO_3	Potassium carbonate
KPa	Kilo Pascal
KOH	Potassium hydroxide
LaB_6	Lanthanum hexaboride
$LiAlO_2$	Lithium aluminium oxide
MPa	Mega Pascal
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide
O^{2-}	Oxygen ion
O_2	Oxygen
OH^-	Hydroxide ion

Pa·s	Pascal second
phr	Parts per hundreds rubber
Sm^{-1}	Siemens per metre
Tan δ	Tan delta (loss factor)
vol%	Volume percentage
$W\ m^{-1}\ K^{-1}$	Watt per metre per kelvin
wt%	Weight percentage
YSZ	Yttria-stabilised zirconia
Ωcm	Ohm centimetre
ρ	Resistivity of the sample
σ	Electrical conductivity

Nomenclature

AFC	Alkaline Fuel Cell
Ag	Silver
CB	Carbon Black
CF	Carbon Fibre
CHP	Combined heat and power
CNT	Carbon Nano Tube
DC	Direct Current
DMA	Dynamic Mechanical Analyser
DMFC	Direct Methanol Fuel Cell
GDL	Gas Diffusion Layer
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
PAFC	Phosphoric Acid Fuel Cell
PDA	Personal Digital Assistant
PDMS	Polydimethylsiloxane
PEMFC	Proton Exchange Membrane Fuel Cell
PPy	Polypyrrole

Pth	Polythiophene
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
SWCNT	Single Wall Carbon Nano Tube
TGA	Thermal Gravimetric Analysis
PVD	Physical Vapour Deposition

1. INTRODUCTION

This chapter gives a general introduction to the dissertation, background information, research issues, research problems, methodologies used to solve the problems, significance of the study, and finally an outline of the dissertation.

1.1 Background to the Research

Energy drives the economic development of a country, as well as being an indication of the comprehensive national strength and citizen living standard of the country. Since the Industrial Revolution in the middle 18th century, fossil energy has been extensively used. The use of fossil fuel has caused an exponential increase in carbon dioxide and other green house gas concentrations in the air, the rise of global temperature and sea levels as well as huge climate change. All these have become major environmental pollutions of the day.

In order to control green house gas concentrations, prevent further environmental pollution, the United Nations has issued several directives about emission control regulations globally. Statistics have shown that current oil reserves will only last 50 years maximum according to present consumption rates today. Therefore how to reduce the use of fossil fuel and find alternative fuel solutions have become key research projects worldwide.

Among wind energy, hydrodynamic energy, solar energy and other renewable energies, fuel cell technology has exhibited promising potential and drawn great attention for research and development work for both academics and industries.

Although fuel cells are often called batteries, they do not have to be disposable (causing pollution), and do not require recharging as rechargeable batteries do. They use fuel to generate electricity, mostly hydrogen or alcohol depending on the type of fuel cells.

Because of development in electronic industries, many appliances have become smaller and portability has been considered key. There is a great demand for a power source for these portable electronic devices such as cell phones, laptops, portable TVs and PDA (Personal Digital Assistant). Micro fuel cell is a promising solution.

However, miniaturization of fuel cells remains a problematic with respect to size and weight, and on the other hand, power output and efficiency. Consequently, a new composite material is proposed and studied in this dissertation in a fuel cell structure bipolar material perspective.

1.2 Research Problem

The problem addressed in this research is:

Can polymer composite be successfully utilized in a fuel cell structure?

Utilization of polymer composite in fuel cell structure will give direct benefits to the mass and size reduction of conventional fuel cell models, however, selection of polymer and fillers as well as different properties of the polymer composite need to be investigated.

1.3 Delimitations of Scope

This research proposes and develops a polymer composite polydimethylsiloxane (PDMS) with nano/micro structure fillers and evaluates its suitability for fuel cell fabrication, with the aims, to

- Complete a comprehensive literature review of materials used for fuel cell structures and investigate the feasibility of utilizing PDMS composite for such application

- Synthesize polymer polydimethylsiloxane (PDMS) composite with fillers such as Carbon Black and Silver powder
- Evaluate the thermal, mechanical and electrical properties of the composite so that it can be utilized for fuel cell fabrication.

1.4 Research Sub-Problems

To solve the research problem, several issues need to be addressed step by step. These include:

How to prepare the polymer composite?

Are the samples mechanically stable to support the fuel cell structure?

Can the samples conduct electricity? Does the electrical conductivity meet the requirement?

Are the samples thermally stable under fuel cell operation conditions while heat is a byproduct?

Relevant literature and more information on fuel cells are reviewed in chapter 2, while answers to these research questions will be discussed in the following chapters.

1.5 Source of Data and Methodology

The data in this research has been collated by various scientific experiments with calibrated equipment. Furthermore, the methodologies chosen have been widely used with specific aims for the different research questions. Literature study was focused on the current research and development of various types of fuel cells and structure, materials used in fuel cells and their advantages and drawbacks.

1.6 Significance

Composite material has been used in fuel cell fabrication by other researchers as found in the literature, which will be discussed in depth in chapter 2. However, the utilization of a PDMS based polymer composite is being proposed in this research for the first time. Carbon Black, Silver powders will be used as fillers and tests will be conducted to investigate their feasibility.

Polydimethylsiloxane (PDMS) is a silicone elastomer widely used in packaging, in cosmetic and food industries because of its transparent, flexible, non-toxic and non-flammable properties. PDMS has also received growing attention recently in the biomedical and microfludic application (Mata et al., 2005; Fujii, 2002; Abbasi et al., 2001; McDonald and Whitesides, 2002; Fujii et al., 2003). It is biocompatible, chemically inert, thermally stable, easy to process as well as being low cost. Because of these excellent properties, PDMS has been selected as the polymer matrix to study.

The research will add value to the PDMS based composite as well as the fuel cell research community.

1.7 Outline of the Dissertation

This dissertation is structured into five chapters, each chapter will have its own theme forming a logical flow in the resolution of the main research problem. Chapter 1 is an introduction to the research, research problem and questions raised. Chapter 2 gives detailed information on the fuel cell and existing knowledge of materials used in fuel cell structure. In chapter 3 methodologies used to answer the research questions are presented, results are analyzed and discussed in chapter 4. In chapter 5, conclusions are drawn based on the

experimental results regarding the initial research questions, while also presenting the limitations of the research and recommendations for the future studies.

2. RESEARCH ISSUES

2.1 Introduction

Chapter 2 presents the theory of fuel cell technology, different types of fuel cell, fuel cell structures and bipolar plate. Relevant literature corresponding to the research questions is reviewed.

2.2 Fuel Cell

Fuel cell converts chemical energy into electricity, as does a battery, both are electrochemical power sources. But unlike a conventional battery that stores energy in a chemical form, a fuel cell operates continuously with an external fuel supply. The fuels are mostly hydrogen, alcohol or hydrocarbons and oxidants including oxygen, chlorine and chlorine dioxide depending on the fuel cell type.

In term of a working principle, fuel cells can be regarded as power generators which consume fuel and generate electrical power. However, conventional generators first combust fuel to generate heat, then the heat is used to drive the turbine to generate mechanical energy, and then electricity. During the chain of energy conversion, byproducts such as noise, heat, and waste are generated and energy is lost. On the other hand, fuel cells convert chemical energy directly into electricity in a simple chemical reaction with water being the only byproduct. Therefore, a simple process, no pollution and noise and high efficiency make fuel cells a promising new generation of power source.

For example, in the Proton Exchange Membrane Fuel Cell (PEMFC), the core component is a polymer electrolyte membrane. When hydrogen enters the anode, it will react with the catalyst then be ionized into electron and hydrogen ions:

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

The hydrogen ions go through the membrane and move to the cathode side, the electrons go through the external circuit and back to the cathode, and electricity is generated by the moving electrons in the external circuit. On the cathode side, hydrogen ions, electrons and oxygen molecules deoxidize with the aid of a catalyst to produce water:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

And the overall reaction of a fuel cell can be expressed as the follows:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

2.3 Fuel Cell Types

Fuel cells can be classified by the different types of electrolyte used, which determine the chemical reaction in the fuel cell, the fuel required, the fuel cell operation temperature and power output. These include Alkaline Fuel Cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). Each type of fuel cell is explained and basic details are shown in Table 2.1

Table 2-1 Data for different types of fuel cell

Fuel cell type	Mobile ion	Operating Temperature	Applications and notes
Alkaline Fuel Cell(AFC)	OH^-	50-200°C	Used in space vehicles, e.g. Apollo, Shuttle.
Direct Methanol Fuel Cell(DMFC)	H^+	20-90°C	Suitable for portable electronic systems of low power, running for long times
Molten Carbonate Fuel Cell(MCFC)	CO_3^{2-}	~650°C	Suitable for medium- to large-scale CHP systems, up to MW capacity
Phosphoric Acid Fuel Cell(PAFC)	H^+	~220°C	Large numbers of 200-kW CHP systems in use.
Proton Exchange Membrane Fuel Cell(PEMFC)	H^+	30-100°C	Vehicles and mobile applications, and for lower power CHP systems
Solid Oxide Fuel Cell(SOFC)	O^{2-}	500-1000°C	Suitable for all sizes of CHP systems, 2kW to multi-MW.

2.3.1 Alkaline Fuel Cell (AFC)

Alkaline fuel cells use potassium hydroxide (KOH) or sodium hydroxide (NaOH) as the electrolyte, pure hydrogen and oxygen as the anode and cathode reagents respectively. CO_2 gas must be strictly removed from the supplied gases, since CO2 reacts with the KOH or NaOH in the electrolyte and produces K_2CO_3 or Na_2CO_3 which will "poison" the cell by blocking the pore in the membrane and reduce efficiency. Alkaline fuel cells can be operated reversibly, so they are mostly utilized in aerospace applications. They can generate electricity

with hydrogen fuel, and the byproduct water can be electrolyzed again to produce oxygen and hydrogen. But the disadvantages are high cost, short lifetime, and highly purified hydrogen is also required (Gülzow, 2004).

2.3.2 Proton Exchange Membrane Fuel Cell (PEMFC)

The Proton Exchange Membrane Fuel Cell, also known as the Polymer Electrolyte Membrane Fuel Cell, was used by the National Aeronautics and Space Administration (NASA) on the first manned space vehicle in the 1960s(Larminie et al., 2004). It uses an ion conducting polymer as the electrolyte, hydrogen as the fuel and oxygen or air as the cathode reagent. Most PEMFCs operate at a low temperature around 80ºC. It has a high power density, long lifetime and is easy to maintain, hence it can be used as a portable power source for laptops, cell phones, personal digital assistants (PDA), as well as home appliances and electric motor vehicles. PEMFC has drawn great attention in the research and development over the past several decades.

2.3.3 Direct Methanol Fuel Cell (DMFC)

A Direct Methanol Fuel Cell (DMFC) is similar to a PEMFC, it uses a polymer as the electrolyte and proton as the charge carrier. However, diluted ethanol (CH_3OH) is used as the fuel instead of hydrogen in a PEMFC, the CH_3OH is oxidized at the anode generating carbon dioxide (CO_2). The advantages of DMFC are easy storage of fuel and room temperature operation. But due to the low energy density of CH_3OH, DMFC has a relatively lower power output.

2.3.4 Phosphoric Acid Fuel Cell (PAFC)

The Phosphoric Acid Fuel Cell uses concentrated phosphoric acid as the electrolyte. The phosphoric acid is retained on a solid carbon paper which also contains platinum that

functions as the catalyst on both electrodes. It uses hydrogen as the fuel and oxygen or air as the cathode reagent. The use of acid as the electrolyte has eliminated the problem of a CO2 impurity in the hydrogen. However, the presence of CO could poison the Pt catalyst and affect the power output. Therefore the CO concentration has to be limited to under 0.5%. PAFC is a reliable power source, it is mostly used as an uninterruptible power supply (UPS) for commercial buildings. But because PAFC has a typical efficiency of 40%, and a long start-up time, it is not suitable for mobile power sources.

2.3.5 Molten Carbonate Fuel Cell (MCFC)

The electrolyte of MCFC contains molten carbonate salt mixed in a ceramic matrix of $LiAlO_2$. (Larminie et al., 2004) It operates around 650ºC, its anode reagent is typically hydrogen or carbon monoxide, the cathode reagent oxygen or air. Due to the high operating temperature, precious metals are not inessential for the catalyst, therefore multiple fuels such as natural gas even carbon oxide can be used as fuel without any external reformer. The exhaust heat from MCFC can also be utilized to generate steam for other applications thus further increasing the overall efficiency. However, durability is a main drawback for MCFC, the corrosion of cell components is critical under such high temperature operation conditions.

2.3.6 Solid Oxide Fuel Cell (SOFC)

Yttria-stabilised zirconia (YSZ) is the most widely used electrolyte for SOFC because of its thermal stability at high temperature (1000ºC) on both anode and cathode sides. Similar to MCFC, both hydrogen and carbon monoxide can act as fuels in SOFC. On the cathode side, oxygen or air is used as reagent, negatively charged oxygen ions are transferred from the cathode through the electrolyte to the anode, water or carbon dioxide are produced as a byproduct depending on the fuel used. Typical stack designs of SOFC are tubular design and planar design. The exhaust heat of SOFC can also be recycled to improve efficiency.

2.4 Fuel Cell Structure

Different types of fuel cells have different structures. In this dissertation, the Direct Methanol Fuel Cell (DMFC) will be studied in detail. DMFC has a similar structure to the PEMFC since DMFC utilizes the proton exchange membrane and is fed with methanol instead of hydrogen.

A typical Direct Methanol Fuel Cell (DMFC) is built from four primary components, namely: Membrane Electrode Assembly (MEA), bipolar plate (flow field plate), current collector, and end plate (Mehta and Cooper, 2003). Figure 2-1 shows a schematic DMFC structure and components.

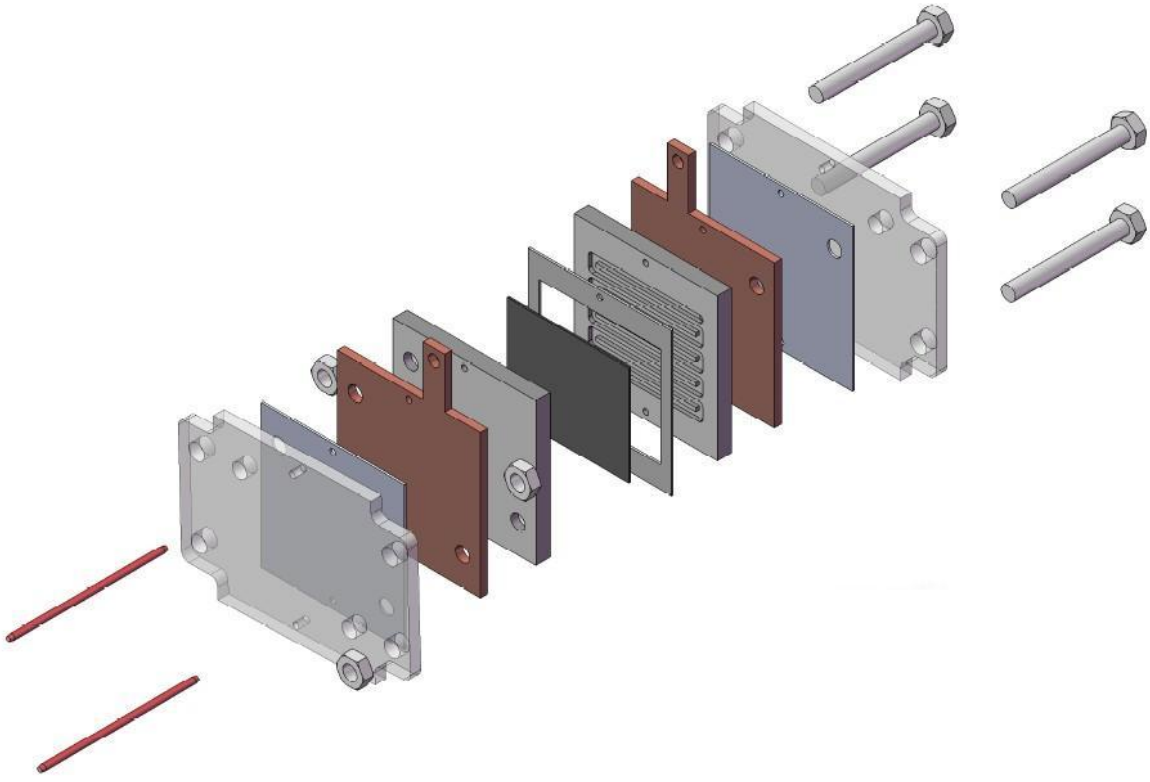


Figure 2-1 Schematic of DMFC structure and components (from side to the centre: end plate, gasket, copper current collector, graphite flow field plate, MEA and gasket)

- **MEA (Membrane Electrode Assembly)**

MEA is the core component of the cell, it is assembled with a proton exchange membrane, a catalyst and gas diffusion layer (GDL). The most commonly seen commercial proton exchange membrane is manufactured by Nafion. The Nafion membrane is sandwiched between the electrodes, it has low permeability in preventing fuel crossover and it is proton conductive so that the proton can be transferred from the anode to the cathode. The catalyst is used to separate the protons and electrons from the reagent molecules. The protons go through the membrane, electrons are collected and lead to the external circuit to power the load. The gas diffusion layer (GDL) consists mainly of porous carbon or graphite paper, its porous structure makes the reagents easily pass through and be uniformly distributed to the electrodes and react with the catalyst. The other function of the GDL is to conduct the electrons on both electrodes, so it has to be highly electrically conductive.

- **Bipolar plate (Flow field plate)**

Bipolar plate has different types of flow channels, it provides the flow path of the reagents to enter the cell as well as mechanical support of the fuel cell stack. It also needs to be highly electrically conductive and thermally conductive, because during the cell operation, heat is generated and needs to be dissipated efficiently.

- **Current collector**

Current collectors are normally made of copper plate, its main function is to conduct the electrons from the electrode to the external circuit and load. If the resistance of the current collector is high, the electrical power will be lost due to the added internal resistance.

- **End plate**

Its primary function is to provide mechanical support and protect the cell stack. Aluminium or Perspex are mostly used to manufacture the end plates.

2.5 Bipolar Plate

Bipolar plate (also known as flow field plate in a single cell configuration) is a key component in a fuel cell with functions such as distributing fuel, conducting current, removing heat, and preventing fuel leakage (Middelman et al., 2003).

Bipolar plates are used in a fuel cell stack to interconnect the unit cells, therefore it has opposite polarity on each side. It implements the serial connection to build up the potential of each unit cell. Bipolar plates represent a significant portion of the fuel cell volume, weight and capital cost. For transport and portable power source applications, bipolar plate plays a vital role in the volume, density and power density. Bipolar plates account for 60%-80% of the total weight and 40%-50% of the cost in a fuel cell stack design (Dhakate et al., 2008). Hence research around the bipolar plate material has been a focus worldwide.

Several types of material have been proposed for the fabrication of bipolar plate. These materials can be generally classified as non-metal, metal, and polymer composite (Hermann et al., 2005). Flow channels are fabricated on both sides of the bipolar plate to create the flow path of the reagents. To date, flow field manufacturing techniques mainly include mill machining of flow paths on a flat plate (metal or graphite) which is very costly, and injection moulding or hot press for composite materials. Note that for transport applications, the weight of the bipolar plates is even more important, as weight affects the fuel efficiency, handling and travel range. Suitable material for bipolar plate should be lightweight, electrically conductive, thermally conductive, low gas permeable, easy to process and

inexpensive (Huang et al., 2005; Kuan et al., 2005; Hermann et al., 2005). Figure 2-2 is a photograph of two graphite bipolar plates.

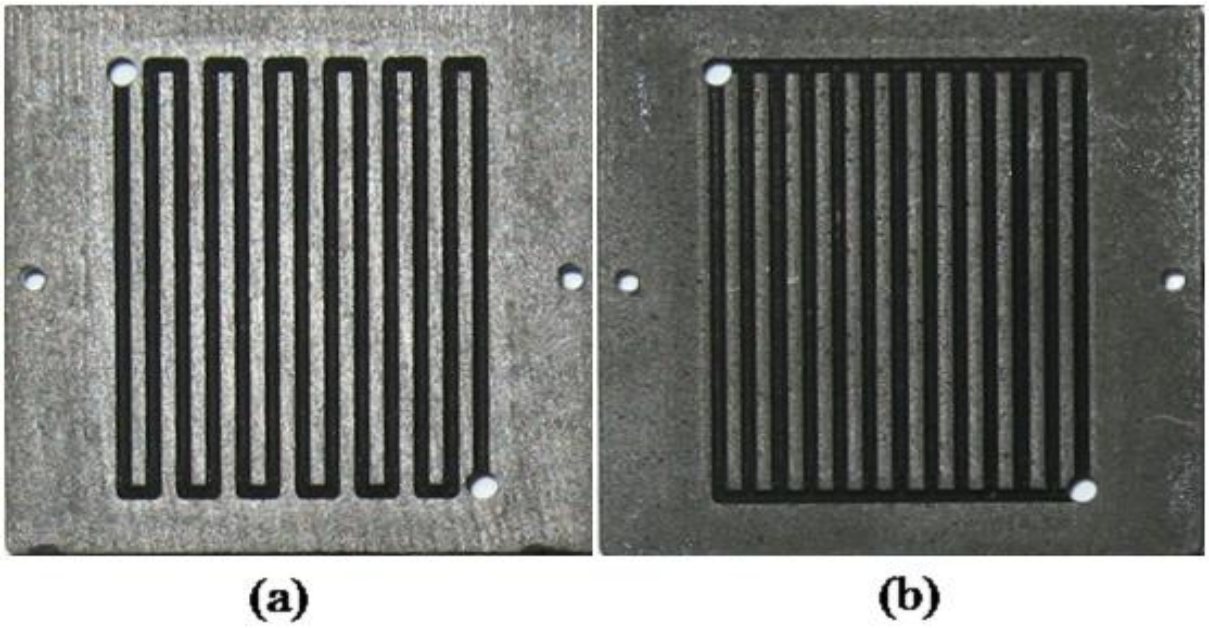


Figure 2-2 Photograph of graphite two bipolar plates (a) Serpentine (b) Interdigital

2.5.1 Functions and requirements of Bipolar Plate

As a multifunctional core component of the fuel cell, the role of the bipolar plate can be summarized as followings (Mehta and Cooper, 2003; Hermann et al., 2005): it

- Provides a flow path for fuel and reagents to the MEA uniformly and removes product water
- Interconnects the individual cells in a fuel cell stack, collecting and transporting electrons from the anode to the external circuit and back to the cathode. (electrical conductivity >100Scm^{-1})(United States Department of Energy, 2009)
- Provides mechanical support for the membranes and electrodes as well as the cell stack

- Removes heat from the stack and keep the system thermally stable(thermal conductivity >10 W m^{-1} K^{-1})
- Prevents leakage of reagents and coolants

In order to keep the fuel cell operational in its performance of the above mentioned functions, ideal bipolar plate should also meet the following requirements (Huang et al., 2005; Du, 2008):

- Chemical compatibility (no emissions affecting the electrode performance, no plate surface degradations occurring)
- Low volume, lightweight, and low cost
- Easy manufacturability and rapidly processable

2.5.2 Materials Selection Criteria

2.5.2.1 Chemical Compatibility

Materials for individual components should be chemically compatible. This allows each component of the fuel cell to carry out its intended functionality undisrupted. During the operation or non-operation of a fuel cell, the constituent materials should not breakdown or react with each other, unless the functional design demands otherwise. Since the fundamental workings of a fuel cell are based on chemical reactions, this criterion is of primary importance to the efficiency of the overall system.

