EFFECT OF CARBON NANOTUBE ON THE PROPERTIES OF GRAPHITE–CARBON BLACK-POLYPROPYLENE COMPOSITE FOR BIPOLAR PLATE

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A thesis submitted in fulfilment of the requirement for the degree of the Bachelor of Mechanical Engineering

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2019

DECLARATION

"I here declare that the result in this report is my own research except as cited in the references. The thesis has not been accepted for ant degree and is not concurrently submitted in candidature of any degree."

Signature :.....

Name : NUR FITRAH BIN DAINIL

Date : 14 JUNE 2019

DEDICATION

TO

my beloved family

DAINIL BIN MD DEWA

My Supervisor,

PROF MADYA DR. MOHD ZULKEFLI BIN SELAMAT

Other

My friends especially to Muhammad Firdaus Bin Sahrani, Dilip Rhaj A/L Baskaran and Amirul Hanif Bin Mohd Rasid and all people that had guided me throughout completion of this project.

APPROVAL

"I hereby declare that I have read this thesis in my opinion this report is sufficient in term of scope and quality for the award of Bachelor of Mechanical Engineering (with Hons.)"

Signature : .....

Name of Supervisor: .....

Date : .....

SUPERVISOR'S DECLARATION

I have checked this report and the report can now be submitted to JK-PSM to be delivered back to supervisor and to the second examiner.

Signature :.....

Name of supervisor :

Date :

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ABSTRACT

Nowadays, pure-graphite bipolar plate had been targeted replace to conductive polymer composite (CPCs). This is because CPCs bipolar plate has low manufacturing cost and low density in PEMFCs. The first objective is to study the effect of the CNTs on the properties of G/CB/PP composite. While second objective is to determine the critical loading of CNTs in G/CB/PP composite. In this research, the ratio of filler (G/CNTs) and binder (PP) is fixed at 80:20. The CB fixed at 25%, 10 grams. The additional small amount of CNTs which is 0, 1, 2, 3 wt% (calculate from the total weight of filler 80%) respectively. Before hot press moulding, the G/CB/CNT need to mix with ball mill. Then mix with PP also by ball mill machine in order to determine the effect of CNTs in G/CNTs/PP composite such as electrical and mechanical properties. Moreover, there are several tests to obtain the result which is electrical conductivity, flexural test, density test, shore hardness test (type D) and microstructure analysis. The results show that 2 wt% of CNTs at electrical conductivity test has the highest electrical conductivity which is 124.7544 S/cm. Result of flexural test also has 41.92 MPa for 1wt% of CNTs. 3 wt% of CNTs which has the lowest shore hardness, 1 wt% has the highest result of shore hardness which is 74.2 Shore-D, while increase weight loading of CNTs, decrease of density of composite in result by densimeter.

ABSTRAK

Pada masa ini, plat bipolar grafit tulen telah disasarkan menggantikan komposit polimer konduktif (CPC). Ini kerana plat bipolar mempunyai kos peekilangan rendah dan kepadatan rendah dalam PEMFCs. Objektif pertama adalah mengkaji kesan CNT terhadap sifat komposit G / CB / PP. Tujuan kedua adalah menentukan pemuatan kritikal CNT dalam komposit G / CB / PP. Dalam kajian ini, nisbah pengisi (G / CNTs) dan pengikat (PP) ditetapkan pada 80:20. CB tetap pada 25%, 10 gram. Tambahan kecil CNT adalah 0, 1, 2, 3 wt% berat (dari jumlah berat pengisi 80%). Sebelum proses pembuatan menggunakan penekan panas, G / CB / CNT perlu dicampur dengan pengisar bola mesin. Kemudian campurkan dengan PP juga dengan pengisar bola mesin bagi menentukan kesan CNT dalam komposit G / CNT / PP seperti sifat elektrik dan mekanikal. Tambahan pula, terdapat beberapa ujian untuk mendapatkan hasil seperti kekonduksian elektrik, ujian kekuatan lenturan, ujian ketumpatan, kekerasan ujian kepadatan (jenis D) dan analisis mikrostruktur telah dilaksanakan. Keputusan menunjukkan bahawa 2wt% berat CNT pada ujian kekonduksian elektrik mempunyai kekonduksian elektrik tertinggi iaitu 124.7544 S / cm. Keputusan ujian lenturan juga mempunyai 41.92 MPa untuk 1wt% CNTs. 3 wt% CNT yang mempunyai kekerasan terendah, 1% berat mempunyai hasil kekerasan tertinggi iaitu 74.2 Shore-D. Sementara penambahan beban berat CNT meningkat, tahap ketumpatan komposit dalam hasil oleh densimeter semakin menurun.

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LIST OF ABBREVIATION

CNTs	Carbon Nanotubes
CB	Carbon Black
G	Graphite
PP	Polypropylene
PEMFCs	Proton Exchange Membrane Fuel Cell
DC	Direct Current
DOE	Department of Environment
CPC	Conductive Polymer Composite

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Proton exchange membrane fuel cells (PEMFCs) is a good contender for portable and automotive propulsion applications because of their advantages of high-power density, solid state construction, high efficiency of conversion of chemical to electrical energy, near zero environmental emissions and low temperature operation1.

The bipolar are key components of PEMFCs. They are responsible for functions of vital importance to the long-term operation of these electrochemical devices. The performance of fuel cells is depending on bipolar plate roles in water and gas management, mechanical stability and electrical performance. It is a good application for automotive propulsion because it has high efficiency to convert chemical energy to electrical energy without environment emission. Fuel cell required a very important and expensive component such as bipolar plate. It contributes 70-80 % of stack weight and up to 45 % of the cost [1]. Thus, it shown that it is a critical issue to investigate on cost or performance material of bipolar plate.

Iijima was the first scientist to identify the carbon nanotubes (CNTs) in 1991 [3]. After that, it has been investigated in various field because of it can improve the mechanical and

electrical properties of a component. In 2003, R. Andrews and M.C. Weisenberger were presented their experimental measurements of single shell failure for multiwalled carbon nanotubes that displays fracture strength by using CNTs as discontinuous support for polymer matrices. The strength multiwalled carbon nanotubes had been proved by providing the first direct measurements for tensile fracture strengths of MWCNTs that are near the ultimate strength estimates of quantum mechanics calculation [6].

The metal bipolar plate is usually made of special alloyed steel because of high strength, high chemical stability, ease of mass production and low cost. But, stainless steel is not suitable for bipolar plate due to its very low of surface contact resistance and inexpensive mass production. Thus, graphite is the most currently used material for bipolar plate, because graphite has a good conductivity and higher corrosion resistance under 2g/m³ of density. However, in term of mechanical strength and ductility of graphite are in low level. In this case, composites materials are the best solution to make sure the bipolar plate criteria of conductivity of electricity performance and mechanical properties are balance. Various graphite with polymer composites and those on the basics of the inorganic binding agent such as Carbon Black, Carbon Nanotubes.

Bipolar plate (BP) is a most costly and main component in PEMFCs, therefore study on performance of bipolar plate (BPs) has become a famous and critical issue now. All materials have standpoint, bipolar plate (BPs) application also should present a balance of physical properties and chemical properties. Thus, the bipolar plates can be different on their properties with the different of composites of BPs. However, the BPs must follow the target properties that specified by Department of Energy (DOE). These targets have been developed with input from the automotive and energy companies and specifically the Fuel Cell Technical Team. The guideline helps to assist component developers in evaluating

progress without testing full systems. The properties requirement shown in Table 1.1 should be satisfied for fabrication of a bipolar plate.

Table 1.1: DOE target for bipolar plate (Source: Yeetsorn et al, 2012 [14])

Properties	Value
Electrical conductivity	>100 S/c
Thermal conductivity	>10 W/Mk
Flexural strength	>25[MPa]
Shore Hardness	>50
Bulk Density	<5[g/c]

To achieve the requirements stated by the U.S. DOE for bipolar plate, materials/composite properties of the CPCs must be considered for achievable design for a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight [2].

1.2 PROBLEM STATEMENT

There are many researches about Polymer Electrolyte Membrane Fuel Cells (PEMFCs) because they want to change of pure graphite or metal based bipolar plates. In

2015, Mohd Zulkefli Selamat was studied the effects of CNTs loading in multi filler with Graphite (G), Carbon Black (CB) and Carbon Nanotubes (CNTs) as reinforcements and Polypropylene (PP) as a polymer matrix. composite for bipolar plate PEMFC shows that incorporating CNTs composites produces a synergistic effect that enhances the electrical conductivity, flexural strength, bulk density and hardness of the composite which are exceeded of Department of Energy (DOE) requirement [4].