The chemical compatibility of fuel-cell materials should also be considered in an environmental context. Materials that are sustainable and do not impact on the greater environment are most favourable.

2.5.2.2 Resistance to Corrosion

A highly corrosive environment exists between the MEA and bipolar plates of a PEM micro fuel-cell. Corrosion is simply the mass-wasting of a material and in context occurs as a result of the chemical reactions at the field plates/electrolyte interface. At this interface the fuel, typically hydrogen gas, decomposes into its elementary particles. In the case of a DM fuel cell, the exhaust carbon-dioxide produced at the anode combines with water vapour present to form a carbonic acid gas which accelerates the corrosion (Joh et al., 2008).

Appropriate materials should therefore be chosen to minimize this corrosion thereby vastly improving the durability and longevity of the cell.

2.5.2.3 Electrical Conductivity

Certain components of a fuel cell are required to be highly electrically conductive. The most significant components with this requirement are the anode and cathode, and in the case of a fuel-cell stack, the bipolar plates. Since they are the carriers of electrons to the external load, the materials used must allow electrons to flow freely with a maximum current density. Typically, graphite material is used in the construction of bipolar plates because it is highly conductive and is resistant to corrosion.

In contrast, total electrical insulation is necessary for materials that are used in the packaging and support of the micro fuel-cell. This is to ensure that the cells are not short-circuited and that no damage occurs to the system utilizing them.

In selecting suitable materials for the conductive elements, the ability to maintain superior electrical contact between elements must be considered. The ability of these materials to bond impacts appreciably on the conductivity between components. Therefore, the contact

resistance between conducting elements should be reduced such that parasitic currents are minimized to prevent unnecessary energy losses.

2.5.2.4 Weight/ Volume

A key requirement is to achieve a compact and lightweight fuel cell design. Even though materials may possess favourable behavioural properties, their densities and consequently volumes may become significant. Commercial micro fuel-cells should be compact enough to be used practically in cell-phones and hand held electronics.

The cost and size of bipolar plate is a major hurdle in PEMFC commercialization. Bipolar plates account for 60%-80% of the total weight and 40%-50% of the cost in a fuel cell stack design (Dhakate et al., 2008), therefore lightweight and low cost durable materials should be used (Gamburzev and Appleby, 2002). The bipolar plates however usually account for the bulk of the weight since they are made from graphite or sometimes metals. The efficient use of materials with minimal weight and volume is therefore a definite requirement.

2.5.2.5 Manufacturability

In addition to producing PEM and DM micro fuel cells using superior materials, another focus is on making these materials easily manufacturable (Virginia Tech, 2010). Materials that can be machined easily enable the fuel-cell to be assembled easily, thereby reducing production time and costs. Furthermore, individual components should not require complicated processes. These factors ultimately enable a fuel-cell design that has fewer functional complications and is maintainable.

2.5.2.6 Thermal Conductivity

Direct methanol fuel cell operating between 60°C -70°C (Nguyen and Chan, 2006) has an efficiency level of less than 30% with the rest of the total input energy being converted into

heat (Broussely and Archdale, 2004). Therefore, bipolar plate material needs to be able to dissipate the heat generated during the operation efficiently (Li and Sabir, 2005), underlining the need for materials that are resistant to high temperatures.

In most systems, excess heat is often undesirable as it leads to the wearing of materials, affects performance as well as significantly reducing its lifetime of operating.

The effect of scaling has a significant impact on the ability of the materials to rid themselves of excess heat. Materials must therefore also exhibit good thermal conductivity when they are scaled down to proportions of a micro fuel cell (Morse, 2007). The scaling should account for the increased surface to volume ratio which determines the ability to remove excess water and heat (Morse, 2007).

2.5.2.7 Cost

Considering the above mentioned criteria, perhaps the cost of materials and processing is of central importance and ultimately determines the feasibility of producing micro fuel-cells commercially.

Materials currently being used for bipolar plates are expensive to machine on flow field patterns. These materials include graphite and metals (Macdonald and Berry, 2000).

Additionally, the setup of cost effective fuel storage containers requires inexpensive materials which are easily disposable. Packaging materials should be readily obtainable and require little processing.

Ultimately, materials that are easily processed and inexpensive ensure that developmental costs surrounding infrastructure are minimal. This would also mean that these fuel-cells can be made available to a wider market, more especially to developing nations.

2.5.3 Materials for Bipolar Plate

There are a number of suitable materials for the fabrication of bipolar plates, the most common being metal, metal alloys with or without coating, graphite, carbon-carbon composite and carbon polymer composite(Brett and Brandon, 2007; Cunningham and Baird, 2006).

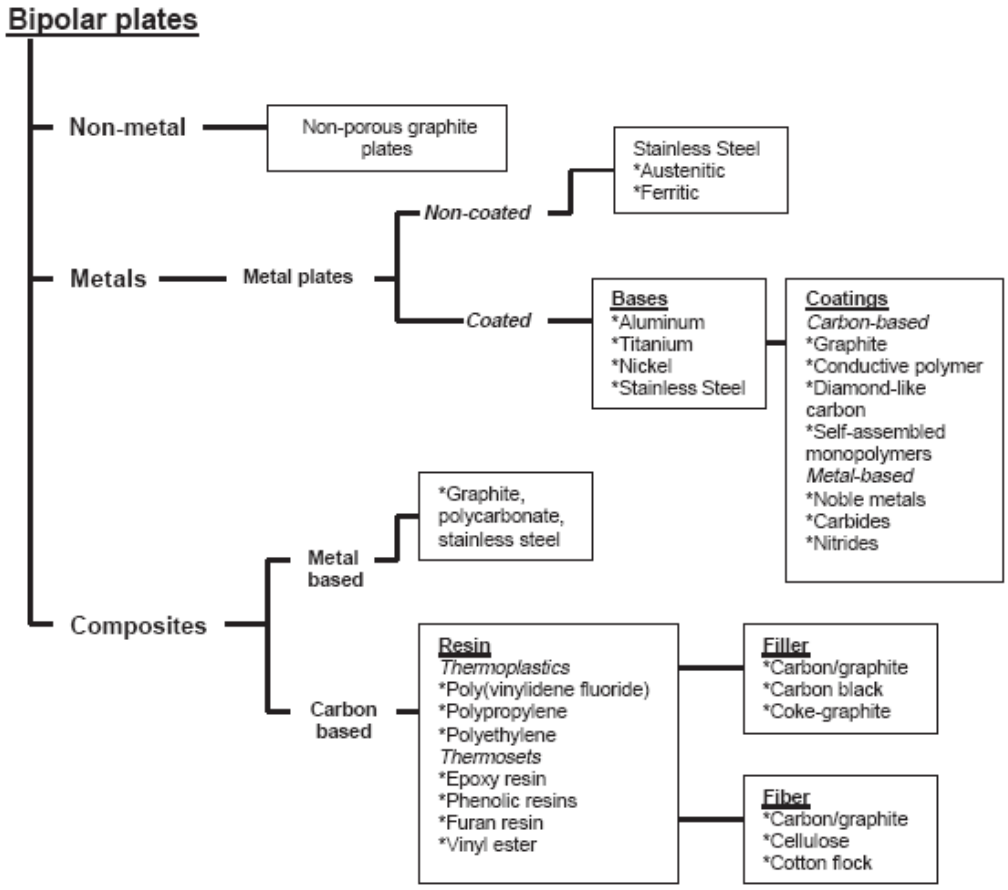


Figure 2-3 Classification of materials for bipolar plates used in PEM fuel cells (Hermann et al., 2005)

When metal material is used to manufacture bipolar plates, a corrosion resistance layer is normally coated on the surface of the plate, while graphite has to go through a sealant

treatment to decrease the gas permeability. In recent years, research has been conducted to develop low cost, high performance and lightweight bipolar plates. In this section, different bipolar plate materials are discussed and reviewed. Figure 2-3 illustrates the classification of materials for bipolar plates in PEM fuel cells (Hermann et al., 2005) and figure 2-4 shows the main material developer in the fuel cell community (Brett and Brandon, 2007).

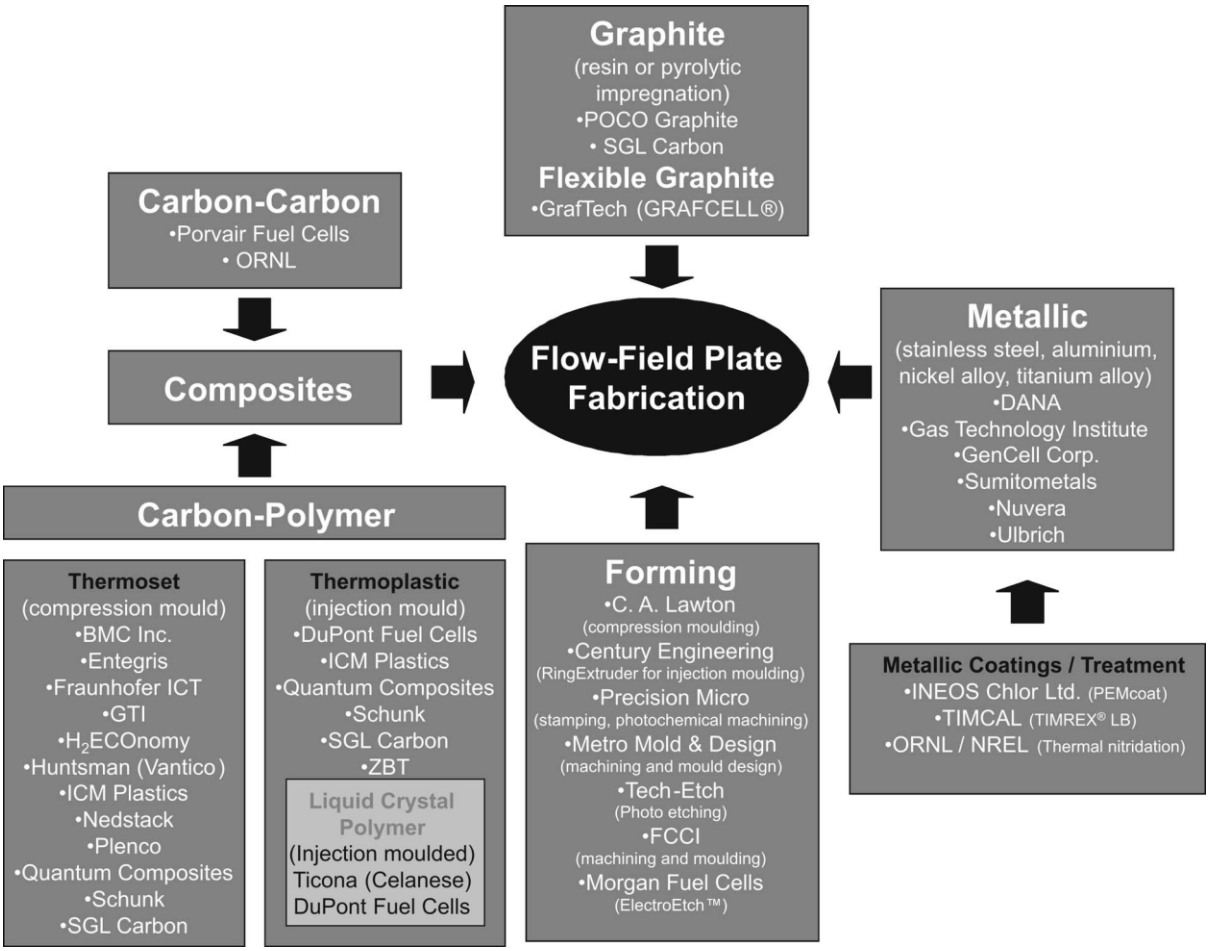


Figure 2-4 Summary of the main developers of bipolar plate materials (Brett and Brandon, 2007)

2.5.3.1 Graphite plate

Traditionally, the most popular material for bipolar plate is graphite plate because of its high electrical conductivity, chemical resistivity and low density. However, graphite is porous and brittle.

To use graphite plate as the bipolar plate material, pretreatment such as impregnation with a resin or pyrolytic (a sealing process that seals the pores several microns under the surface of the plate) is required to lower its gas permeability. Without such treatment, when gas fuel such as hydrogen is used in the fuel cell, the gas would easily permeate through the graphite plate and cause fuel loss and pressure drop.

Another disadvantage is the mechanical property of graphite, due to its brittleness, a few millimeters thick plate has to be designed to provide substantial mechanical support to the fuel cell stack. Thus, although graphite has a low density, the fuel cell stack becomes bulky and heavy.

Machining of flow channels on the graphite is also a costly and time consuming process, and requires careful handling and assembly. However, graphite bipolar plate is still used for some state-of-the-art stacks and quick prototyping, and sets a standard for the electrical conductivity and corrosion resistance for other materials.

2.5.3.2 Metal

The main advantages of using metallic bipolar plates and coated metal bipolar plates are their superior electrical conductivity, low porosity, high thermal conductivity and excellent mechanical properties. Stainless steel, titanium, and aluminium are mostly used for non coated bipolar plates, for metal based coated bipolar plates, two types of coating are widely used, namely, carbon based coating and metal based coating(Mehta and Cooper, 2003).

Carbon based coating materials include graphite, conductive polymer, diamond-like carbon, and organic self-assembled monopolymers while some of the metal coating materials are Noble metals, metal nitrides and metal carbides(Tawfik et al., 2007).

It has been found that metal bipolar plates are prone to corrosion and dissolution when they are exposed to an acidic environment with a PH level of 2-3 and a temperature of around 80°C. The membrane of the fuel cell would be poisoned by the dissolved metal ions hence affecting the ionic conductivity. Moreover, the corrosion layer on the surface decreases the conductivity of the bipolar plates (Hermann et al., 2005).

Metal bipolar plates also have high cost and manufacturing problems. New manufacturing techniques such as continuous rolling or batch stamping instead of laser machining have been developed to meet the mass production requirement of metallic bipolar plates, but these plates are still in the research stage. As bipolar plates account for 60%-80% of the total weight and 40%-50% of the cost in a stack, metal plates not only increase the cost of the fuel cell but also decrease its total efficiency.

In order to improve the corrosion resistivity of metal bipolar plates, surface coating with a conductive and corrosion resistive layer has to be employed. Electroplated aluminium plate was fabricated and tested by Woodman et al.(Woodman et al., 1999). Davies et al.(Davies et al., 2000) reported studies on stainless steel and titanium coated bipolar plates, it was noted that a thicker coating layer provided higher corrosion protection, however, power output was found to be inversely proportional to the coating thickness. Lee et al.(Lee et al., 2005) investigated the corrosion rate of several types of coating materials on aluminium bipolar plates by the physical vapour deposition (PVD) process, results showed good corrosion resistance in a simulated fuel cell environment.

The above mentioned researchers have shown that coating materials on metal bipolar plates can significantly improve the corrosion resistivity. However, the coating process is costly and difficult to perform, and very few studies have been conducted on the durability evaluation.

2.5.3.3 Composites

Among graphite, metal, and polymer composite, conducting polymer composite has the most promising potential because of its electrical and thermal conductive properties, its light weight, and good mechanical and anticorrosion properties (Dhakate et al., 2008; Middelman et al., 2003)

Following the successful synthesis of conducting polyacetylene in 1977 by Shirakawa et al. (Shirakawa et al., 1977), conducting polymers have drawn great attention as a result of their potential application in many fields. Most conducting polymers were made by doping with an oxidative/reductive subsistent or by donor/acceptor radicals (Anand et al., 1998). However, this synthesis process involves chemical reactions and is not easy for reproduction and mass production. An alternative way of preparing conducting polymer is mixing conductive fillers into a polymer matrix (Sandler et al., 1999). This polymer matrix is normally in liquid form at room temperature and can be cured by mixing with a catalyst (cross-linker).

Polymer composites that offer the desired electrical conductivity can be categorized as metal-based and carbon-based composites, depending on the types of filler particles used. The majority of research activities in this area have been focused on carbon-based polymer composites as carbon fillers which provide lower density, are available in large varieties, and can be tailored to obtain the desired particle size and morphology. On the other hand, the metal particles offer higher electrical conductivities than carbon fillers, but they have a higher density, and are prone to corrosion in highly acidic environments in PEM fuel cells. Corrosion, in turn, reduces the electrical conductivity

With the proper selection of polymer matrix, the polymer composite could provide excellent chemical inertness and fuel tightness. Thermoset polymers have been studied from the fuel cell bipolar plate perspective. As reported by Besmann et al.(Besmann et al., 2000) research on phenolic resin and carbon fibres including polyester and polyepoxy with carbon fibres was completed by Feller et al. (Feller et al., 2002). Studies conducted by Ryu et al.(Ryu et al., 2001) with phenol-formaldehyde resin and carbon black. Kumar and Sharma (Kumar and Sharma, 1998) comprehensively reviewed the fabrication of different types of conducting polymers and demonstrated their advantages, versatility, and potential. There could be more options for the polymer such as Polypropylene, Polyaniline, Poly(vinylidene fluoride) with different types of conductive filler such as metal coated graphite powder, carbon fibre, and other metal powder (Lee et al., 2005; Çakmak et al., 2004; Shirakawa et al., 1977).

In the research conducted by Niu et al. (Niu et al., 2007), polydimethysiloxane (PDMS) composites were prepared with infiltration of silver and carbon black particles at different filler fractions; percolation threshold concentration of the silver particles was found at wt83% (weight percentage) and the electrical conductivity of 104 S/m (siemens per metre) was achieved with wt86% silver. In this respect, the United States Department of Energy (United States Department of Energy, 2009) indicated a target value for the electrical conductivity of the fuel cell bipolar plate of 100 S/cm. Mamunya et al. (Mamunya et al., 2004) also reported a high electrical conductivity of 1000 S/cm for copper powder filled epoxy resin with 25% volume fraction.

Furthermore, good thermal properties are also crucial for the composite material. Experimental and theoretical models of the conductivity of heterogeneous composite materials have been reported by Nan et al. (Nan et al., 2003) indicating that as the filler content increases, the thermal and electrical conductivity of the composite material will also increase. In this respect, a Direct Methanol Fuel Cell (DMFC) operating between 60°C -70°C

(Nguyen and Chan, 2006) has an efficiency of less than 30% with the rest of the total input energy being converted into heat (Broussely and Archdale, 2004). Therefore, the bipolar plate material needs to be able to dissipate the heat generated during the operation efficiently (Li and Sabir, 2005). Cong and Pan (Cong and Pan, 2008) also observed that silver filled PDMS composite exhibited an excellent thermal conductivity of 71-81 W m^{-1} K^{-1}(watts per metre per kelvin) which is close to the conductivity of Iron (80 W m^{-1} K^{-1}). Compared with pure PDMS, the thermal conductivity improved in the order of 102. Furthermore, Single Wall Carbon Nano Tubes (SWCNT) were used as conductive filler in Epoxy Resin matrix by Choi et al. (Choi et al., 2003) showing an increased thermal conductivity of 300% with 3wt% SWCNT loading.

Kuan et al. (Kuan et al., 2005) found that with 4phr (parts per hundreds rubber) CNT filled polyurethane, the tensile stress of the composite increased 370% and the tensile modulus increased by 170.6%. In addition, Ghosh and Maiti (Ghosh and Maiti, 1996) pointed out a drastic decrease in the tensile modulus of silver filled polypropylene composite at 1.3vol% concentration, Therefore, as (Ruge and Büchi, 2001) indicated, for fuel cell application it is important to measure, tailor, and optimize the electrical, thermal, and mechanical properties of the polymer composite to fulfil the required standards with respect to the material and manufacturing designs (Ruge and Büchi, 2001).

Table 2.2 is a summary of studies conducted on different polymer composites and their electrical, thermal and mechanical properties.