By changing bipolar plates can make fuel cell more high-power density, low operating temperature. They are several materials is currently use to produce bipolar plate. The first option material that suitable combination of thermal and electrical properties is pure graphite. It is high corrosion resistant, but inherent brittleness and high manufacturing cost. While another material is metal plate, but it is too heavy compare to pure graphite heavy, corrosion-protective coating is typically required to improve lifetime [4].

Now, new bipolar plate material has been developed and through composite approached where two types of materials were used. That materials are fillers and binder. Normally the fillers or conductive fillers such as G, CB and carbon fibre. While the binders used thermoplastic or thermoset. The mixer of these material is Conducting Polymer Composite (CPC). CPC have advantage such as ease of shaping, low density and wide range of electrical conductivities as well as corrosion resistance when compare with the metallic conductor [8].

Mostly researcher used for bipolar plates is graphite material because it has good corrosion resistance, high electrical conductivity and low density than other materials. On the other hand, graphite is a very high cost of machining channels into the surface and their vulnerability will cause the fuel cell stack becomes heavy and voluminous [7].

1.3 OBJECTIVE

The main objective of this research is:

- To study the effect of Carbon Nanotubes (CNT) on the properties of Graphite (G), Carbon Black (CB) and Polypropylene (PP) composite.
- To determine the critical loading of CNT in G, CB, and PP composite.

1.4 SCOPE OF PROJECT / GENERAL METODOLOGY

This research will study the effect of CNT loading on the electrical and mechanical properties of G, CB, and PP composite. The critical loading of CNT in G/CB/PP composite needs to be determined and to be used as composition of G/CB/CNT/PP composite for bipolar plate. The ratio of filler (G/CNT) and binder (PP) is fixed at 75:25. The amount of G also will be fixed 25% and by adding of small amount of CNTs into CB/CNT/PP composite thus will gives synergy effect on electrical conductivity and mechanical properties. The small amount of CNTs which is 0, 5, 10 and 15 wt. % (from the total weight of fillers 75 %) will be added into G/CB/PP composite. The filler of G, CB and CNTs will be mixed used ball mill before the fabrication process using the hot press. To determine the effect of CNTs content in G/CNT/PP composite, the tests such as electrical conductivity, flexure test, density test, hardness and microstructure analysis will be performed.

CHAPTER 2

LITERATURE REVIEW

2.1 FUEL CELL

Fuel cell is a device of electrochemically like a battery that can convert from chemical potential energy of gaseous or liquid reactant into direct current (DC) electricity. The different between fuel cell with battery is the fuel cell requires the source of hydrogen (fuel) and oxygen (air) as reacting gases to generate electrical energy. Fuel cell also can produce electricity continuously for as long as fuel and oxygen are supplied.

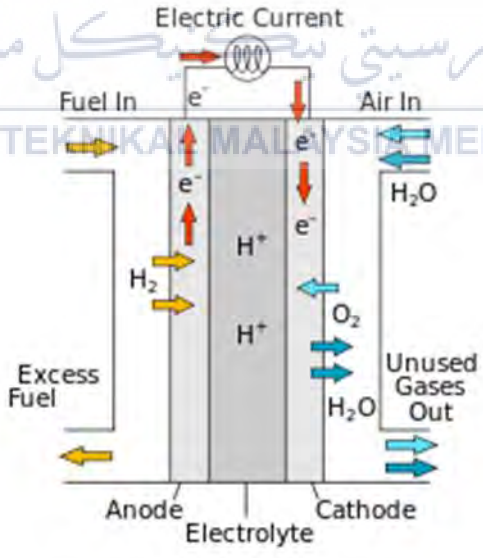


Figure 2.1: Basic Fuel Cell [15]

Fuel cell consist of anode cathode and electrolyte that block the negative charged of electron pass through was shows in figure 2.1. At anode, the fuel (H2) will undergo oxidation reaction to form positively charged hydrogen ions and electron. At the same time, electron from anode flow from anode to cathode though external circuit produce direct current electricity. At cathode, there are form of water by the reaction of hydrogen ions, electron and oxygen [9]. There are many types of fuel cells as shown at table 2.1. All types of fuel cells require a fuel that reacts with oxygen and in the process releases the chemical energy contained in the fuel.

	Low Temperature Fuel Cells			**High Temperature Fuel Cell**		
	DMFC Direct Methanol Fuel Cell	**PEMFC** Proton Exchange Membrane Fuel Cell	**AFC** Alkaline Fuel Cell	**PAFC** Phosphoric Acid Fuel Cell	**MCFC** Molten Carbon Fuel Cell	**SOFC** Solid Oxide Fuel Cell
Electrolyte	Proton-conducting membrane	Proton-conducting membrane	Caustic Potash solution	Concentration phosphoric acid	Molten Carbonate	Ceramic
Temperature Range	< 100 °C	< 100 °C	< 100 °C	~200 °C	~650 °C	800-1000 °C
Fuel	Methanol	Hydrogen	Hydrogen	Hydrogen	Natural gas, coal	Natural gas, coal
Power Range	Watts/ kilowatts	Watts/ kilowatts	Watts/ kilowatts	Kilowatts	Kilowatts / megawatts	Kilowatts/ megawatts
Application Example	Vehicle/ small appliances	Vehicles/ small generator, domestic supply, power station	Outer space	Block type heat, power station	Power plant, combined heat and power	Power plant, combined heat and power

Table 2.1: Type of Fuel Cells Characteristic

2.2 PROTON EXCHANGE MEMBRANE FUEL CELLs (PEMFCs)

The Department of Energy (DOE) is focusing on the PEMFCs as the most important of vehicles applications. There have been many successful shows of this technology in recent years. It able to efficiently to generate high power density and low operating temperature about 60 to 80 degrees Celsius. Despite PEMFCs have many advantages such as hydrogen can be produced in an environment friendly manner, while oil extraction and refining are very damaging, clean exhaust gases, modular design and low noise production [9].

The purpose of Proton-exchange membrane fuel cells (PEMFCs) are to changes the energy for suitable applications with difference requirements. The material combinations of PEMFCs that used also must difference. But need to get the properties of bipolar plates the properties for bipolar plates are as follows:

- Have electrical conductivity that >100 S cm bulk conductivity.
- The thermal conductivity must >20Wcm
- High chemical and corrosion resistance.
- Mechanical stability toward compression forces.
- The low permeability for hydrogen.
- Mass production techniques must have low-cost material being process able.
- Low volume and weight.

2.3 MAIN COMPONENT OF PEMFCs

Figure 2.3 shows the structure diagram of PEMFCs. There are three main components of PEMFCs which are Membrane Electrode Assembly (MEA) Bipolar plate (BPs) and End plate.