Table 2-2 Summary of different properties of polymer composite

	Electrical conductivity ($S \cdot m^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Mechanical property (Pa)
PDMS	$3.4*10^{-13}$ (Dow Corning)	0.17 (Yamamoto et al., 2002)	$7.5*10^{5}$ (Young's modulus) (Armani et al., 1999)
PDMS-CB	30 (Niu et al., 2007)	4.72 (Chen et al., 2010)	Not available
PDMS-Ag	10^{4} (Niu et al., 2007)	71-81 (Cong and Pan, 2008)	$1.3\text{-}3.2 *10^{6}$ (Young's modulus) (Cong and Pan, 2008)
Silicone elastomer-MWNT	3.6 (Liu et al., 2004)	1.8 (Liu et al., 2004)	$1.71\text{-}2.34 *10^{6}$ (Elastic modulus) (Wu et al., 2009)
PDMS/CF/PPy (Çakmak et al., 2004)	230 -400	Not available	$2.2\text{-}2.8 *10^{9}$ (Young's modulus)
PET/graphite/carbon fibre (Huang et al., 2005)	In-plane $1.8\text{-}3.0*10^{4}$	Not available	$4.8\text{-}5.2 *10^{7}$ (Tensile strength)
Epoxy-carbon fibre (Hwang et al., 2008)	$3*10^{4}$	20	$5.2 *10^{8}$ (Tensile strength)
phenolic resin-graphite (Dhakate et al., 2008)	$1.1\text{-}1.5*10^{4}$	Not available	$4.9\text{-}5.4 *10^{7}$ (Flexural strength)
epoxy resin-CNT (Gojny et al., 2006)	0.01	0.252	Not available
polyvinyl acetate-Silver (Lee et al., 2005)	33	Not available	Not available
Polypropylene/Carbon black/Graphite (Mighri et al., 2004)	250-1000	Not available	$8\text{-}19 *10^{9}$ (Flexural Modulus)
Vapour-Grown Carbon Fibre/Phenolic (Patton et al., 2002)	Not available	0.54-0.62	$0.92\text{-}2.76 *10^{9}$ (Flexural Modulus)

2.5.4 Using Polymers as Structural Materials

Presently, research and development programmes are exploring the characteristics of alternative carbon-based materials in the construction of micro fuel-cells (Hinds, 2004). These engineered polymeric materials are now recognized as a key material in PEM fuel-cell for frames, bipolar plates, electro-catalysts and ion-conducting membranes. Polymeric materials are already being used and developed in the storage of electricity, molecular based information storage and processing, molecular composites as well as in healthcare and housing (Cancela et al., 2003).

However, utilizing these polymers for fuel-cells still requires considerable testing to optimize the extent of their application.

A fundamental reason influencing the research into polymeric materials is that they can be easily produced using a process called moulding and micro machined later if necessary at low cost(Steele and Heinzel, 2001). This significantly reduces the cost of the final product and therefore makes these fuel-cells more affordable.

In a broader sense, plastics and polymer substrates provide the appropriate combination of characteristics that are necessary to produce practical PEM and DM micro fuel-cells (Morse, 2007).

A polymer that has recently been of particular interest as a structural material for micro fuel-cells is Poly-dimethylsiloxane or PDMS. Poly-dimethylsiloxane has extensively been used in the field of micro-fluidics which is concerned with the behavior and characterization of fluids on a micro-scale. The most attractive reason for utilizing PDMS in commercial micro-fluidic devices is because it can be made compact, inexpensive and machined more easily than conventional materials.

Although polymers have been recognized as key materials in the construction of fuel-cells, there still remain a few uncertainties around its usage for specific components. In particular, PDMS and its extent of usage in fuel-cell elements are discussed. This includes a critical review of literature on trade-offs while selecting these materials. In addition, the possibility of utilizing well defined graphite-polymer composites is also explored.

Utilizing polymers for encasing is more suitable since it has shown to maintain structural integrity of cells for long periods of time i.e. durability (Hinds, 2004). The cell frame is used to keep all the components together and prevent any leakages of fuel.

Polydimethylsiloxane is used for packaging the fuel-cell because of its excellent flexibility and chemical inertness (Zhong et al., 2008). In a real environment, this allows the fuel-cell to cope with improper usage, wrong handling and other mechanical forces.

Its incredible ability to permanently bond to itself as well as other surfaces makes PDMS even more attractive (McDonald and Whitesides, 2002). Considering certain condition and environment in which the fuel-cell may be exposed to, solid PDMS does not permit aqueous solvents to infiltrate into the material. Therefore there can't be any deformation of the material. As a result the seals remain intact and there is no compromise on the structure and its resilience. On the other hand, most organic solvents will diffuse into PDMS and cause severe swelling. These solvents include hexanes, ethyl ether, toluene, dichloromethane, acetone and acetonitrite.

In general, a disadvantage is that proxy radicals are formed during the reduction of oxygen at the electrodes making the polymer with C-H bonds that are highly vulnerable to degradation (Bruijn, 2005).

The use of conductive polymers or graphite composites is at not necessary this stage since the encasing/support of a fuel-cell should be insulating to protect the device during operation.

Zhong et al. (Zhong et al., 2008) presented the design of a compact DM fuel-cell based on Silicon (Si). It can be noted that the cell also makes extensive use of PDMS for support, between components. The PDMS is placed to form seals and impart robustness to the design.

The heavy parts of the fuel-cell are the bipolar plates and it is possible to make use of PDMS to fabricate them (Bruijn, 2005). At present, graphite is used for the bipolar plates in a fuel-cell stack and copper is used for the anodes and cathodes (Bruijn, 2005). These materials are costly and often require expensive processes to fabricate (Bruijn, 2005).

Using PDMS for fabricating bipolar plates would definitely be favorable. In this way, a significant reduction in weight can be achieved. This would mean that flow field patterns must then be transferred on to the PDMS.

Polymers provide a good alternative to micromachined fuel-cell bipolar plates because of their increased flexibility and low density. However, since PDMS is virtually non-conducting, it cannot be used without being modified (Bruijn, 2005). Maintaining sufficient electrical contact between adjacent cells is a requirement for efficient operation and integrating conducting structures into PDMS is especially critical (Niu et al., 2007).

However, patterning conducting metallic structures on to PDMS is a difficult task as embedded electrodes may be required for signal detection (Niu et al., 2007). In an attempt to solve this, carbon black-PDMS and Ag-PDMS composites are being developed. Consequently, it will reinforce the electrical and thermal conductivity of the PDMS (Niu et al., 2007). The result would be a superior lightweight composite capable of conducting electric current. These composites would also allow the machining of flow-fields directly

onto the surface. Furthermore, a single component may then serve to replace the use of a bipolar plate and a reinforcement copper plate in some fuel-cells.

Recent studies have shown that PDMS typically begins to improve its conductivity if the volume fraction of conducting graphite/carbon black is greater than 10%. A problem could arise when the concentration of the solid conducting particles is too high. The resulting composite becomes rigid and tend to break easily. The mechanical properties of PDMS then begin to change and the composite becomes difficult to process (Niu et al., 2007).

These graphite/polymer composites could extensively be used for the anode/cathode as well. It may result in thinner plates consequently reducing the overall size of the fuel-cell. A disadvantage could be the inability of PDMS to resist the infiltration of fuels within the flow fields.

Table 2-3: Important properties of PDMS vs Graphite.

	PDMS	Graphite
Electrical Resistivity	4 x 1013 Ωm	7.837 μΩm
Melting Point	< 50 °C	3675 °C
Tensile or fracture strength	2.24 MPa	4 – 55 MPa
	Very Flexible	Brittle
Density	0.97 kg/m3	2.03 - 2.23 g/m3

In Table 2.3 above, selected properties of PDMS and graphite are compared. There appears to be a significant difference in the resistivity of both materials. PDMS is observed to be far less

conductive Even though composites may not practically approach the conductivity of pure graphite, it is possible to make PDMS a suitable electrical conductor. The graphite is also very fragile despite the high tensile strength compared to the polymer. Graphite is also approximately twice as dense as the PDMS despite graphite's porous nature.

The quest to make PDMS conductive is a difficult task, but the advantages far out-weight the disadvantages. Conductive composites for bipolar plates therefore offer a mixture of properties that are well suited to the possible applications.

Polymers dramatically reduce time and complexity of manufacturing and processing components fabricated from them (McDonald and Whitesides, 2002). Injection molding is a relatively inexpensive process used widely for fabricating polymer based parts (Hinds, 2004). In turn, this reduces the manufacturing and micromachining costs associated. Furthermore, PDMS can be processed at room temperature and expensive clean room facilities are not required. This means that PDMS can be handled easily primarily because it is in liquid form at room temperature. Also, these polymers are less expensive than silicon and easier to assemble with other fuel-cell component (Pichonat and Gauthier-Manuel, 2007).

However, handling PDMS in liquid form could be untidy as it easily adheres to objects. On a commercial scale, this could lead to a mass wastage of PDMS in mixing containers. Adequate procedures must then be designed to maximize its usage. Additionally, contact resistances are complicated to manage as it vastly affects performance of fuel-cells (Morse, 2007). In fact, PDMS significantly increases contact resistances at the current collector (Morse, 2007).

Poly-dimethylsiloxane has shown many significant advantages over conventional materials in the different elements that constitute a micro fuel-cell. The shortfalls of PDMS still require immense research and testing to construct micro fuel-cells that are practical, compact and can be made available commercially.

2.5.5 Environmental Considerations of PDMS and Polymers

An essential consideration whilst selecting engineered materials should be around the development of a sustainable solution. While the material may possess all the desired characteristics, it may not necessarily be an environmentally compatibility material. Taking into account the lifespan of fuel-cells, the time frame for the workability of these cells is finite and thought should be given in the event of disposing them. However, polydimethylsiloxane in particular is of utmost sustainable in its use in micro fuel-cells because of the following reasons (Dow Corning, 1998):

- As it makes contact with soil, it degrades into lower molecular weight compounds. These compounds oxidize in the environment to form naturally occurring silica, carbon-dioxide and water.
- It has been shown to have no adverse effect on plant and animal life as well as other terrestrial life.
- Its non-toxicity means that it does not contaminate the materials which it makes contact with and thus remains harmless. This is one of the important reasons for its extensive use in health care.
- PDMS is non-volatile which means that it does not evaporate into the atmosphere and can therefore do not contaminate the air.

The same conclusions cannot be drawn for all polymers as each may behave differently. These remain specific to PDMS and it is clear that this substance is definitely worth researching and developing further as a potential candidate for use in major micro fuel-cell components. It is certainly a unique polymer and that may be applied in a sustainable and environmentally conscious way. The ideal way would be to use as structural materials that are recyclable and do not need disposing.

2.6 Conclusions

The development of PEM and DM micro fuel-cells for commercial low-power applications has received much interest in recent years. The performances of many available fuel-cells at present are not sufficient in delivering adequate power and in most cases are too bulky to be portable. Current research into new materials to replace specific components is definitely a means to develop compact, durable and practical low-cost micro fuel-cells.

A thorough literature survey was conducted around the possible use of polymers, specifically Poly-dimethylsiloxane, as the structural materials in micro fuel-cells. An evaluation of the criteria that should be considered in selecting appropriate materials was extensively discussed. The materials in present "micro" fuel-cells are inadequate in providing commercially viable cells and have many associated problems. However, polymers have indicated many favourable characteristics in the fabrication of microfluidic devices, in particular fuel-cells. PDMS provides a unique compact, durable and inexpensive solution to manufacture major components.

Considering that bipolar plates and packaging or cell-supports constitute most of the weight/volume in fuel-cells, PDMS provides a lightweight and robust alternative in producing a truly "micro" fuel-cell. The possibility exists to machine flow-fields onto these polymers, however, PDMS is virtually non-conductive. Therefore, graphite composite materials must be developed to make PDMS more conductive. Composites can then possess properties of both graphite and polymers to individual components.

An evaluation of the influence of materials on the performance of cells was comprehensively illustrated. Fuel-cells under development have shown to only perform well, 1000's of hours, under steady-state conditions. Their overall performance lacks in more harsh environments

and cannot cope with many stresses. Also, advances in fuel storage and replacement are currently premature and more research and development is necessary.

The future of polymers in micro fuel-cells is promising and has a vast potential for being explored extensively. For this to be realised, a systematic understanding of the complex interactions at the material level must be gained. Focusing on details of failure mechanisms in materials should pave the way for more advanced methods and components in PEM and DM micro fuel-cells. The ultimate triumph would be to develop a highly cost effective commercial micro fuel-cell capable of providing power to devices for prolonged duration of time.

In this chapter, a brief introduction to fuel cell technology was given. Focus was placed on bipolar plate and bipolar plate materials, relative literature was studied and summarized. This chapter attempts to give readers a background to the intended research. Based on the literature studied, polymer composite material shows the potential not only to make the fuel cell smaller, lighter and more compact but also to reduce the manufacturing cost. Finally, based on the information and literature gathered in this chapter, the next chapter will describe the methodology, experimental approaches and equipment used in this project.

3. METHODOLOGY

3.1 Overview

In order to utilise polymers in a fuel cell structure, the polymer needs to be conductive. To achieve this, different methods can be approached. One can modify the surface of the polymer to create a conductive path for the electrons to flow, this can be done by spin coating, printing or cold spraying of conductive materials on the polymer surface. Cold spraying process applies coating with a supersonic jet of gas. The gas is loaded with micro conductive particles of the size from 5 to 50 um in diameter that can be accelerated to a high speed (up to 1500m/s). These particles will then be jetted and deposited onto the substrate therefore forming a conductive layer. (More information and advantages of Cold Spraying process can be found in Appendix 1) Alternatively, conductive fillers can be mixed into the polymer matrix to form a conductive path throughout the polymer structure for the electrons to flow.

Based on the literature study and research questions in the previous chapters, the objective of this project is to develop a conductive polymer material for the fabrication of fuel cell bipolar plates. Due to the availability of equipment and materials, development and characterization of conductive PDMS polymer composite was researched. To complete the research project, several issues needed to be addressed, namely, the experimental apparatus, materials selections, sample preparation and testing procedures are documented.

3.2 Experimental Materials

The materials selected for polymer composite development include polymer matrix and conductive fillers. The detailed information about polymer matrix and fillers is discussed as follows.

3.2.1 Polymer Matrix

The polymer matrix selected is Polydimethylsiloxane (PDMS), a silicone elastomer widely used in packaging, cosmetic and food industries owing to its transparent, flexible, non-toxic and non-flammable properties. PDMS has also received growing attention recently in the biomedical and microfludic application (Mata et al., 2005; Fujii, 2002; Abbasi et al., 2001; McDonald and Whitesides, 2002; Fujii et al., 2003). It is biocompatible, chemically inert, thermally stable, easy to process as well as low cost. Polydimethylsiloxane (PDMS) was selected as the polymer matrix for this project because of its properties such as easy processability, soft lithographic reproducibility, and mechanical flexibility.

PDMS (Sylgard 184 Silicone Elastomer) was supplied by Dow Corning in two-part liquid component kits comprised of a base and a curing agent. The two parts mix in a ratio of 10: 1, and when the two liquids are mixed thoroughly, the mixture cures at 60°C to form a flexible elastomer. Table 3.1 illustrates the properties of PDMS.

Table 3-1 Properties of PDMS (Dow Corning)

Property	**Value**	**Unit**
Viscosity	4575	mPa·s
Thermal Conductivity	0.16	Watt·meter^{-1}·K^{-1}
Linear Coefficient of Thermal Expansion	325	10^{-6}/°C
Volume Resistivity	2.9 x 10^{14}	ohm·cm
Young's modulus (Armani et al., 1999)	750	KPa

3.2.2 Conductive Fillers

Carbon black (CB) and silver (Ag) particles were selected as the conductive filler. Both fillers have very high intrinsic electrical conductivity. The amorphous structure and large surface area of carbon black can deliver the desired high electrical conductivity to the composite. Furthermore, incorporating carbon black filler into the polymer matrix can enhance the mechanical property and thermal property of the composite which is also highly desirable for the fuel cell bipolar plate perspective.

Typical carbon blacks are composed of nearly pure carbon in colloidal entities of aciniform morphology. The term aciniform, meaning "clustered like grapes", refers to the characteristic appearance of the colloidal entities composed of spheroidal particles fused together in clusters of branched, irregular shapes as presented in Figure 3-1. The entities are generally called aggregates. Within each aggregate, the carbon atoms are arranged in imperfect graphite layers. The arrangement of carbon atoms and layers is referred to as microstructure. The layers are arranged more or less concentrically within each particle or growth centre, with a fair degree of parallelism between adjacent layers in small regions or crystallites. The layers are continuous from one particle to the next within the aggregate.

Carbon black Vulcan XC-72 was supplied by Cabot Corporation. The main carbon black characteristics in terms of processability and conductivity are the specific surface area, surface chemistry, and wetting properties. Because of this material's high surface area, which increases with particle porosity, more porous carbon blacks should produce more conductive blends (Mighri et al., 2004). The physical and chemical properties of Vulcan carbon black are recorded in Table 3.2.

Silver filler offers a higher electrical conductivity, and because of its higher density, high filler loading in the composite can be achieved. However, in turn of the high filler loading, other properties such as corrosion resistance and mechanical property are often compromised.

Silver powder (327085, silver powder, 2-3.5 μm, ≥99.9% trace metals basis) was supplied by Sigma Aldrich, it has a particle diameter of 2-3.5 μm, a density of 10.49g/cm3, and resistivity of 1.59 μΩ-cm at 20°C.



Figure 3-1 Vulcan XC-72 Carbon black

Table 3-2 Properties of Cabot VulcanXC72 Carbon Black (Cabot Corporation, 2010)

Appearance	Black pellets, powdery
Odour	None
Density	1.7 -1.9 g/cm3 @ 20℃
Bulk Density	200-680 kg/m^3 (Pellets) 20-380 kg/m^3 (Fluffy)
Mean Particle Size	30 nm
Surface area	250m^2/g

3.3 Experimental Apparatus

The experimental apparatus used in this project was provided by the Council of Scientific and Industrial Research (CSIR) and its collaborator Sreenidhi Institute of Science and Technology (SNIST) in India. These include a Polymer blends mixer (CSIR), Oven (CSIR), Four Point Probes resistivity measurement equipment (CSIR), Thermal Gravimetric Analysis (TGA) (CSIR), Cut-bar thermal conductivity facility (SNIST), Dynamic Mechanical Analyser (CSIR), Scanning Electron Microscopy (SEM) (CSIR). The specific models for experimental apparatus are detailed in Table 3.3. More detailed information and images of the experimental apparatus can be found in Appendix 2.

Table 3-3 Experimental Apparatus Model

Apparatus	Model
Polymer blend mixer	In-house made mechanical mixer
Oven	EcoTherm LABOTEC
Four Point Probes resistivity measurement equipment	Microtech and KEITHLEY 4200
Thermal Gravimetric Analysis (TGA)	TA Instrument TGA Q500
Cut-bar thermal conductivity facility	Designed in-house
Dynamic Mechanical Analyser (DMA)	Anton-Paar Physica MCR 501 rheometer
Scanning Electron Microscopy (SEM)	JEOL JSM 7500F field-emission scanning electron microscopy

3.4 Sample Preparation

The composites were fabricated by mixing the conductive fillers and polymer resin received from suppliers. The processing procedures included the material selection, blend mixing, blend degassing, moulding, and sample properties testing.

For the carbon black, Vulcan XC-72, which is a very fine particle but in pellet form, the first processing step was to disperse carbon black pellets in methanol to obtain a homogenous dispersion with the aid of ultrasonication. The carbon black pellet was first dispersed in methanol then ultrasonicated for 30 min, which process broke down the carbon black pellets into original nano size particles. The carbon black methanol dispersion was then mixed with the PDMS base. The blend was mechanically mixed for 24 hours to obtain homogenous dispersion, and then the curing agent was added and further mixed with the blend. The well mixed blend was then degassed in vacuum to remove bubbles. The mixture was oven baked to cure for 8 hours at 60ºC. The solvent methanol added evaporated during the mixing, the vacuuming process and baking and the weight of the methanol was eliminated because of its low boiling point (64.7ºC). It is to be noted that the Carbon black particles were easy to mix with PDMS gel owing to their good wetting properties which in general led to a uniform distribution in PDMS(Niu et al., 2007).

For the silver powders, a similar procedure was followed, except that the silver powder was not dispersed in methanol, simply because the silver powder was supplied in its original particle size of 2-3.5 μm. The silver particles were directly mixed with the PDMS base.

In order to meet the test requirement for different experimental equipment, two types of mould were designed. For the cut-bar thermal conductivity measurement, samples were moulded into a disk shape with a diameter of 3 mm and a thickness of 1mm. For the dynamic mechanical measurement, samples were moulded into a rectangular shape, with a dimension

of 45mm*6.7mm*1.6mm. For the four point probe electrical conductivity, SEM and TGA, the same samples of the rectangular shape were used.

Table 3-4 Sample compositions used in this study

Carbon black (CB) composition wt%	Silver powder composition wt%
10%	50%
13%	55%
16%	60%
19%	65%
22%	70%
25%	74%
	77%

3.5 Testing Procedure and Analysis

Based on the relevant literature, the problems to be investigated were focused on the electrical conductivity, thermal conductivity, thermal stability and mechanical properties of the polymer composite. In this section, experimental procedure is described.

3.5.1 Electrical Conductivity

The electrical conductivity of the samples was measured with the four point probe technique. The four point probe measurement consists of a DC current source, an ammeter, a digital voltmeter and four probes. As shown in Figure 3-2, probe 1 and 4 are connected to the DC power supplier and probes 2 and 3 are connected to the voltmeter. When the four probes come into contact with the sample, the current flows through the outer probes (1 and 4). Due

to the sample resistance, there was a potential drop along the measured sample. The voltage difference between the inner probes (2 and 3) was measured by the connected voltmeter.