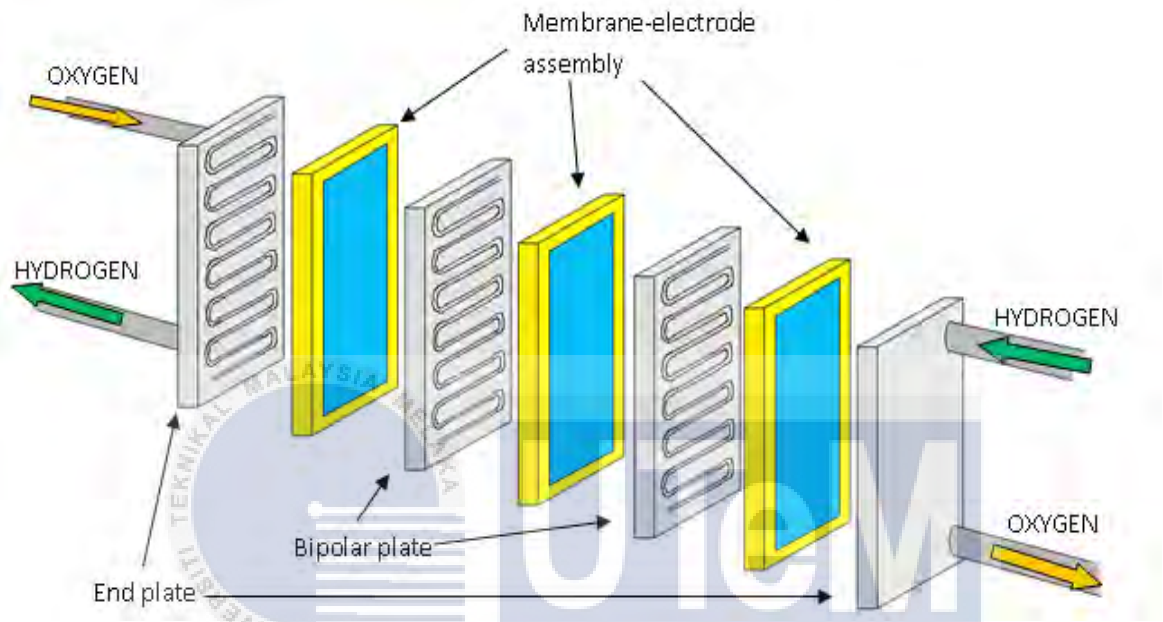


Figure 2.3: Structure Diagram PEMFCs, [15].

2.3.1 Membrane Electrolyte Assembly (MEA)

The MEA is the heart component of PEMFCs and work currently being done to find cheaper and thinner membranes whilst maintaining durability.

2.3.2 Bipolar Plates (BPs)

Allen Hermann, [10] stated that bipolar plates (BPs) play major role with multifunctional character of proton exchange membrane fuel cells (PEMFCs). The BPs can distribute fuel gas and air uniformly, remove heat from the active area, conduct electrical

current from cell to cell and prevent leakage of gases and coolant. It also contributes significantly to the volume, weight and cost of PEMFCs stacks.

The requirement in order to improve the quality of BPs are as below:

- High corrosion and chemical resistance.
- Mechanical stable when compressed.
- Low permeability for hydrogen.
- Low cost material.
- Recyclable material.

There are 3 types of BPs. Each type of BPs has their own classification of materials for BPs used in fuel cell as shown at figure 2.3.2. Graphite material is the best choice for composite bipolar plates because the material can give more lifetime. Graphite is not sufficiently to separate the hydrogen and air from cooling channels but there is various method to improve the properties.

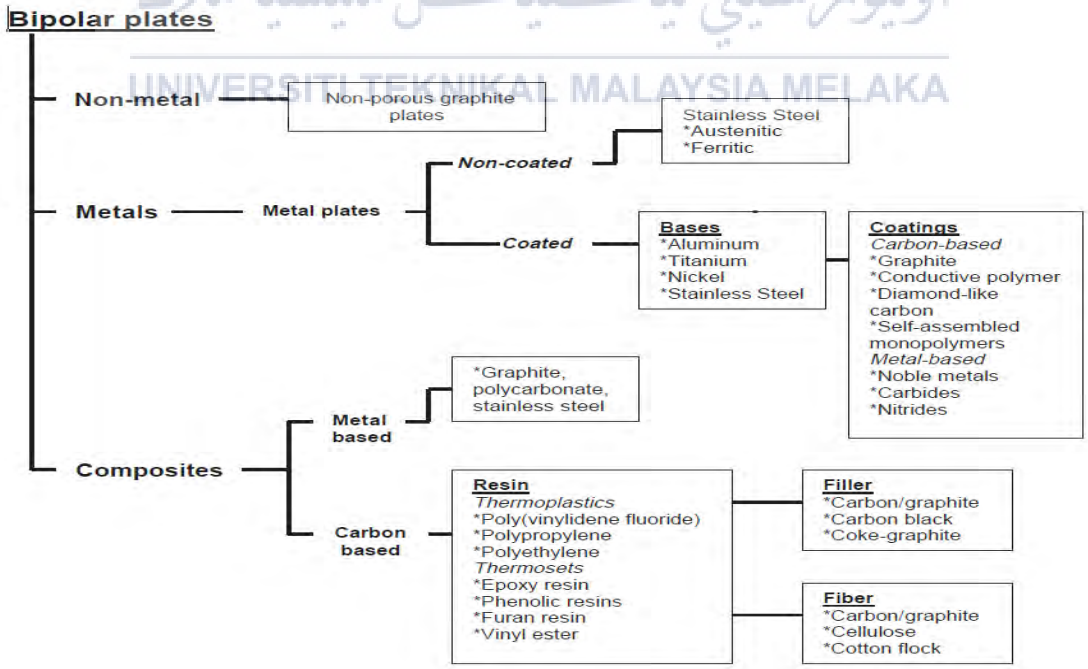


Figure 2.3.2: Classification of materials for BPs. [10]