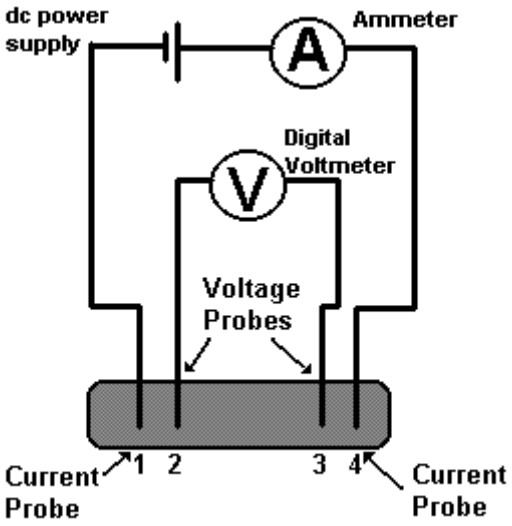


Figure 3-2 Four point probe schematic (Scientific instruments, 2010)

The resistance R of the sample is the ratio of the voltage difference to the output current of the DC supplier. Therefore the resistivity ρ of the sample can be calculated from equation

$$\rho = \frac{\mathrm{R} * \mathrm{L}}{\mathrm{w} * \mathrm{t}}$$

Where ρ is the resistivity of the sample, L is the distance between probe 2 and 3, w and t and the width and thickness of the sample. Then the electrical conductivity σ can be obtained from

$$\sigma = \frac{1}{\rho}$$

3.5.2 Dynamic Mechanical Properties

The mechanical properties are one of the most important aspects of the structural materials in a fuel cell, because the bipolar plate material has to be mechanically stable to prevent fuel leaks and also to keep the membrane in position. Rheology is defined as the science of deformation and flow of materials such as polymers and composites. It is a branch of physics and physical chemistry since the most important variables come from the field of mechanics. Rheological experiments reveal information about the flow behaviour of liquids and the deformation behaviour of solids. These experiments are done using a rheometer. There are two types of rheometers used in research nowadays, namely (1) rotational and (2) oscillatory rheometers. Liquids and solid materials can be investigated using both rheometers. Rotational tests are performed to characterize the viscous behaviour of materials, while creep and viscoelastic behaviour, as well as relaxation tests can be carried out using oscillatory tests (Mezger, 2006). Rheological tests were used to investigate the dynamic mechanical for PDMS composites with different filler loadings.

The Anton-Paar Physica MCR 501 rheometer was used to investigate the thermal dynamic mechanical properties of all the samples in this study. All samples were tested with a temperature sweep from -150°C to 100°C, at a frequency of 6.28 rad s-1, for a strain of 0.02 %. Storage modulus and loss modulus were recorded as a function of temperature.

3.5.3 Thermal Stability

Thermal stability was characterized by Thermal Gravimetric Analysis (TGA). The principle of the TGA technique is that the material thermal stability is monitored by sample weight loss in a given temperature range with a constant heating rate under specific atmospheric conditions. Thermal Gravimetric Analysis (TGA) for thermal stability/degradation was performed on a TA Instrument TGA Q500 in nitrogen and oxygen atmospheres. The heating

rate was 10°C/min. The measurement range was from room temperature to 800ºC. Samples ranging from 5 to 10 mg were analyzed.

3.5.4 Thermal Conductivity

A widely used Cut-Bar method was employed for the thermal conductivity measurement. A Cut-bar test facility is a proven system for the measurement of thermal conductivity and thermal contact conductance over a wide range of temperatures. A schematic configuration is shown in Figure 3-3. For the most part, the unknown sample is sandwiched between two similar samples with known thermal conductivity. The working principle (illustrated in Figure 3-4) of the cut-bar technique is that the heat flux through the unknown sample and known sample is measured, therefore the conductivity of the unknown sample can be calculated using the equation below with other known parameters.

$$\frac{Q1 + Q2}{2} = K * A * \frac{\Delta T}{\Delta X}$$

where Q1 and Q2 are the heat flux through the two known samples, K is the thermal conductivity of the unknown sample, A is the cross-sectional area of the sample, $\frac{\Delta T}{\Delta X}$ is the temperature gradient.

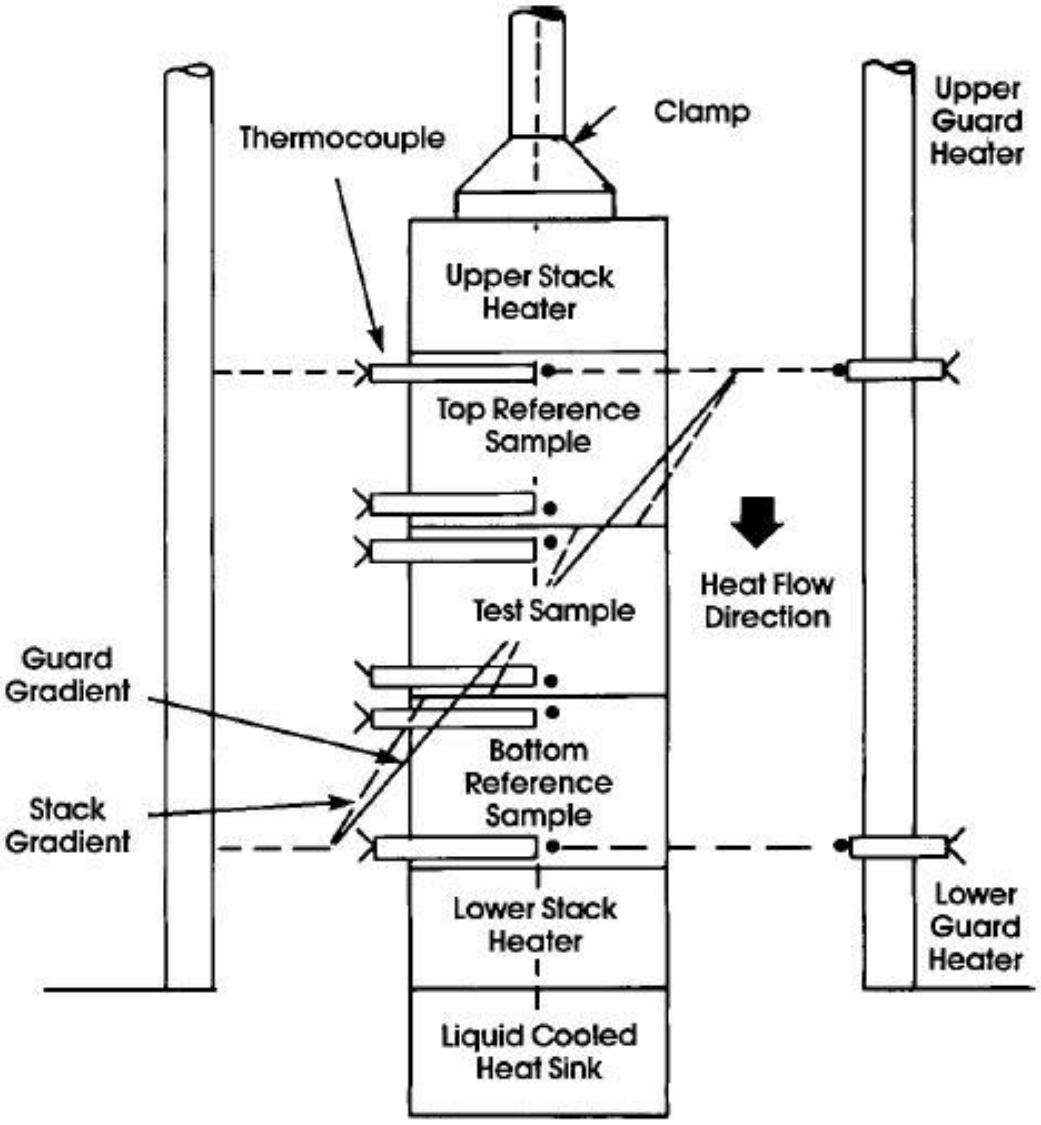


Figure 3-3 Schematic configuration of the setup

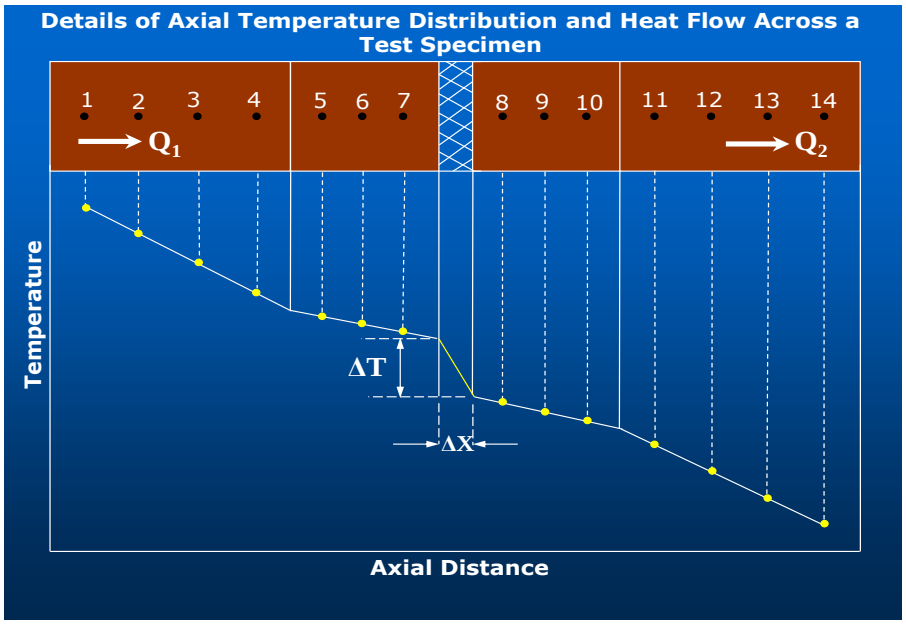


Figure 3-4 Sample testing explained

3.5.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a technique whereby a beam of energetically well defined and highly focused electrons are scanned across a sample. The microscope uses a lanthanum hexaboride (LaB_6) source and is pumped using turbo and ion pumps to maintain the highest possible vacuum. The technique can provide information about the topography, morphology and crystallography of the material. The basic principle of the system is that the electron beam impinges the surface and generates a splash of electrons, called secondary electrons, with kinetic energies much lower than the primary incident electrons. An image of the sample surface is constructed by measuring the secondary electron intensity as a function of the primary beam position. Advantages of the SEM over traditional microscopes are (i) its large depth of field, which allows more of a sample to be in focus at one time and much higher 5 0 resolution, so that closely spaced samples can be magnified at much higher levels, and (ii) its use of electromagnetic lenses which give much more control over the degree of magnification. A simplified layout of a SEM is shown in Figure 3-5.

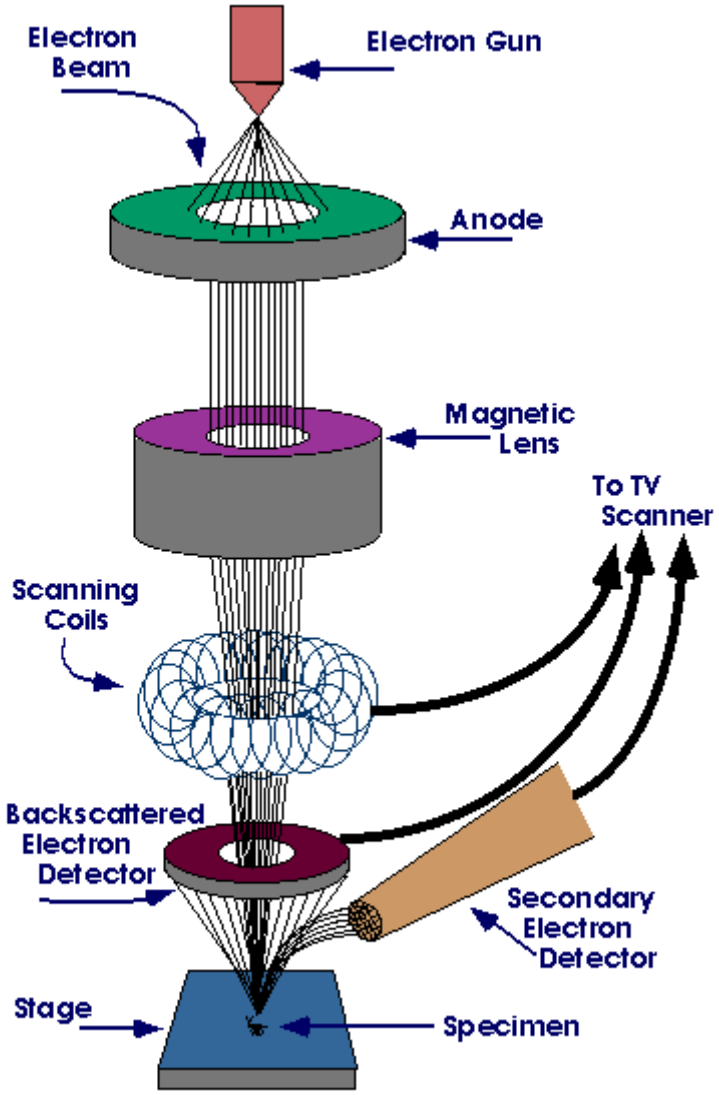


Figure 3-5 A simplified layout of the scanning electron microscope (PURDUE University, 2012)

The SEM micrographs were obtained by the JEOL JSM 7500F field-emission scanning electron microscopy (FE-SEM). Before the images were taken, all the samples were frozen in liquid nitrogen for 24 hours, and fractured by simply breaking the samples into an appropriate size to fit into the sample chamber, and then mounted onto the holder. The surfaces of the samples were coated with carbon by an electro-deposition method to impart electrical conduction before recording the SEM micrographs. This was done to prevent the accumulation of a static electric charge on the sample during electron irradiation.

3.6 Conclusion

Chapter 3 focused on determining, applying methods and conducting experiments in order to solve the research questions posed in chapter 2 and support the hypotheses classified in chapter 1. This chapter forms the main structure and foundation of the thesis. The following chapter will present and discus results of the experiments conducted.

4. RESULTS AND DISCUSSION

In order to investigate the feasibility of using PDMS-Carbon black and PDMS-Silver composites in fuel cell structural material applications, several experiments were carried out to study the thermal, mechanical and electrical properties of the composites. In this chapter, the experimental results are presented and discussed with comparison to literature.

4.1 Electrical Conductivity

High electrical conductivity is required for polymer composites to be used as fuel cell bipolar plates. However, PDMS is a nonconducting polymer, hence the integration of conducting structures into bulk PDMS has been a critical issue. PMDS can be formed into conductive material by the addition of carbon black in a concentration higher than 10% by weight, as described by Unger et al(Unger et al., 2000). The electrical, rheological, and morphological properties have also been studied by Rwei et al(Rwei et al., 2002).

In this project, carbon black and silver particles were used as conductive fillers mixed into the PDMS polymer matrix. The electrical conductivities of the composites is presented and discussed in this section.

4.1.1 PDMS-Carbon black composite

Electrical resistances were measured using the four point probe technique with sample dimensions of 1mm thick, 45mm long and 6.7mm wide. The resistivity ρ was calculated using the equation

$$\rho = \frac{\mathrm{R} * \mathrm{L}}{\mathrm{w} * \mathrm{t}}$$

Electrical conductivity σ is the inverse of the electrical resistivity ρ, therefore

$$\sigma = \frac{1}{\rho}$$

Where L is the distance between the two inner probes which measure the potential difference. A distance of 1 mm was used in this experiment.

The conductivity of the PDMS-Carbon black composite is shown in Figure 4-1, plotted as a function of weight concentrations of the carbon black fillers. The conductivity exhibited a plateau from 10wt% to 19wt%, and then rapidly increased beyond 19wt% to 25wt%. The rapid increase in this range can be regarded as the percolation threshold. "Percolation threshold" is understood as at some critical loading, the conductivity increases many orders of magnitude with very little increase in the filler loading. This finding also agrees with the results reported by Niu et al(Niu et al., 2007).

From Niu's results in experiments conducted at the same range of filler concentrations, at 26wt% carbon black loading, a conductivity of 0.25 S/cm was achieved. And in this project, conductivity of 1.03 S/cm was found at 25wt%, four times higher at an even less filler concentration. This improvement could be attributed to the sample preparation method that was used in this project. The carbon black particles were obtained in pellet form, prior mixing to PDMS, these pellets were dispersed in methanol by ultrasonication. This step has broken the carbon black into its original nano sized particles therefore increase the surface area that leads to a higher conductivity.

From the pattern of conductivity against filler weight concentration, it can be assumed that higher carbon black loading (>25wt%) would further increase conductivity, however, at 25wt% loading, the composite blend before became very viscous. A higher concentration will cause difficulties for composite processing and also affect the filler distribution homogeneity.

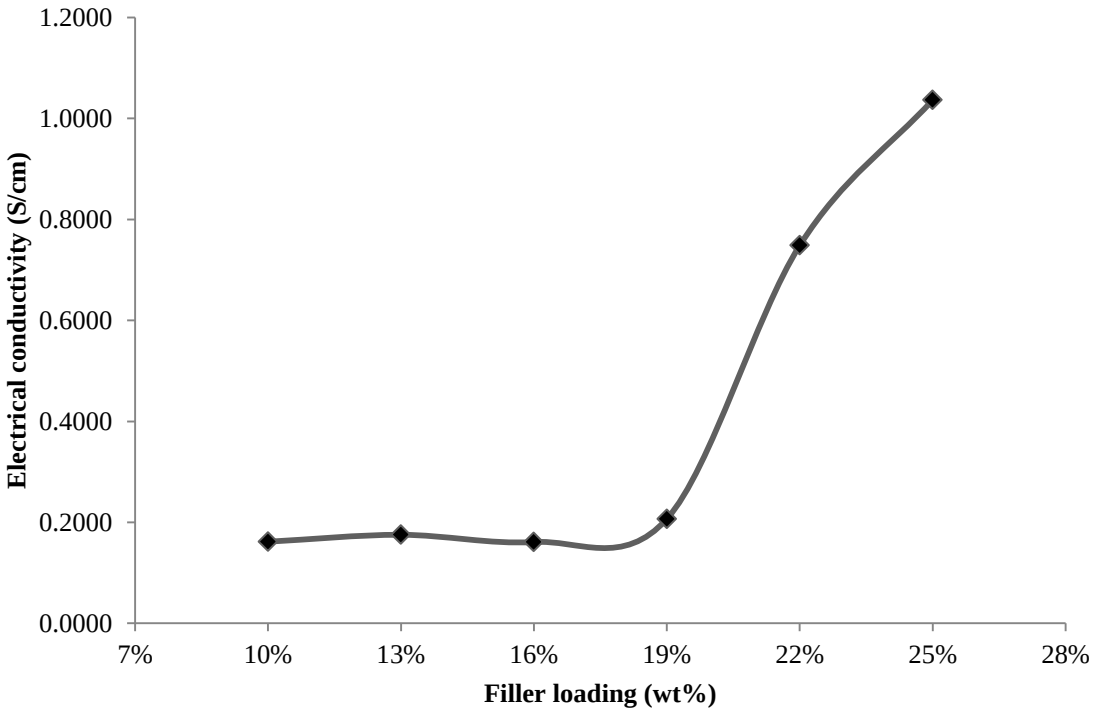


Figure 4-1 Conductivity versus carbon black filler weight concentration

4.1.2 PDMS-Silver composite

The goal of this project is to investigate the feasibility of a PDMS composite in a fuel cell structural material context. To increase the electrical conductivity of PDMS by incorporating different conductive fillers is one of the primary objectives of the study. Silver is known to be the best electrical conductor with a conductivity of 6.3×10^5 S/cm. The synergistic effects of silver micro powders in PDMS polymer matrix follows.

The conductivity measurement results are illustrated in Table 4-1 and the corresponding graphs are shown in Figure 4-2. The conductivity of each filler concentration was measured with a pulse current of 1mA at 1Hz for 20 pulses, and the average was obtained.

Table 4-1 Electrical conductivities of PDMS-Silver composites

Filler concentration (wt%)	Conductivity (S/cm)
50%	0.0081
56%	0.2672
60%	1.1982
65%	2.1347
70%	3.8833
74%	6.2896
77%	8.5230

The electrical conductivity of pure PDMS was 3.45×10^{-15} S/cm (Dow Corning), while the 50wt% silver filled had a conductivity of 0.0081S/cm, which improved in the magnitude of 10^{12}. Between the ranges of 50wt% and 77wt%, 7 samples were prepared to establish the trend of conductivity. In general, conductivity increases as filler loading in the polymer matrix increases. However, unlike Carbon black PDMS composites, the plateau was not found at lower concentrations, instead, the conductivity showed a drastic growth pattern in the range of 70wt% to 77wt%, and this was where the percolation threshold was reached. Comparing the figures Niu et al (Niu et al., 2007) presented for the silver PDMS composite electrical conductivity, moreover, the threshold was found to be at 70wt% in this work, and at 83wt% in Niu et al's(Niu et al., 2007) study. This means the threshold was successfully shifted to a lower concentration by 13wt%. This would not only improve processability since high filler loading in the polymer matrix causes high viscosity of the blend and inhomogeneous distribution of particles, but also reduce the manufacturing cost of the bipolar plate.

Although the threshold was shifted to a lower concentration in this project, the 77wt% sample still achieved a conductivity of 8.5230 S/cm which was approximately similar in value to Niu(Niu et al., 2007)'s results with a 86wt% sample.

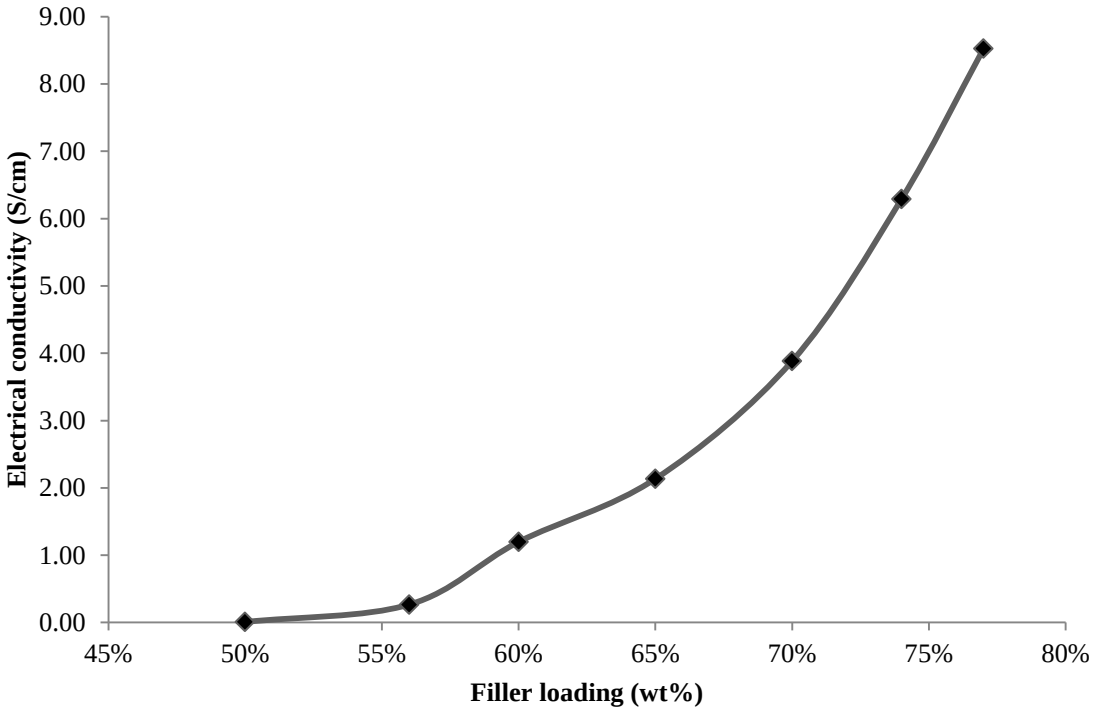


Figure 4-2 Conductivity versus silver filler weight concentration

4.2 Thermal Conductivity

In a fuel cell bipolar plate itself as well as form a structural material perspective, the thermal properties of the PDMS composite are as important as its electrical properties simply because large amounts of heat are generated during the operation of the fuel cell. Hence the PDMS composite as the structural bipolar plate material has to be able to dissipate the heat efficiently and be thermally stable. It was found that there is a lack of literature available on the thermal stability and thermal conductivity of the PDMS-Carbon black and PDMS-Silver composites.