2.3.3 End Plate

End plates also called clamp plates are needed at the end of a stack of fuel cell. It can provide pressure on the cell to prevent the gases escape from between the plate. A completed end plate normally has holes for the bolts to screw the stack of fuel cell together. There are also got some end plates is served as flow field plate with flow channel on one side. When a metal plate is flow field plate, the end plates is located at anode and cathode side also as flow field plate as shown in Figure 2.3.

2.4 MATERIALS FOR BIPOLAR PLATE

There are 3 common of material to produce a BPs which is pure graphite, metal based and CPCs. The amount of these materials must control to make an optimum stage which the bipolar plate can achieve well in mechanical and electrical properties.

2.4.1 Pure Graphite

Pure Graphite is extremely soft and cleave with very light pressure. It is a crystalline allotrope of carbon, a semimetal, a native element mineral, and a form of coal. Graphite also is the most stable form of carbon under standard conditions. Optimization of graphite for the highest electrical conductivity is increasing until 170ºC which is 50S/cm² of

electrical conductivity stated by Dr Mohd Zulkefli Selamat, (2015) [4]. Thus, the highest value of electrical conductivity of fuel cell when the filler loading at 20 wt%.

2.4.2 Metal Based

Metal Based is a common and inexpensive metal. It can be corroding relating easily and react with diluted hydrochloric acid to form hydrogen and distinguished oxidizing.

2.4.3 Conductive Polymer Composite (CPCs)

Conductive polymer composites (CPCs) is widely studied as alternative materials to conventional carbon plates. CPCs are made of two main materials which are conductive fillers and binder. CPCs is the mixer of filler and binder which aim to improve the mechanical and electrical properties of composite bipolar plate. Usually, the use of thermoplastics, thermosets or elastomers as a matrix material for CPCs conductive binder.

There are some material that can improve the high electrical conductivity and good mechanical strength such as Graphite (G), Carbon Black (CB), and Carbon Nanotubes (CNTs). These composites are produced via melt mixing and injection or compression moulding. They possess good corrosive behaviour due to insert complex structure of polymer. The higher the concentration of filler, the higher the probabilities to have a porous structure or inferior mechanical properties.

2.5 MATERIAL

The materials that able to produce the CPCs sample are G, CB, and CNTs powder. Besides, the binder is Polypropylene (PP) as shows in Table 2.5.

Table 2.5: Percentage of Composite (Source: M.Z Selamat et al 2016, [13])

Sample	Fillers (%)			Binder (%)
	G	CNT	CB	PP
1	55	0	25	20
2	54	1	25	20
3	53	2	25	20
4	52	3	25	20

2.5.1 Filler

Filler function in fuel cell is to achieve a good conductivity of the component. It is combination of multi-filler had been used in bipolar plates. The reinforcement filler such as G, CB and CNTs. These fillers which will mix into composite to improve the electrical properties and mechanical properties of bipolar plate.

2.5.1.1 Graphite (G)

Graphite is a naturally-occurring form of crystalline carbon. It is extremely soft and cleave with very light pressure. Based on the research of Dr Mohd Zulkefli Selamat in 2015 [4], it stated that optimization for the highest electrical conductivity is increasing until 170oC which is 50S/cm2 of electrical conductivity. Therefore, the highest value of electrical conductivity of fuel cell when the filler loading at 20 wt%.

Figure 2.5: Graphite powder (Source: http://www.epoxy-superstore.com)

2.5.1.2 Carbon Black (CB)

The most common use of carbon black is in automobile tires as a pigment and reinforcement. It also can help to keep the conduct heat away from the tread and tire, reducing the thermal damage and increase the lifespan. Moreover, it can make in product such as non-tire runner goods, belts and hoses [12].

This is due to the carbon black is a controller in the production process and form aggregates also vary in surface chemical, porosity and size. It contains around 95% of pure

carbon and minimal quantities of oxygen, hydrogen and nitrogen. Bipolar plate which mix with carbon black can increase it ductility. Besides, it also can decrease the flame-treatment temperature, while the flexural strength decreases due to the carbon black increase its brittleness. Therefore, the optimum of the carbon black is investigated to optimise the mechanical properties and chemical properties. On the other hand, Treacy in 1996 [11] was stated that by applied higher pressure, the ultimate value varies from 145 to 250 S/cm with increasing CB and electrical conductivity is 25vol%.

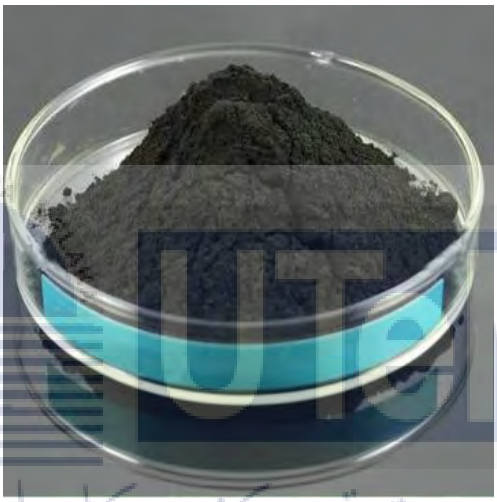


Figure 2.5.1: Carbon Black powder (Source: www.okorder.com)

2.5.1.3 Carbon Nanotubes (CNTs)

Nanoscopic particles of carbon nanotubes are tubular structures formed by carbon atoms. Diameter size between 1 and 50 nm for the normal duration of one micrometre up to a few centimetres. Therefore, the ratio of CNTs can be very large. Advantages of CNTs are available in commercial form multiwall or in the laboratory as a wall. Since their discovery, the physical characteristics unique has led to enormous interest. With a very large elastic modulus, carbon nanotubes known as a reinforcing agent effectively. Depending on their molecular structure, carbon nanotubes with small diameter show either semi-conducting or metallic behaviour.

Figure 2.5.2: Carbon Nanotube Powder (Source: dir.indiamart.com)

2.5.2 Binder

Binder consist 2 type of composite which is thermoset and thermoplastic. Binder level influences the conductivity, permeability and strength properties of the plate. Based on the data from test plates shown in the table 2.5.2 below was stated by Iljima, (1991) [3], binder level 20% -30% provides the optimum flex stress with well permeability and minimum loss of conductivity as indicated by increase in resistance.

Sample	A	B	C
Binder (%)	10	20	30
Thickness (inch)	0.132	0.13	0.131
Resistance (Ω)	1.1	1.18	2.86
Nitrogen Permeability, (10^{-16} m^2)	62.8	105.3	103.1
Flex Stress (MPa)	11.486	25.538	39.992

Table 2.5.2: Result with Different % of Binder in Test Plates

2.5.2.1 Polypropylene (PP)

Polypropylene (PP), is a thermoplastic polymer used in a wide variety of applications. It is produced via chain-growth polymerization from the monomer propylene. PP have the advantages of low cost, good processability, well balance physical and mechanical properties that stated by Dr Mohd Zulkefli Selamat (2016) [13].

Figure 2.5.2.1: polypropylene [4]

2.6 MANUFACTURING PROCESS

There is some manufacturing method that can be used to fabricate bipolar plate. Compression moulding and injection moulding are two main processes for current manufacturing of bipolar plates as shown at figure 2.6.