This section, the detailed thermal conductivity measurements of the CB-PDMS composites are presented. PDMS composite samples with specific wt %(10-25%) of carbon black and wt

%(50-77%) of silver loadings were tested. These ranges were chosen because these composites had shown good electrical conductivities in this particular range (Niu et al., 2007). Their thermal properties were then compared with those of other polymer composites recorded in the literature.

4.2.1 PDMS-Carbon black composite

The thermal conductivity (k) of the test specimens was measured using a cut-bar test facility under steady state conditions. The system was assumed to have attained steady state conditions when all the temperature sensors (thermocouples) indicated a constant value with a variation of less than ±0.5°C. The variation in thermal conductivity as a function of mean bulk temperature was determined.

Figure 4-3 shows the variation of thermal conductivity k as a function temperature for PDMS composites filled with carbon black with different filler fractions ranging from 10-25 wt %. The measurements of the thermal conductivity were made in the temperature range of 50-200°C. The general trends showed that the thermal conductivity decreased with an increase in temperature for all the specimens considered in the present investigation up to about 90°C. However, thermal conductivity remained constant with minor variations up to a temperature of 180°C. For the specimens with 22 wt % and 25 wt % carbon black, thermal conductivity appeared to increase beyond 180°C up to 200°C. The experiments were terminated at 200°C due to possible degradation of the samples. When compared with pure PDMS, there was a remarkable enhancement (an order of magnitude) in thermal conductivity of PDMS loaded with carbon black nano-particles in varying proportions. For example in specimens with 10 wt % carbon black, the PDMS acquired thermal conductivity of 2.07 $Wm^{-1}K^{-1}$ as against 0.17 $Wm^{-1}K^{-1}$ for PDMS without carbon black. The experimental results also showed that the thermal conductivity of the samples increased in general with the percentage (10-25%) of

carbon black present in the composite. This was attributed to the increase in conductive pathway and network density with an increased number of filler particles (Burden et al., 1998).

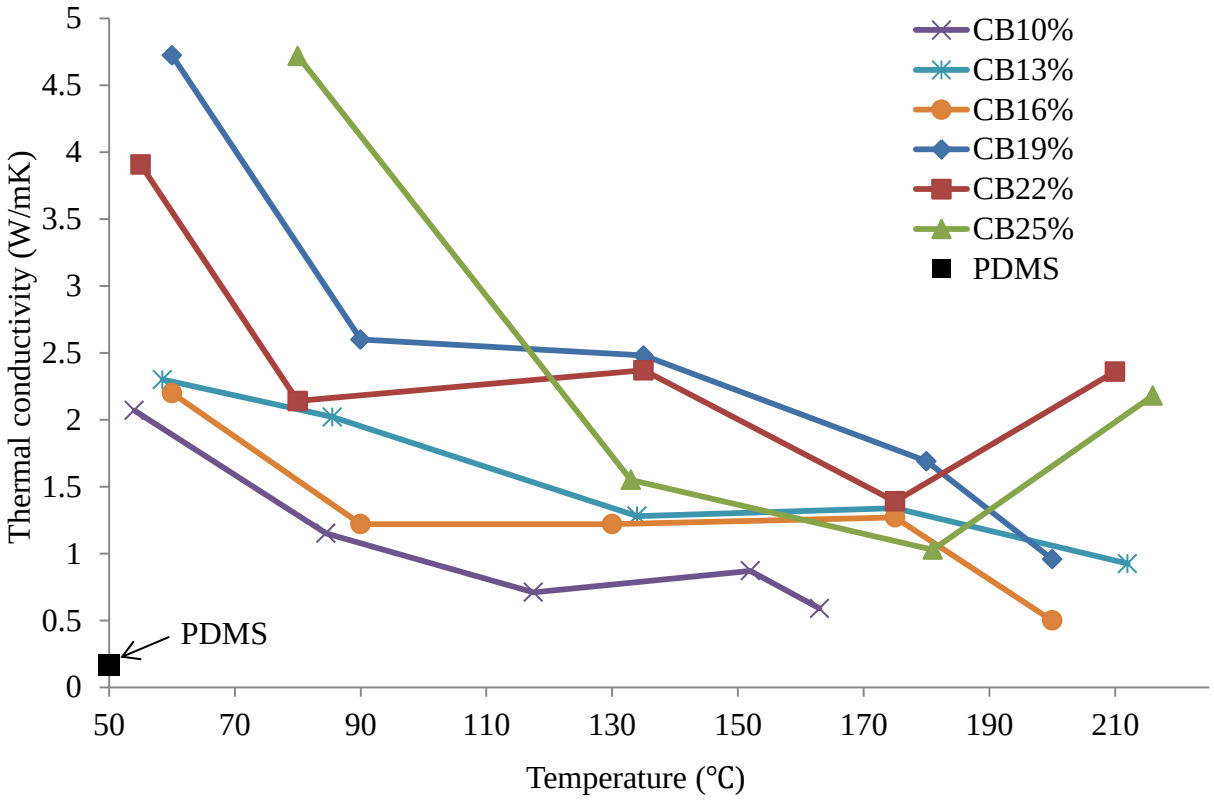


Figure 4-3 Thermal conductivity vs temperature for carbon black-filled PDMS composites with different filler loadings (10–25 wt %) The solid dot represents pure PDMS thermal conductivity value

The thermal conductivity data of the present experimental investigation is more promising when compared with the investigations carried out earlier by other researchers. For example, the thermal conductivity of epoxy resin with 70 wt% carbon black nanofiller is 1.8 $Wm^{-1}K^{-1}$ (El-Tantawy et al., 2002). Whereas in the present experimental investigation, it was found that a thermal conductivity value of 2.07 $Wm^{-1}K^{-1}$ could be achieved with a 10 wt% of

carbon black in PDMS. This means, a lesser wt% (almost seven times) of carbon black was needed in the case of PDMS when compared with epoxy resin to achieve the same or slightly higher values of thermal conductivity. Carbon black as nanofiller in PDMS is more effective in improving thermal conductivity than in epoxy resin.

Furthermore, it is to be noted from the data published by Liu et al. (Liu et al., 2004) that both carbon nano tubes and carbon black at equal loading in PDMS equally improve a thermal conductivity in a comparable way. Thus, there was no significant difference in thermal conductivity values between carbon nano tube and carbon black filled PDMS in their experiments. However, carbon black is much less expensive when compared with the carbon nano tubes. Thus, the choice of carbon black as nanofiller in PDMS would be a better choice in the context of the mass production of the CB–PDMS based fuel cells.

4.2.2 PDMS-Silver composite

Thermal conductivities of silver PDMS (Ag-PDMS) composites are presented in Figure 4-4. Silver filler loading varies from 50wt% to 77wt%, and the thermal conductivity is plotted against temperature ranges from 40°C to 170°C.

At a lower temperature range (40°C to 60°C), 65 wt% the silver filled PDMS sample showed the highest thermal conductivity of 2.23 $Wm^{-1}K^{-1}$, followed by the 77 wt% sample, while the rest of the samples presented very similar thermal conductivities with small variations.

It was found that the thermal conductivities for most of the samples decreased with increasing temperature, and this result agreed with the findings of Kline and Hansen (Kline.D.E., 1970), their results showed that natural rubber had a lesser thermal conductivity at 90°C than at 40°C. Although silver fillers were incorporated in the PDMS matrix, and the thermal

conductivity improved, however, due to the low conductivity of pure PDMS, it still dominated the thermal property characters of the composites.

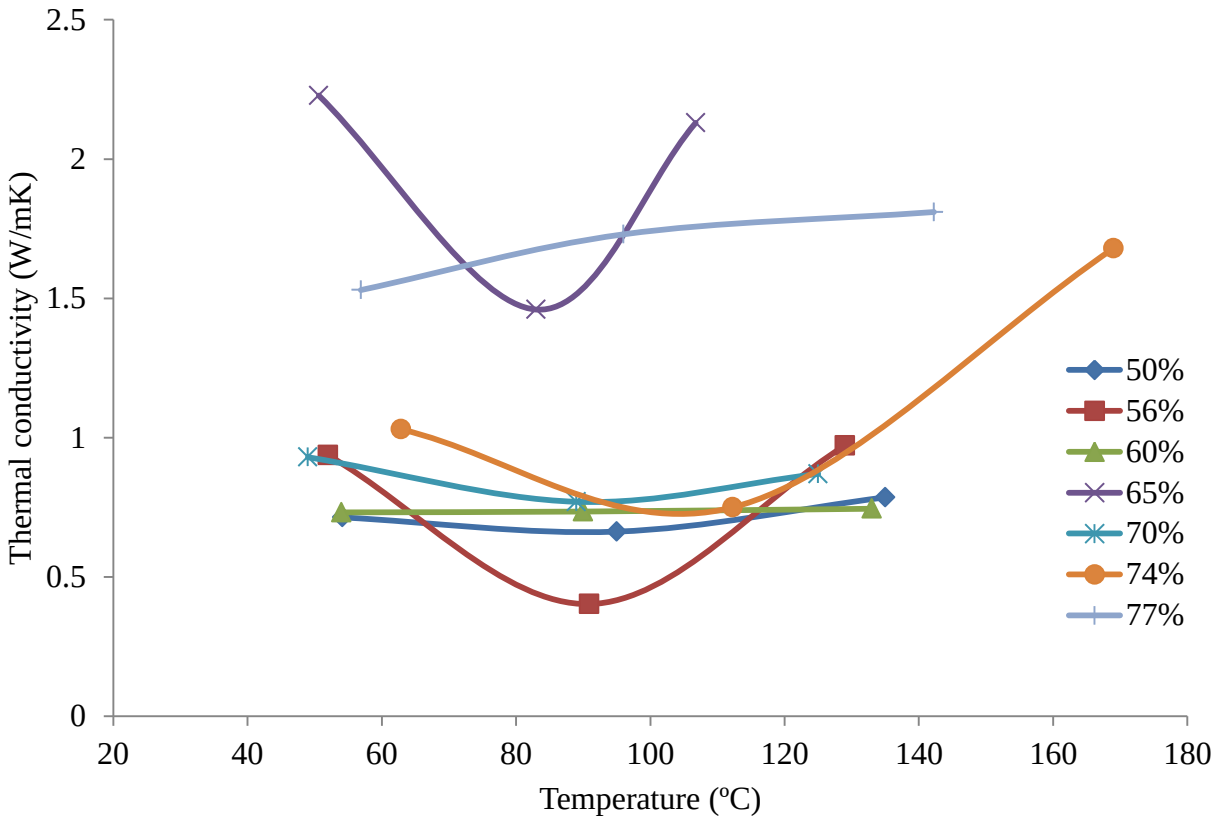


Figure 4-4 Thermal conductivity vs temperature for Silver-filled PDMS composites with different filler loadings (50–77 wt %)

4.3 Thermal Stability

One of the targets for bipolar plate material is that it needs to be thermally stable up to 120°C. For bipolar plates made of metal and graphite, it is not an issue. But for polymer composites especially thermoset polymers, since they generally have low glass transition temperatures and melting points, it is very important to study their thermal stability. In this section, the

thermal stabilities of PDMS-Carbon black composite and PDMS-Silver composite are presented.

4.3.1 PDMS-Carbon black composite

The thermal stability behaviours of the PDMS and PDMS-CB composites with different filler loadings in a nitrogen environment are shown in Figure 4-5. The analysis indicates that the PDMS was thermally stable up to 250 ºC with a weight loss of 1%. Sharp losses of weight occurred at 552 ºC (83% remaining), 709 ºC (53% remaining) and at 800 ºC, 35% of the weight was left.

The TGA of PDMS-CB composites showed that the infiltration of carbon black into the polymer matrix had enhanced the stability of PDMS (Figure 4-6). In the temperature range of 510 ºC to 550 ºC, the sample degraded faster as the filler concentration increased, at 510 ºC, PDMS-CB composite samples had a weight loss of 10%-15% for all concentrations, however, at 550 ºC, the 10% CB loading sample had 76% weight remaining while the 25% CB sample had only 55% weight left. Also at 800 ºC more than 40% was remaining for PDMS-CB as compared to 35% weight for pure PDMS. The thermal stability/degradation performance of the PDMS-CB composites was compared with PDMS/CF/PPy and PDMS-Pth composites in the literature (Çakmak et al., 2004; Sankır et al., 2003). For example, in PDMS-CB composites the weight loss was only 10% – 15% at ~ 500 ºC, which was better than when compared with the 18% weight loss at 399 ºC in PDMS-CF/PPy composites(Çakmak et al., 2004). Also in the case of PDMS-Pth composite, Mehmet Sankir et al (Sankır et al., 2003) reported a derivative peak due to solvent loss at 75 ºC. There was not any such solvent loss low temperature peak for the 22% CB-PDMS sample (Figure 4-7). Further in the PDMS-Pth composite the onset of degradation started at <130 ºC and already

10% weight loss had occurred around 250 ºC. The differences in the above mentioned results between this project and the literature are mainly due to the higher thermal stability of PDMS, the samples reported in literature were prepared with PDMS and other polymers while in this project, PDMS was the only polymer in the composite. In view of these findings recorded in the literature, the PDMS-CB composites in this study had better thermal degradation properties. The composites were very stable at a lower temperature range (30 ºC to 200 ºC), which is typically the operation environment for fuel cells.

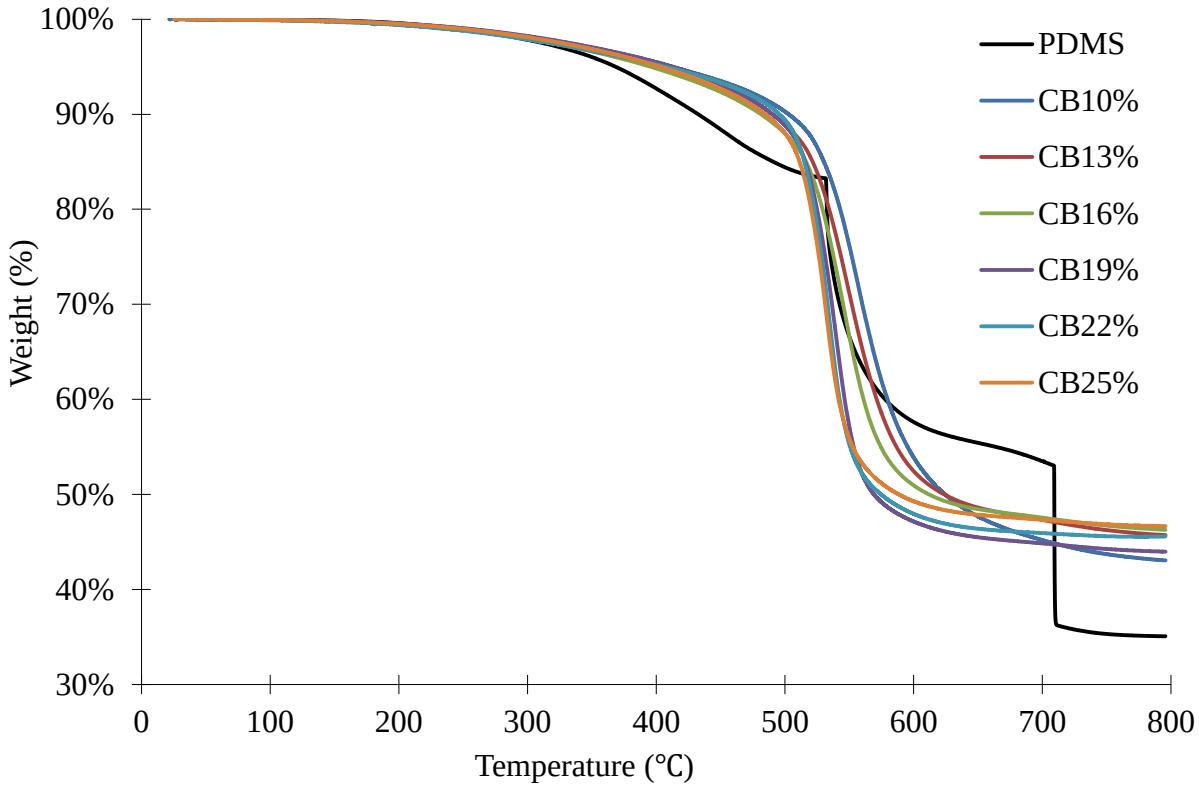


Figure 4-5 TGA analysis of pure PDMS and PDMS-CB composites in Nitrogen

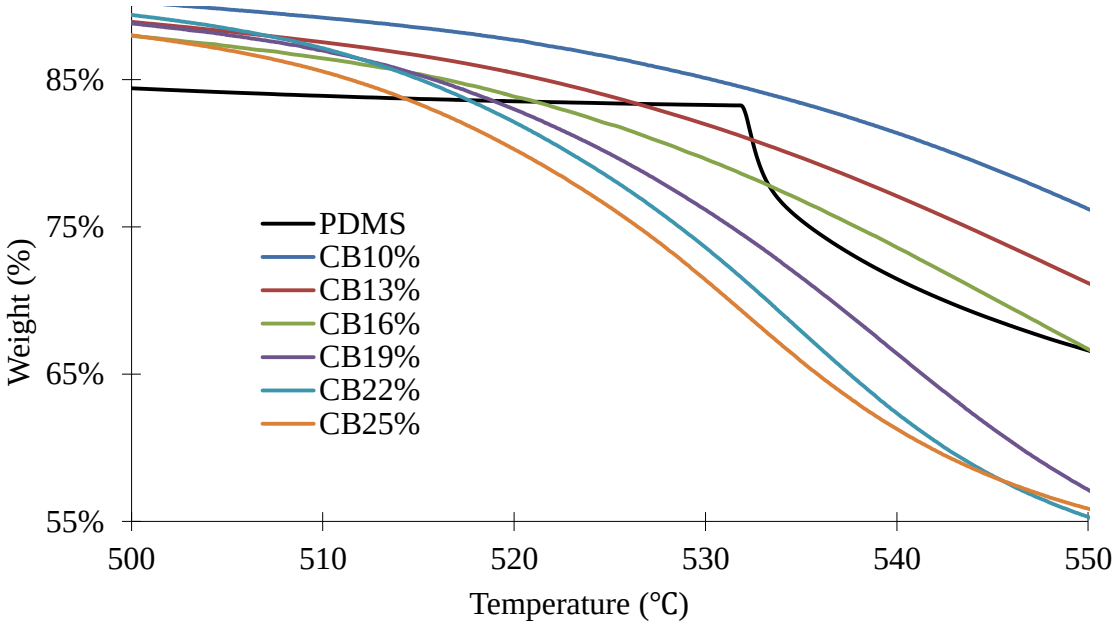


Figure 4-6 A zoom between 500 and 550 ºC of figure 4-2

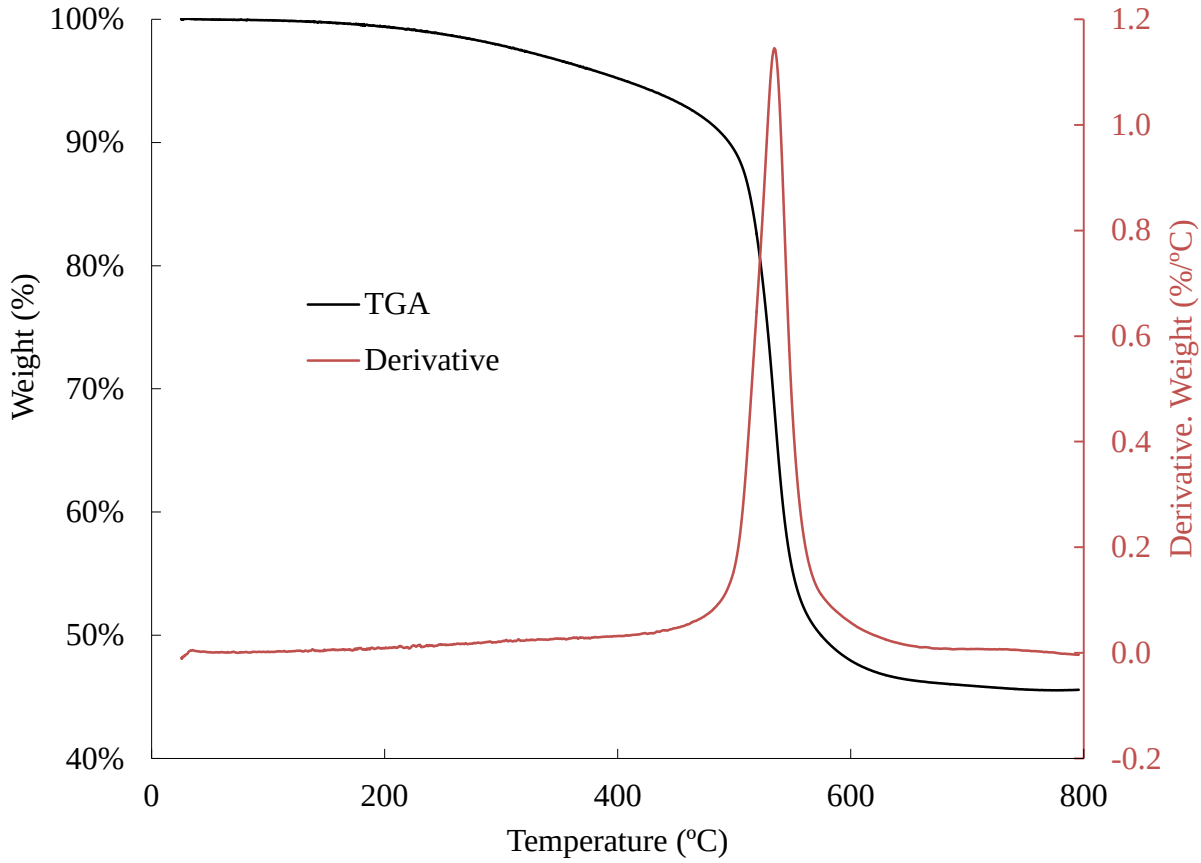


Figure 4-7 TGA and its derivative plot for our 22% PDMS-CB sample in Nitrogen

It is vital that the composite material maintains thermal stability at the high operating temperature of fuel cells. TGA data illustrated in Figure 4-8 presents the thermal stability/degradation of carbon black filled PDMS composites with various filler fractions in oxygen atmosphere. The TGA experiment under oxygen atmosphere was due to the specific application of these composites in the fuel cell context in an oxidative environment.

Results showed that all composites and pure PDMS started to degrade at 300ºC with 1.5% weight loss. The first apparent weight loss for PDMS occurred between 300ºC and 400ºC and a rapid weight loss was found around 500ºC, then 47% of the residual PDMS appeared to be stable up to 800ºC. However, for the samples with carbon filler, the first weight loss peaks were only observed in the range of 450ºC to 550ºC. TGA measurements carried out under nitrogen atmosphere in these samples showed similar results in weight loss. Furthermore, second weight loss peaks rose above 700ºC in all CB filled PDMS samples.

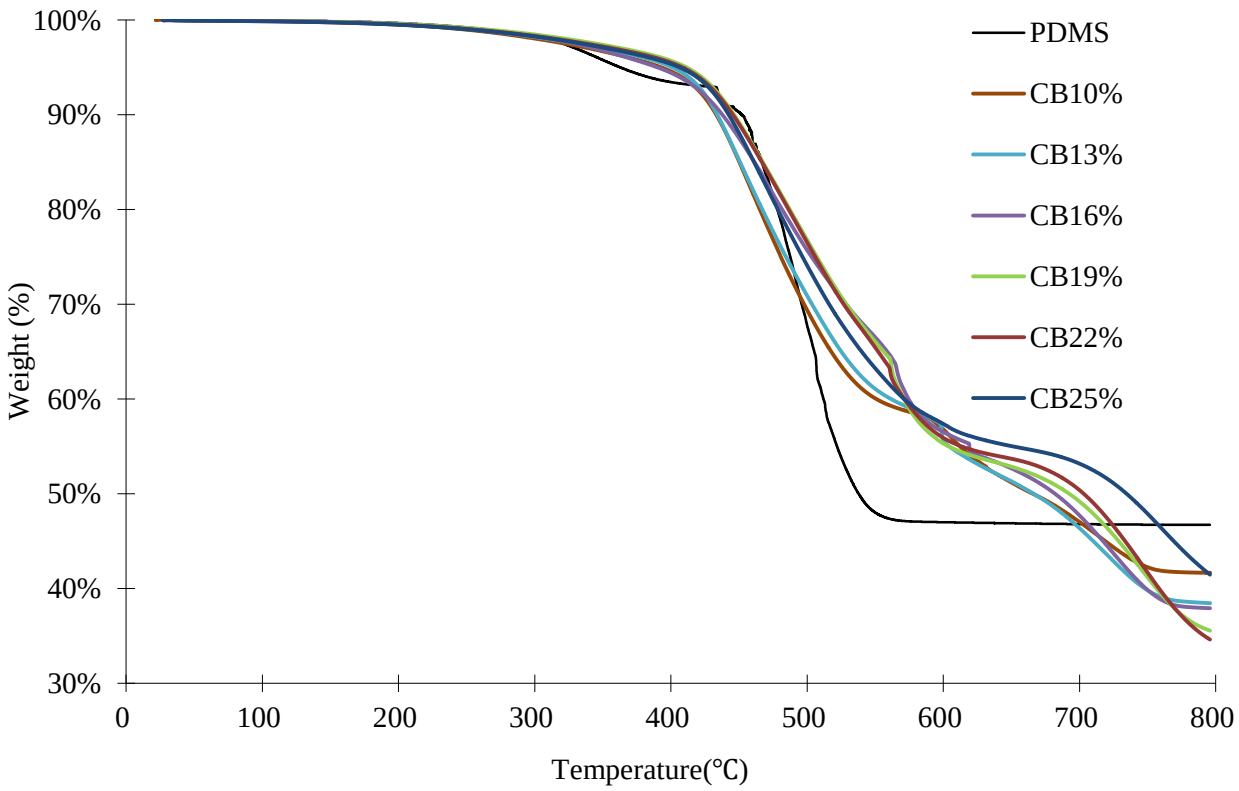


Figure 4-8 TGA analysis of pure PDMS and PDMS-CB composites with filler loadings range 10wt%-25wt% under oxygen atmosphere

Figure 4-9 shows the weight loss and its derivative for 25wt% filled PDMS composite under oxygen and nitrogen atmospheres. From the figure, two major weight losses for the sample under oxygen can be seen, and the corresponding exothermic peaks can be found on the derivative of the TGA curve at 475 and 761°C, respectively. The first weight loss can be ascribed to be the degradation of PDMS polymer matrix with the catalysis of oxygen (Camino et al., 2001; Tiwari et al., 2004). According to Chhina et al. (Chhina et al., 2006), carbon black (Vulcan XC72) is thermally stable and does not oxidise until 700°C in air, and the only weight loss peak was reported at 750°C. It can be assumed that the second weight loss peak was due to the decomposition and oxidisation of the carbon black filler. This also agrees with the TGA studies of carbon black (Vulcan XC72) in the literature (Baturina et al., 2006; Su et al., 2005; Su et al., 2005).

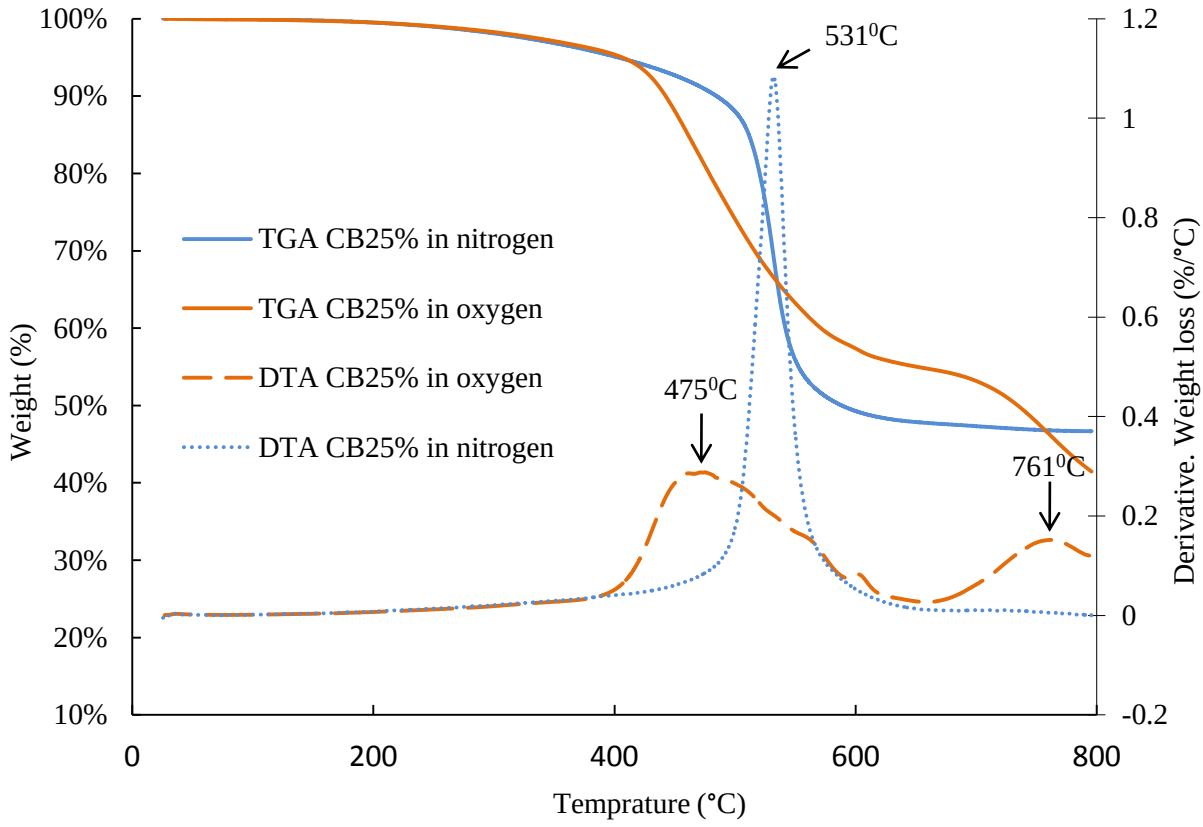


Figure 4-9 Weight loss and its derivative as a function of temperature for 25wt% carbon black filled PDMS composite under oxygen and nitrogen atmosphere

Characteristic temperatures at 50% weight loss of the samples are listed in Table 4-2. It is noticeable that these temperatures ascend with increasing filler fractions. This also indicates that the incorporation of carbon black filler in the PDMS polymer matrix improves the thermal stability of the polymer composite (Jakab and Omastová, 2005; Omastova et al., 2003; Zhang et al., 2003).

Table 4-2 Temperatures at 50% weight loss of CB-PDMS samples under oxygen

Sample	PDMS	CB10%	CB13%	CB16%	CB19%	CB22%	CB25%
Temperature(°C)	537.77	665.65	666.28	681.95	692.38	703.02	734.53

4.3.2 PDMS-Silver composite

Figure 4-10 presents the TGA curves for PDMS-Silver composite samples with filler loadings from 50wt% to 77wt%, performed under nitrogen atmosphere. The TGA curve of PDMS-Ag composite samples showed that weight loss started at 100ºC. In the range of 200°C to 400°C, samples with less silver filler loadings degraded at a higher rate than samples with more silver fillers. Intensive weight loss peaks were found between 433°C and 480°C for all samples. Above 500°C, samples became thermally stable and weight remained constant up to 800°C. It was noticed that in the temperature range, the weight remaining of the samples corresponded to the order of filler loadings and was very close to the silver filler wt% in the samples. This showed that the sample weight residual was mainly silver fillers, PDMS polymer matrix had highly degraded. Compared with the TGA results of PDMS-CB samples under nitrogen, the weight loss peak of PDMS-Ag samples had shifted at about 50°C to a lower temperature.

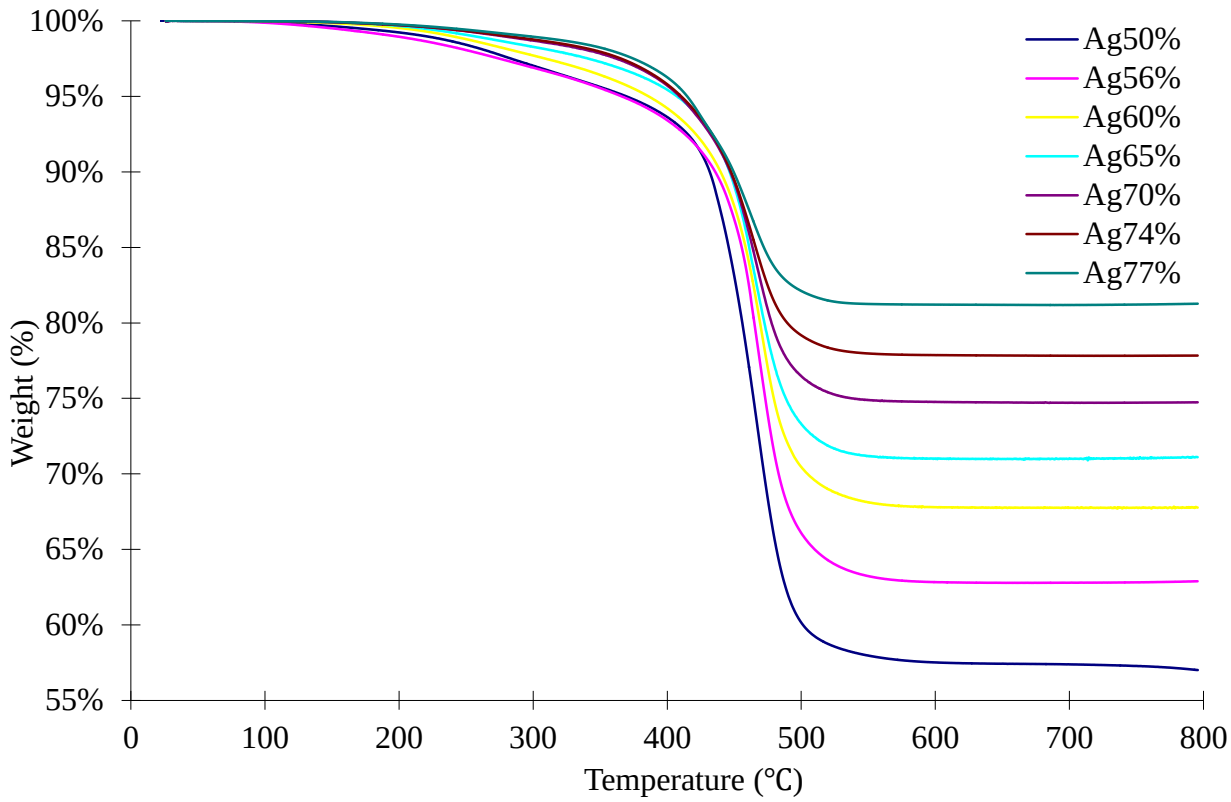


Figure 4-10 TGA analysis of pure PDMS and PDMS-Ag composites with filler loadings range 50wt%-77wt% under nitrogen atmosphere

Figure 4-11 illustrates the TGA of PDMS-Ag samples under oxygen atmosphere. Samples started to decompose from 126°C, weight percentage residual of samples at 300°C as tabulated in Table 4-3, and there was a general trend that samples were more stable with increasing silver filler loading.

Table 4-3 Weight remaining of CB-PDMS samples at 300°C under oxygen

Sample	Ag 50%	Ag 56%	Ag 60%	Ag 65%	Ag 70%	Ag 74%	Ag 77%
Weight remaining at 300°C (%)	98.00	98.14	97.85	98.42	98.55	98.87	99.09

Sharp weight loss occurred at 400°C, and samples became stable from 600°C. Compared with the results under nitrogen, the samples showed similar thermal behaviours, however, less systematic, which could be attributed to the sample shape and size, since all samples for TGA analysis were manually cut by a scalpel, and homogeneity of the filler distribution also played a role.

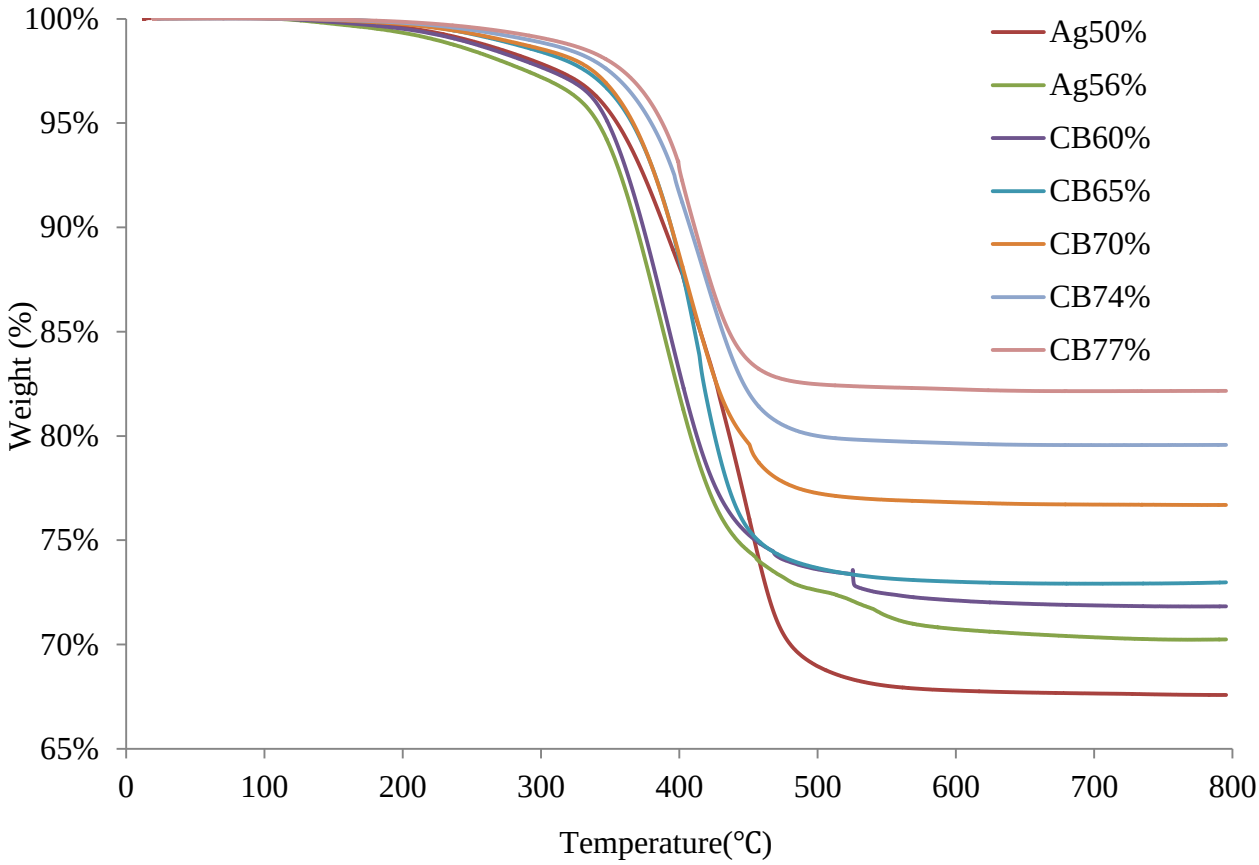


Figure 4-11 TGA analysis of pure PDMS and PDMS-Ag composites with filler loadings range 50wt%-77wt% under oxygen atmosphere.

4.4 Dynamic Mechanical Properties

PDMS has a relatively low mechanical strength. In order to enhance the mechanical properties, Cong and Pan (Cong and Pan, 2008) performed a mechanical tensile test for PDMS and PDMS-silver powder composites, and the results showed that the tensile modulus

increased 2.1-2.5 times with 17–21 vol% silver fillers. However, in many engineering applications, composites are mostly used in a dynamic environment. It is important to understand the dynamic mechanical behaviour of the composite, especially in fuel cell applications, as they are mostly used in mobile devices. In this section, the effect of carbon black particle and silver particle on the dynamic mechanical property of PDMS, with respect to different filler concentrations and temperature range is investigated.

4.4.1 PDMS-Carbon black composite

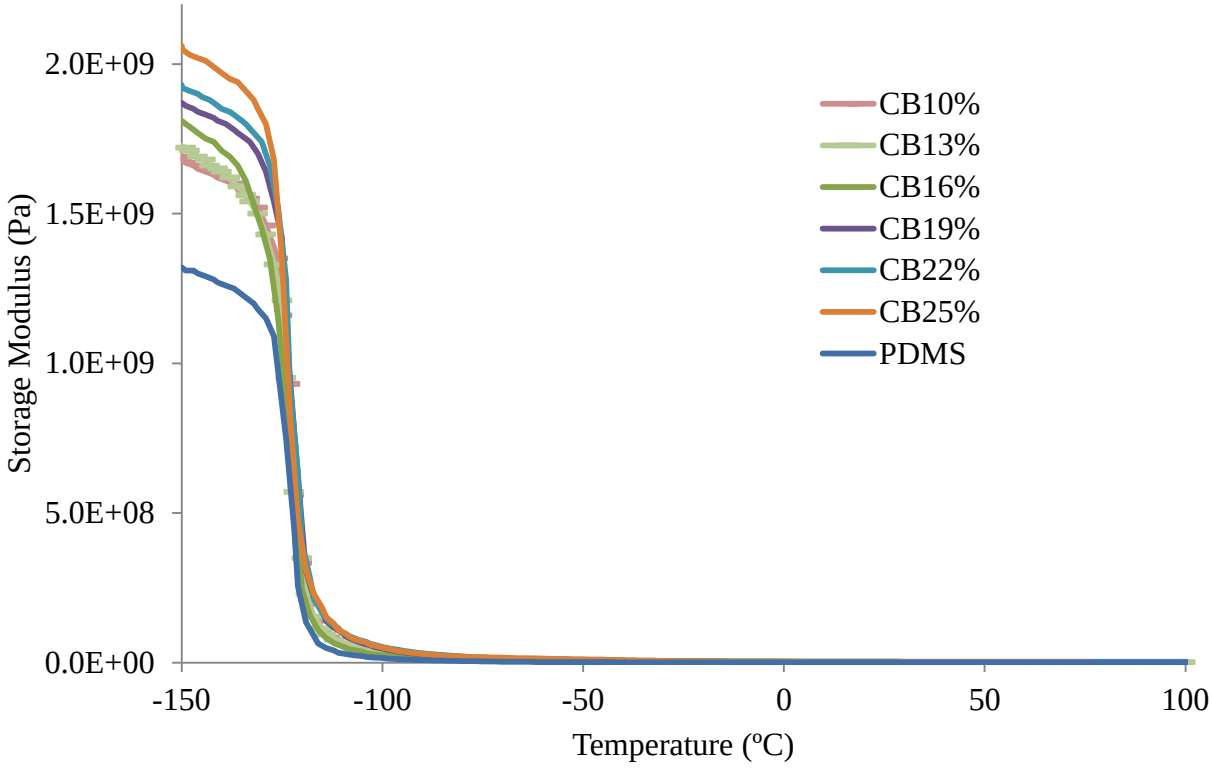


Figure 4-12 Temperature dependence of the storage modulus of pure PDMS and the PDMS-CB composite

The dynamic mechanical response reveals the amount of energy stored as elastic energy and the amount of energy dissipated in the composite upon the application of a harmonic strain, strongly dependent on the level of dispersion-distribution of the fillers and their interaction with the PDMS polymer matrix. The temperature dependence of the storage modulus (*G*')

and Tan δ of the pure PDMS and the composites is shown in Figure 4-12 and 4-13 respectively. The composites showed an observable increase in the elastic modulus compared to that of the pure PDMS, particularly in the glassy region. This was due to the presence of carbon black nano particles, which particles offered a stabilizing effect that resisted the deformation when the composite was subjected to a dynamic strain (Paul et al., 2006). PDMS has a glass transition temperature of -120°C, when the polymer reaches the glass transition temperature, a sharp decrease will be found for the storage modulus as well as a peak for the Tan δ. These are both confirmed in Figure 4-12 and 4-13.

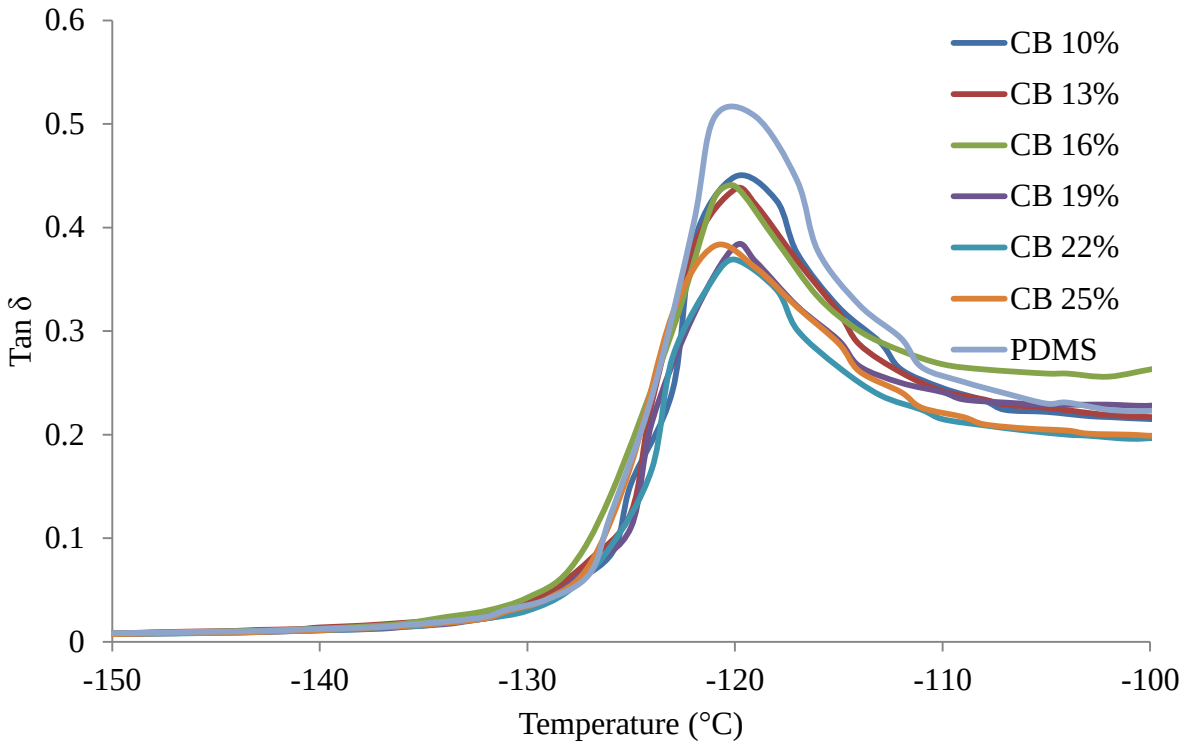


Figure 4-13 Temperature dependence of the Tanδ of pure PDMS and the PDMS-CB composite

4.4.2 PDMS-Silver composite

Figure 4-14 shows the temperature dependence of the storage modulus of pure PDMS and the PDMS-Ag composite. A similar pattern was found in general compared with the results for PDMS-CB composites. However, a remarkable enhancement for 70wt% and 77wt% silver filler loading was noticed compared with the rest of the samples. As compared to pure PDMS polymer, the modulus had increased 2.4 times. An interesting finding was observed with the improvement of electrical conductivities. Both can be explained by the percolation threshold theory, when the random particles in a polymer matrix reach a critical point, the properties of the composite improve significantly. Also the PDMS-Ag composites exhibited a superior modulus than the PDMS-CB composites because of the high concentration of silver particles.

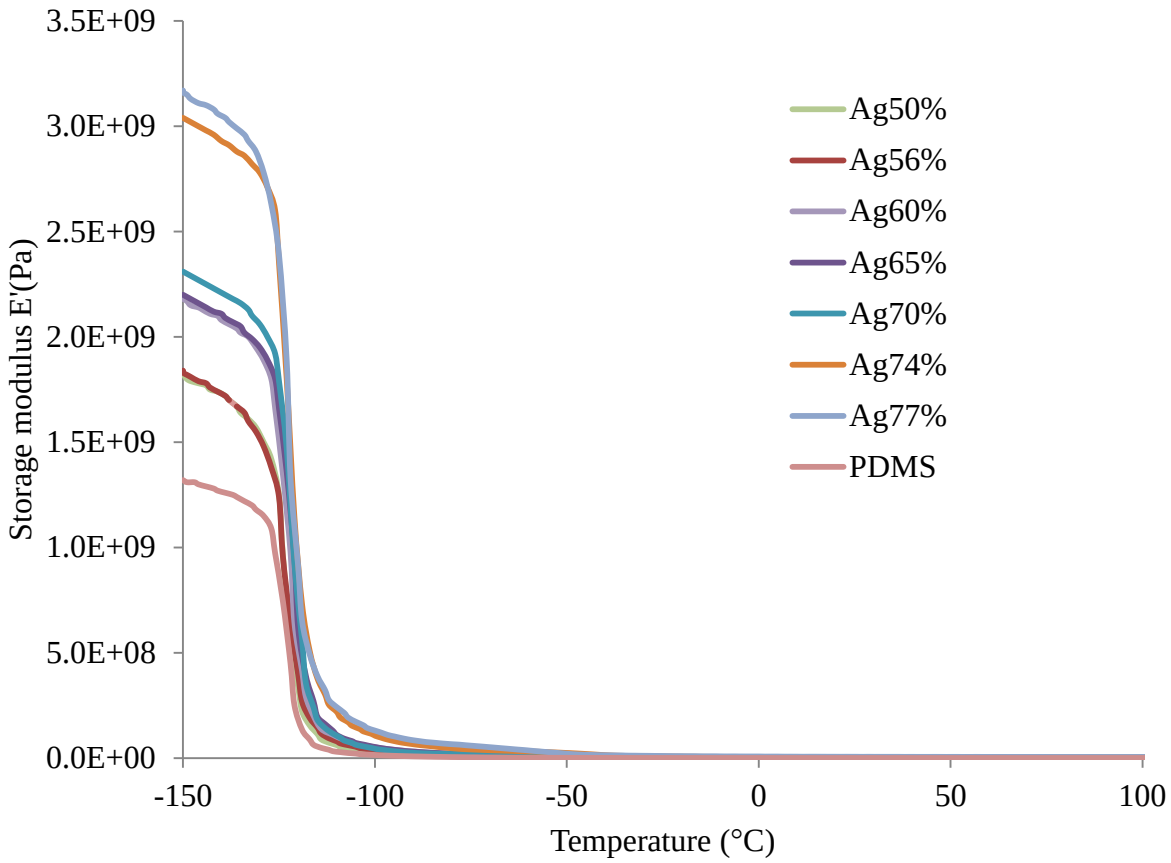


Figure 4-14 Temperature dependence of the storage modulus of pure PDMS and the PDMS-Ag composite

Figure 4-15 confirms the glass transition temperature of -120°C. From the Tan δ Verses Temperature figure for both PDMS-CB composites and PDMS-Ag composites, the conclusion can be drawn that the introduced fillers in the polymer have hardly had any effect in the glass transition temperature of the polymer matrix.

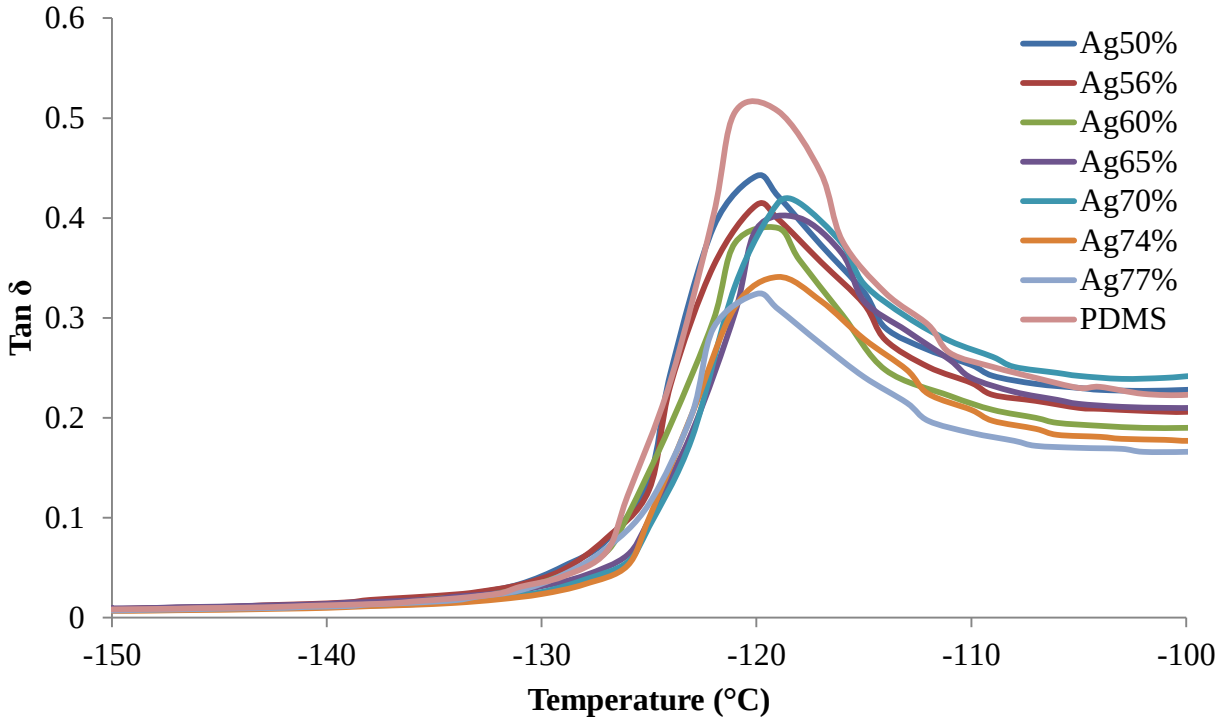


Figure 4-15 Temperature dependence of the Tanδ of pure PDMS and the PDMS-Ag composite

4.5 Scanning Electron Microscopy (SEM)

The morphological characteristics of the freeze-fractured surfaces of PDMS and two different composite systems were investigated by field-emission SEM (FE-SEM). Parts (a) – (d) of Figure 4-16 show the fractured surfaces of the PDMS composites containing (a) 10 wt %, (b) 13 wt %, (c) 16 wt %, (d) 19 wt%, (e) 22 wt% and (f) 25 wt % carbon black loadings. The increasing proportion of carbon black fillers in the PDMS polymer matrix can be clearly seen

in the figures. Relative uniform particle distribution can be observed in Figure 4-16, the scale bar representing one micro metre in all the of 6 images.

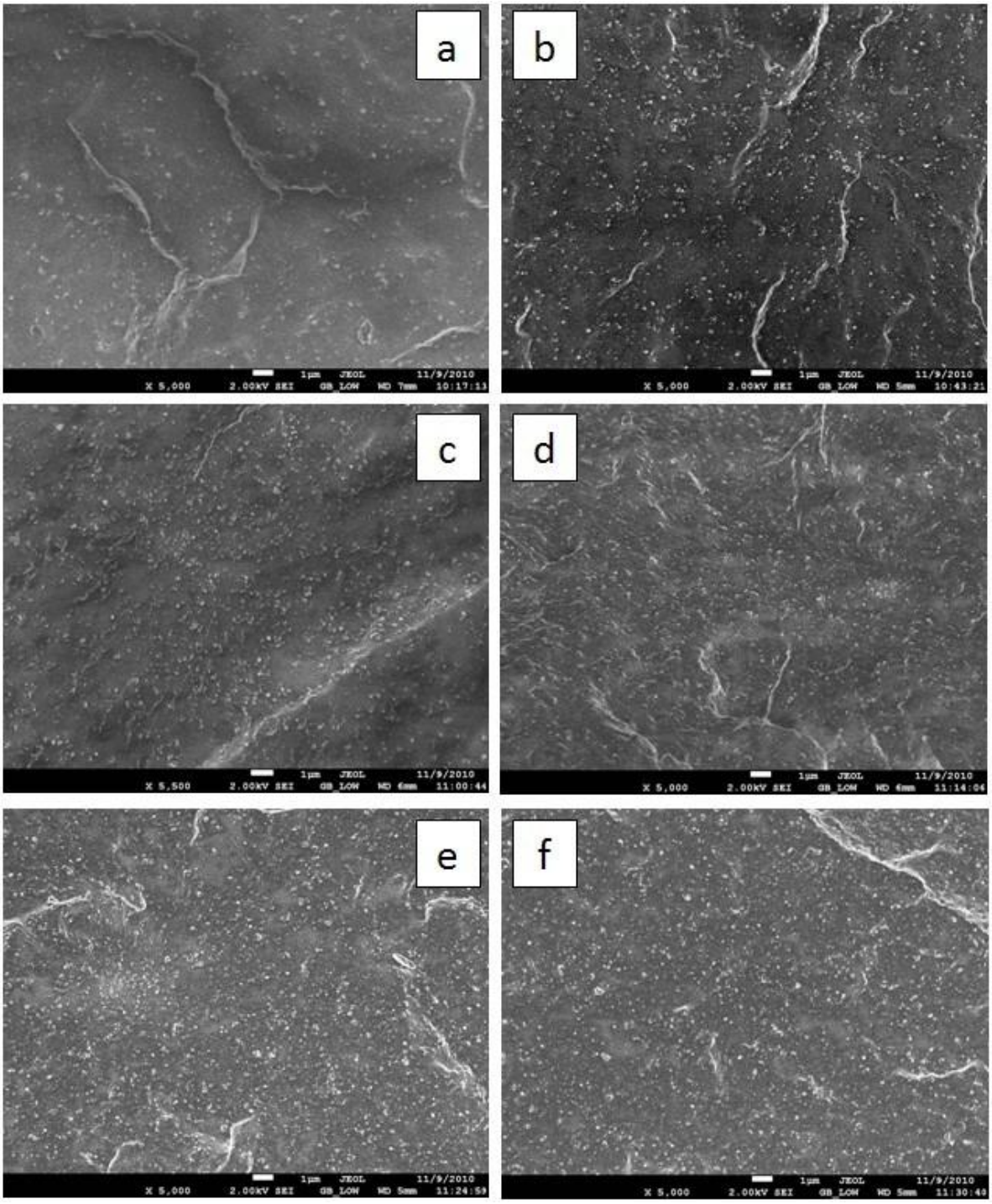


Figure 4-16 SEM images of PDMS composites containing (a) 10 wt %, (b) 13 wt %, (c) 16 wt %, (d) 19 wt%, (e) 22 wt% and (f) 25 wt % Carbon black loadings

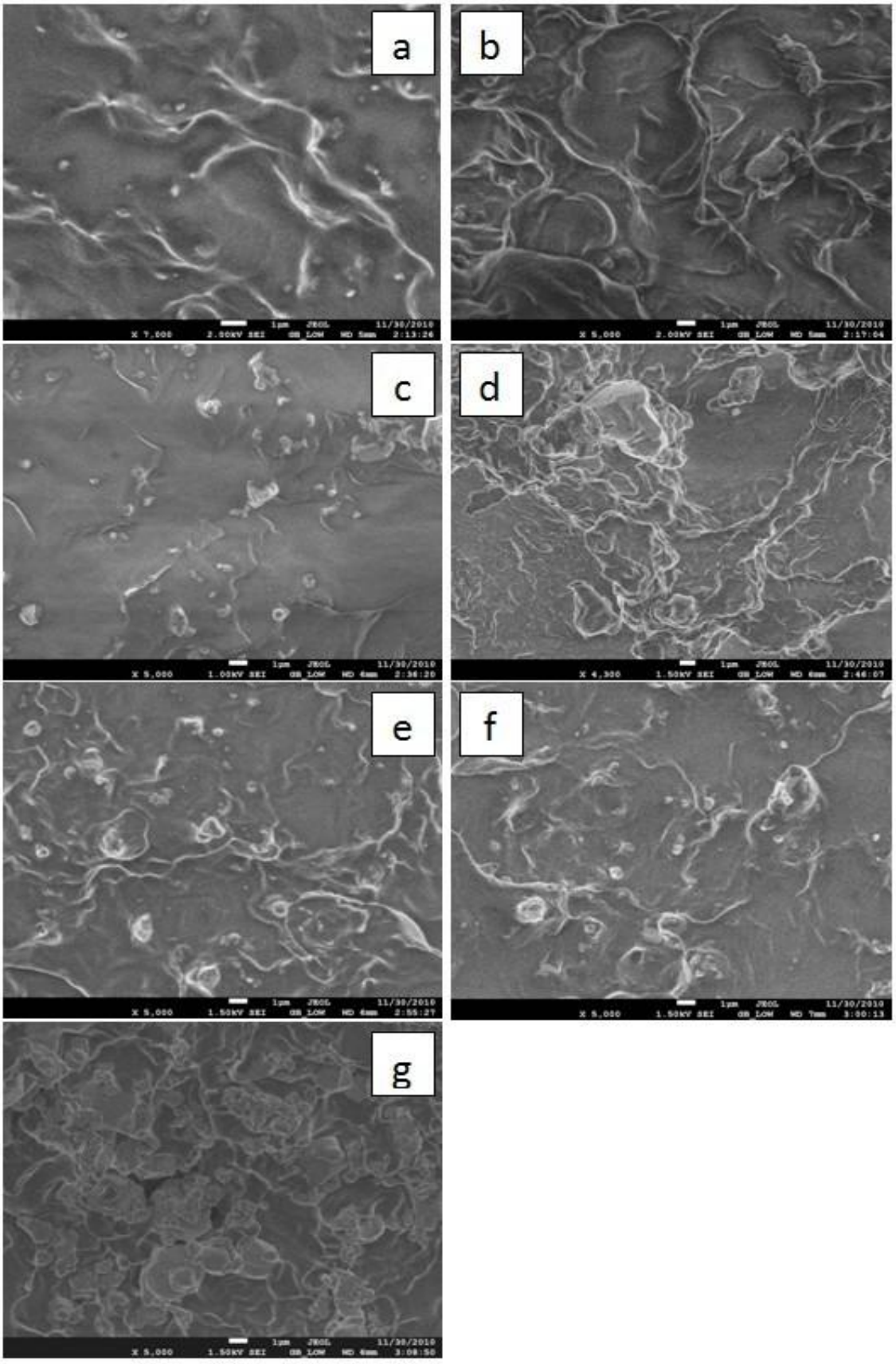


Figure 4-17 SEM images of PDMS composites containing (a)50 wt %, (b) 56wt %, (c) 60wt %, (d) 65wt%, (e) 70wt%, (f) 74wt% and (f) 77 wt % Silver loadings

Due to the higher density of silver particles compared with carbon black, although the PDMS-Ag composites have more filler in weight percentage, much fewer particles can be observed in Figure 4-17 than in Figure 4-16.

In Figure 4-18, the image shows agglomerations of silver particles in the polymer matrix. The agglomeration would not likely result in high conductivity and lead to inconsistent mechanical properties. Further studies should consider a better mixing method for more uniform particle dispersion. Furthermore, some particle sizes are marked with the SEM built-in tool, where the diameter of these fillers ranges from 0.47μm to 1.1μm, however from the supplier data sheet, the particle diameter should be between 2-3.5 μm.

In this image, at 77 wt% silver loading, a certain degree of contact among fillers can be seen, and as a result, more closed electron paths are formed as conductive circuits. A Continuous phase of conductive filler is very critical for electrical conductivity, and this is consistent with the conductivity measurement results where composite with 77 wt% silver loading had a significant increase compared to the rest of samples.

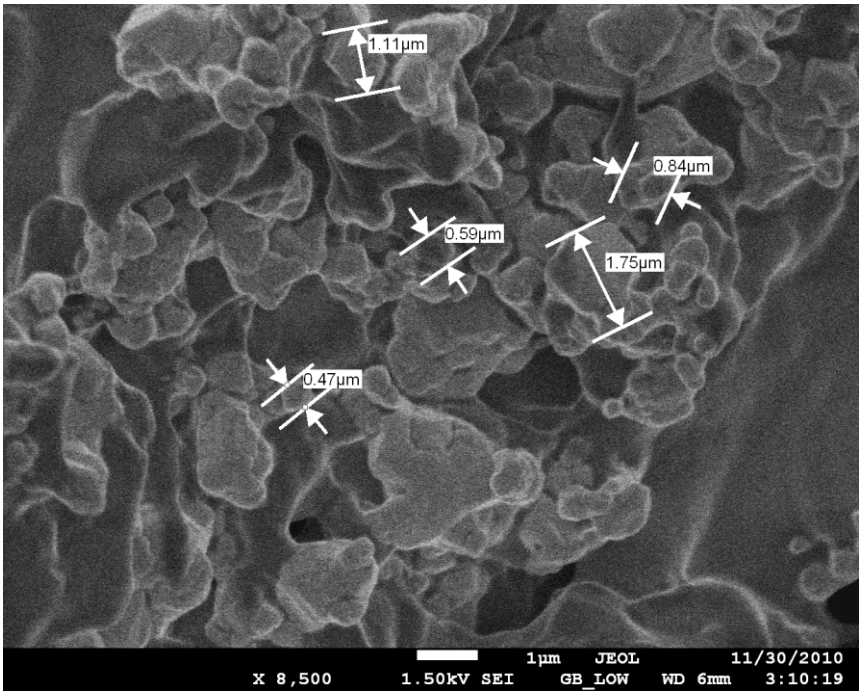


Figure 4-18 Particle size measurement with SEM

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

This project is designed to study the feasibility of using polymer composite in a fuel cell structure. Several experiment methods were employed for the investigation. These included electrical conductivity measurement, thermal conductivity and stability studies, mechanical property study and morphology study.

The first chapter set an overview by introducing the core research problem and why the project has been designed. Then chapter 2 provided the background knowledge and identified current research status and gaps. By using various experiment methods, chapter 3 and chapter 4 answered the research questions. Finally, chapter 5 briefly summarizes the findings and conclusions that can be made based on the whole study.

5.2 Conclusions to the Research Problems

Minimizing the size and weight of a fuel cell is one of the focus areas of the fuel cell research, therefore polymer composites were proposed as fuel cell structural material in this project for several reasons: Their smaller density compared to metal, their mechanical flexibility, and their chemical resistivity. With the proper selection of polymer and conductive fillers, the investigation of utilizing polymer composites in a fuel cell structural material was carried out.

Experiment results showed that the electrical conductivity had been improved by a magnitude order of 10^{13} with 50wt% and 10^{16} with 77wt% silver loading. Compared to carbon black fillers, it had better electrical conductivity. Comparing these results with these recorded in

literature, the electrical conductivity is not superior, for several reasons, the particle sizes are relatively larger (micron size), the dispersing method (mixer was made in-house), and most importantly, the filler loading is less (because of the lack of equipment, 77% silver loading was the limit for this project). Although the results showed increase in the composite electrical conductivity, further improvement is necessary for the composite material to be used in a commercial fuel cell application.

With the incorporation of two different fillers, stability was enhanced and PDMS-CB composites showed better performance over PDMS-Ag composites. An order of magnitude increase in thermal conductivity of 10 wt% CB loaded PDMS–CB composite was observed when compared with that of pure PDMS. Thermal conductivity was also investigated as a function of temperature. A general trend was found, namely, a plateau of thermal conductivitiy for all CB filled PDMS samples (different filler fractions) in the temperature range of 90–180°C. This is a good region for operating the fuel cell, as the thermal conductivity is stable. However, though the thermal conductivity had been improved, the target of 10 $Wm^{-1}K^{-1}$ had not yet been met. More work still needs to be done on this aspect.

The mechanical properties of polymer composites are a very important research topic, since the presence of fillers leads to an increase in mechanical strength of the polymer, but most of the mechanical properties studies of composites have been conducted with tensile stress. In this work, focus was placed on the dynamic mechanical property, which provides information of the polymer composites under constant motion and varying temperatures. Both carbon black and silver particles improved the inelasticity of composites in the glassy region, which is what is needed for fuel cell application. However, at high room temperature range, the filler in the polymer showed very little effect on the composites. The Tan δ results showed that the filler had no influence on the polymerization of the polymer since the glass transition temperature remained unchanged with the incorporation of fillers.

The fillers in the polymer formed a “network-like” structure evidenced by the SEM. This “network-like” structure has significantly contributed to the improvement of the properties of the polymer composites. However, a certain agglomeration was found, but if a more advanced technique could be employed for the sample preparation process, a further impact should be achieved.

5.3 Research Limitations

This research dissertation has aimed to:

- Synthesize the polymer polydimethylsiloxane (PDMS) composite with fillers such as Carbon Black and Silver powder
- Evaluate the thermal, mechanical and electrical properties of the composite so that it can be utilized for fuel cell fabrication.

The research carried out focused on the aims proposed and therefore had its own limitations. These refer to the:

- Polymer matrix and conductive fillers selection
- Sample preparation process
- Other experimental techniques and studies

These limitations are acknowledged by the author, and the limitations should not detract from the findings of the dissertation. Extended research can be done by other students and researchers, as will be recommended below.

5.4 Future Research

Based on the foundation laid in this study, there is scope for further research in this field:

- A wide range of polymers and fillers are available, and so different polymer composites can be studied.
- Further research could include the density, thermal expansion, chemical resistance and corrosion. All critical factors from the fuel cell perspective.
- Although the PDMS composite has obtained improved material properties, for application in the fuel cell, electrical conductivity still needs to be further increased. A combination of multi fillers with different sizes could be introduced to the PDMS, to form a more closed electrical path for electrons.

In this dissertation, research was focused on modifying the material for the fuel cell structure, using fillers in the polymer matrix to improve the properties, lots of efforts were made into the material preparation. However, the key of fuel cell bipolar plate is to conduct electricity, in this case, high electrical conductivity is only necessary on the surface of the material. With this in mind, one could also investigate the use of cold gas dynamic spraying technology (BOTEF, 2013) to treat the material surface. Advantages of cold spray include high electrical and thermal conductivity, creating corrosion-resistant coating, ability to perform rapid prototyping and so on (CSIRO, 2013). More information can be viewed in Appendix 1. The approach can evaluate the impact of replacing graphite bipolar plates with polymer or other materials designed and manufactured using the advantages of cold spraying process. The higher electrical conductivity will lead to increased fuel cell efficiency by decreasing parasitic loss. The thickness of the plate can also be reduced by the cold spraying process which enables the formation of smaller stacks. The consideration of the Cold Spraying

technology in the design and manufacturing of bipolar plates is anticipated to bring new advantages in the development of fuel cells.

5.5 Publication and Conference

- Chen, H., Botef, I., Zheng, H., Mazza, M., Rao, V.V. and Srinivasu, V.V. (2011) 'Thermal conductivity and stability of nano size carbon black filled PDMS: Fuel cell perspective', *International Journal of NanoTechnology, Vol 8 No 6-8.*

- Chen, H., Botef, I., Rao, V.V and Srinivasu, V.V. (2011) Thermal properties of micron size Ag-added PDMS composites: A fuel cell perspective, *South Africa Institute of Physics (SAIP) Conference*, 2011 July 12th- 15th, Pretoria

- Chen, H., Botef, I., Guduri, B. and Srinivasu, V.V. (2010) 'Thermal and bonding properties of nano size carbon black filled PDMS', *International Conference on Advanced Nanomaterials and Nanotechnology 2009 AIP Conference Proceedings* , Guwahati. India.

- 'Thermal and mechanical properties of PDMS nano and micro composites for fuel cell applications' *Advanced materials and Technologies for Global Energy and Environmental Challenges Workshop* on the 7th, Dec 2010 at CSIR ICC, Pretoria

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Appendix 1: Cold spraying process

Cold spray is also called Gas Dynamic Cold Spray (GDCS), it is a coating technology developed by the researchers from the Institute of Theoretical and Applied Mechanics in the 1980s. Particles with size between 1 and 50 micro meters in diameter are accelerated up to 1000 m/s by supersonic gas jet. Then particles bombard the coating substrate and undergo plastic deformation, the spraying nozzle scans the substrate surface, therefore a uniform thickness layer of the particles forms on the substrate. Many types of particle material can be coated using cold spray, these include metals, polymers, ceramics and composites (Hofsajer and Botef).

Cold spray process typically operates at room temperature, unlike thermal spray that preheats the particles and creates thermal stress. The cold spray process has many advantages includes:

- Retaining initial properties of the particles
- Depositing oxygen-sensitive materials without vacuum
- Low oxide content
- High density
- High thermal and electrical conductivity
- High hardness and cold work microstructure
- Creating corrosion-resistant coatings
- Depositing plastic coatings without the need for volatile solvents
- Intermetallic coatings or repair (phase and compositional stability)
- Depositing metal on ceramic or metal on glass
- Ability to perform rapid prototyping.

This technology also offers the opportunity for direct fabrication of low defect parts, repairing defective areas without changing the structure, joining chemically dissimilar materials with bond that gradually transition from one material to other, low temperature alternative to welding, building a composite component using different material in different locations, and rapid prototyping(CSIRO, 2013).

Appendix 2: Experimental apparatus

Polymer blends mixer

The polymer blends mixer was used for composites mixing, and because of equipment availability, was made in-house. It consists of a 12V motor, motor support stand, mixing blade and a beaker. The mixer is powered by a DC power supplier. By varying the power supply voltage, the rotor speed can be varied. Since the first step was to identify the best composites with a certain weight percentage of conductive fillers and polymer, smaller samples were needed. Using this mixer to prepare different composites reduced material waste and the sample preparation time.

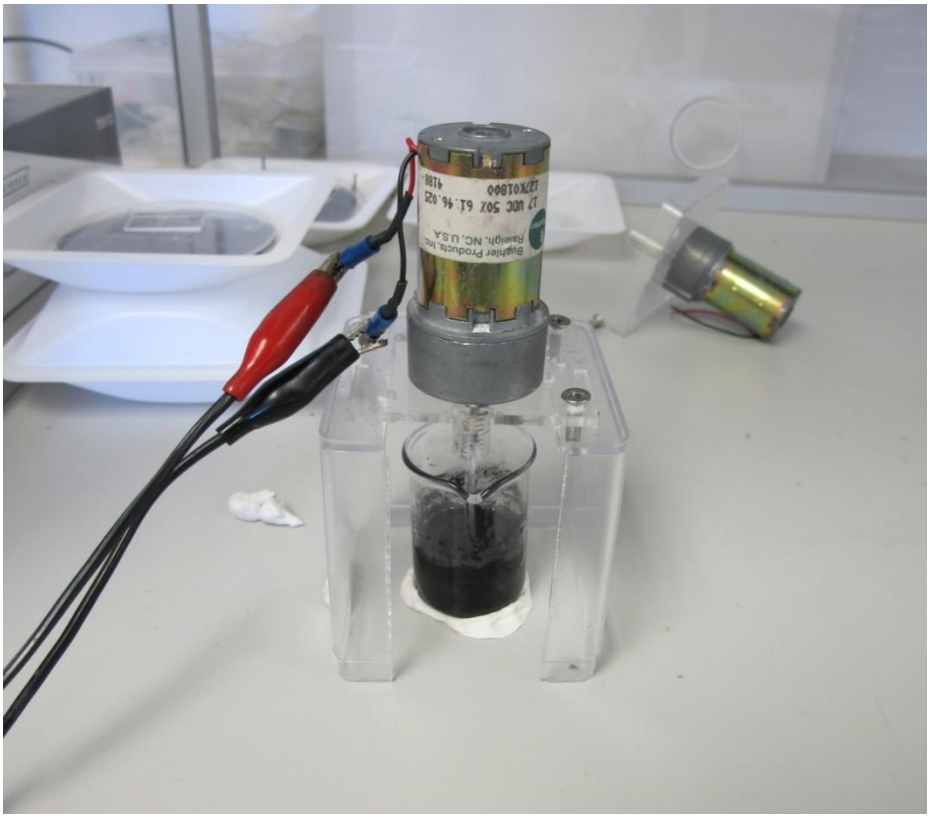


Figure 0-1 Polymer blends mixer

Degassicator

When mixing the polymer matrix and fillers in the mixer, bubbles are very often generated in the blends, if the blend is cured without removing these bubbles, the properties of the composite will be affected significantly. Therefore, degassing before curing is very important. The degassicator chamber is connected to a vacuum pump, the polymer filler blend is degassed when the pressure in the chamber is lower than in the blend, the air bubbles will rise to the surface and are therefore removed.

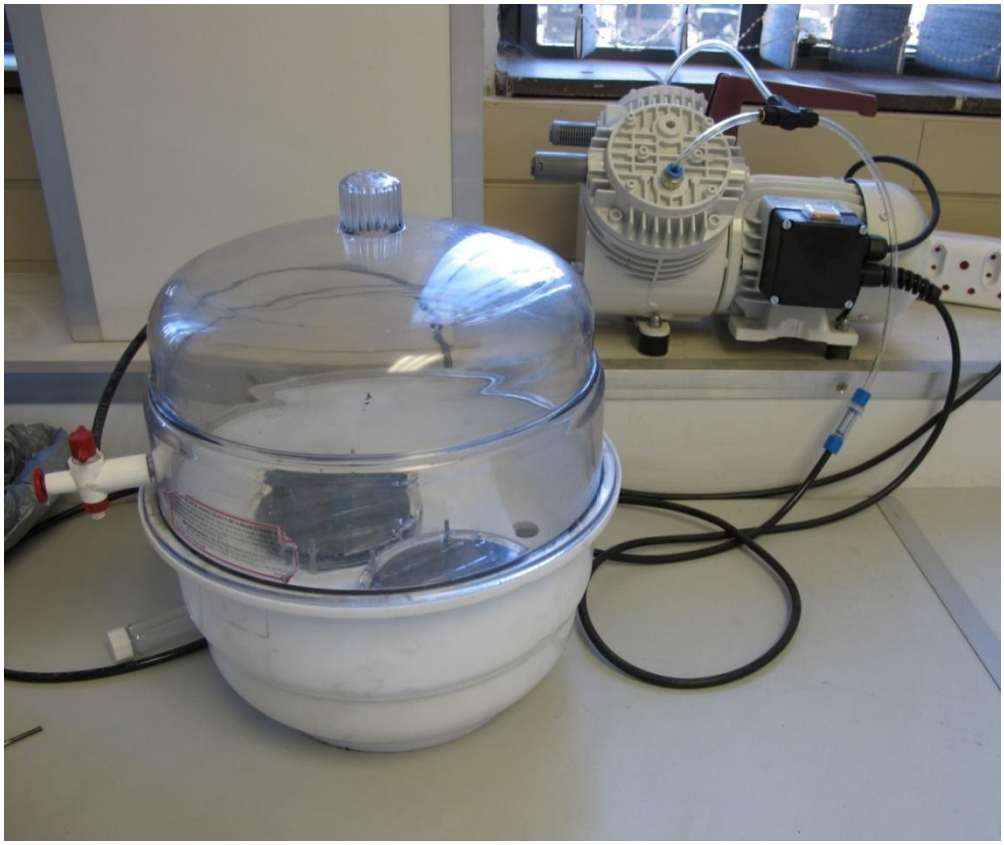


Figure 0-2 Degassicator

Oven

The oven was used to cure the PDMS and PDMS composite. As discussed previously, PDMS is supplied as a kit comprised of a base and a curing agent. The two parts mix in a ratio of 10: 1, when the two liquids are mixed thoroughly, the mixture cures at 60°C in an oven to form a flexible elastomer.

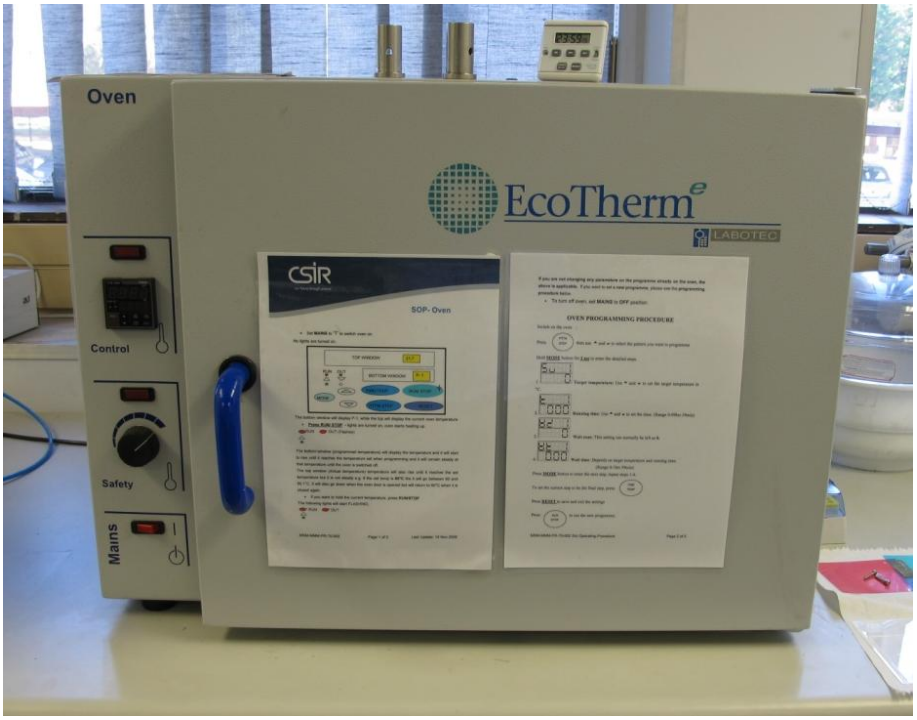


Figure 0-3 Oven

Four Point Probes resistivity measurement equipment

Figure 0-4 shows the four point probes station and Figure 0-5 shows the station and the computer connected to operate it. The distance between the two adjacent probes is 1mm, a current pulse of 1mA was used with 1Hz for 20 pulses, and the average was obtained from 20 measurements.

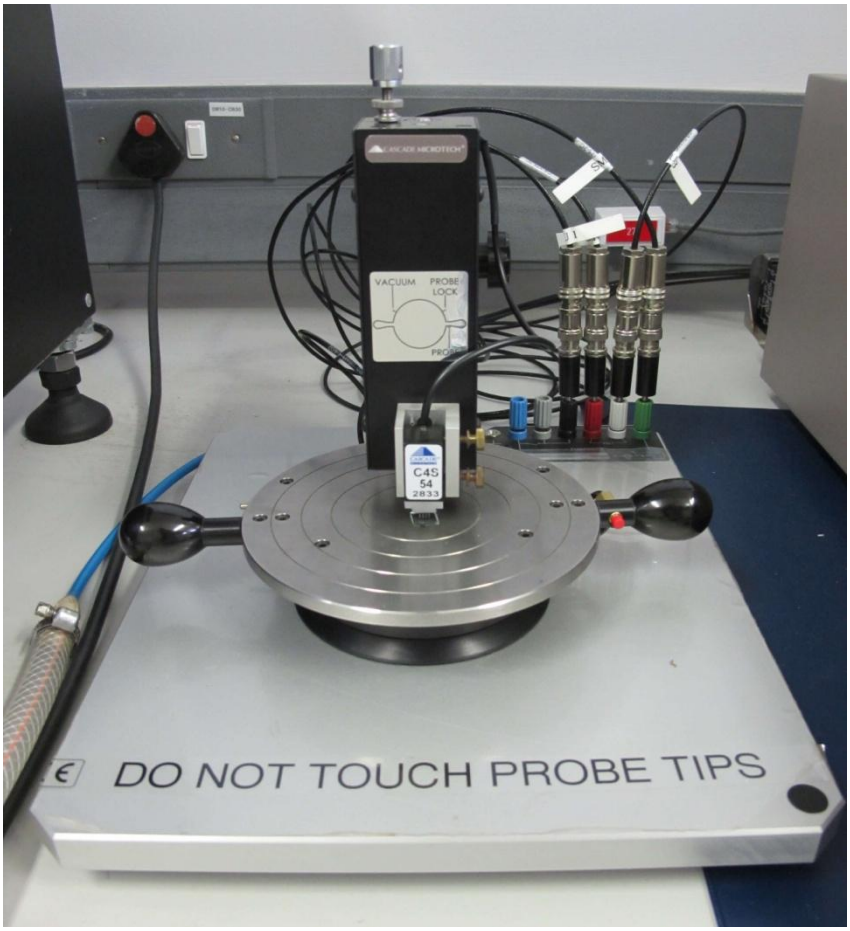


Figure 0-4 Four point probe station



Figure 0-5 Four point probe station and operation computer

Thermal Gravimetric Analysis (TGA)

Figure 0-6 shows the TGA Q500 model (TA Instruments) used for studying the thermal degradation behaviour of the samples. The measurements were carried out at a heating rate of 10°C min^{-1} under oxidative and nitrogen atmospheres from room temperature to 800°C. Samples ranging from 5 to 10 mg were analyzed.



Figure 0-6 Q500 model (TA instrument) thermogravimetric analysis

Cut-bar thermal conductivity facility

The Cut-bar thermal conductivity measurement facility was built in-house. It consists of a contact conductance cell, a hydraulic loading unit, a heating circuit, a cooling circuit, a vacuum system and instrumentation. More details of the test procedures are described in the thesis section 3.5.4.

Dynamic Mechanical Analyser (DMA)

The Anton-Paar Physica MCR 501 rheometer was used to investigate the rheological and dynamic mechanical properties of all the samples in this study. More detailed discussion is described in the following sections.



Figure 0-7 Anton-Paar Physica MCR 501 rheometer

Scanning Electron Microscopy (SEM)

The SEM micrographs were obtained by the JEOL JSM 7500F field-emission scanning electron microscopy (FE-SEM), shown in Figure 0-8.



Figure 0-8 JEOL JSM 7500F model field-emission scanning electron microscopy (FESEM)

Appendix 3: Physical and chemical properties of Cabot VulcanXC72

Appearance	Black Pellets (VulcanXC 72)
Odor	None
PH	4-11 [50g/l water 20°C](non-oxidized carbon black) 2-4 (Oxidized carbon black)
Vapor Pressure	Not determined
Boiling Point	Not applicable
Melting point	Not applicable
Water Solubility	Insoluable
Density	1.7-1.9 g/cm^3 at 20°C
Bulk density	20-550 kg/m^3
Specific gravity	Not determined
Mean particle size	30 nm
% Volatile (by weight)	<2.5% at 950°C (Non-oxidized carbon black) 2-11% (oxidized carbon black)