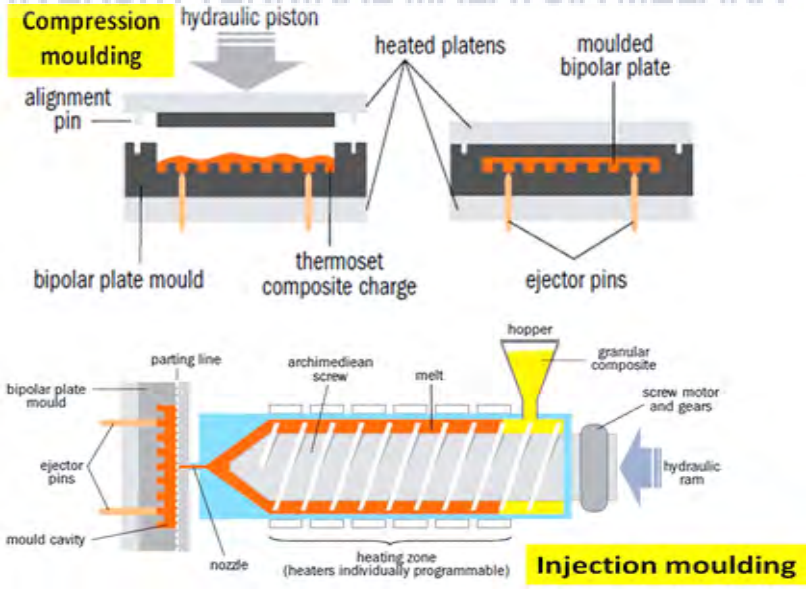


Figure 2.6: Compression Moulding and Injection Moulding [14]

2.6.1 Compression Mould

The compression moulding is a very commonly method for mass production of polymer composites bipolar plate. Compression moulding is stared with the powder compound or bend prepared in an extruder or an internal mixer at a proper temperature from a polymer binder resin and conductivity filler particle. The compression moulding is favoured for both thermoplastic and thermosetting matric composites. Even though both are favoured by compression moulding, once if compression moulding is used, the thermoset has to be cured, and while thermoplastic material has to be cooled. Production time for both processes are sharply increase. Furthermore, the cost-effective mass production would be more readily achievable with thermosets rather than thermoplastics it is due to the shorter cycle times for thermosets. In addition, by using compression method the compression moulded thermoset composite can be cured comfortably in less than 10 minutes, resulting in cycle times less than those required for thermoplastics.

2.6.2 Injection Mould

Injection moulding machines is thought of as an attractive manufacturing method for composite bipolar plates. This is due to the high productivity inherent to the process that need to favour the massive production rates necessary to reduce production cost. Furthermore, by using the injection moulding is a low cost and high productivity manufacturing method. However, other process like extrusion with appropriated die, rolling and thermoforming may be alternative progressions to producing composited bipolar plate.

Although the injection moulding process favours the massive production rates that are essential to reduce production cost, the electrical conductivity. At the same time, the high shearing will promote the rupture of conductive network structure in bipolar plate composition.

2.7 TESTING METHOD

There is some method have to apply on bipolar plate to determine the properties of the sample which is electrical and mechanical properties.

2.7.1 Mechanical Properties

Mechanical properties in this research that need to test such as flexural strength, bulk density test and hardness test. The flexural strength is most critical because the composite bipolar plate will undergo bending force during clamping with the fuel cell. For bulk density, also known as dry bulk density is the weight of dry soil divide by the total soil volume. While the hardness test will be measured with the help of stereoscopic hardness tester.

2.7.2 Electrical Conductivity

Electrical conductivity is a measure of a material ability to allow the transport of an electric charge or the ratio of the current density to the electric field strength. The reciprocal of the electrical conductivity is electrical resistivity.

CHAPTER 3

METHODOLOGY

3.1 GENERAL METHODOLOGY

For this research, there have several actions that need to be carried out to achieve the objective in this project. First, I will find as much as literature review like journals, articles or many materials that regarding the project will be reviewed. After reviewed, the experimentation is setup. Fabrication of bipolar plate with small amount of CNTs which is 0, 1, 2 and 3 wt. % (from the total weight of fillers 80 %) will be added into G/CB/PP composite. In order to determine the effect of CNTs content in G/CNT/PP composite, the tests such as electrical conductivity, flexure test, density test, hardness and microstructure analysis will be performed.

Next, the method for fabricate the sample was by hot press. Hot Press is a one of the fabrication process of fuel cell. It is a simultaneous application elevated temperature and compressive stress. The densification parameter is determined individual. For each different layer, it was hot press in a single step. Additionally, hot press can improve interfacial contact and reduce the polarization losses. Besides, hot pressing can also reduce the time and cost spend.

After fabricating those bipolar plates, result analysis will be applied on each plate. They are several tests will be conducted in order to determine the properties of G/CNT/PP composite. The result such as electrical conductivity, flexure test, density test, hardness and microstructure will be recorded by table and graph.

Final step is the study will be written clearly in report at the end of project.

3.2 EXPERIMENTAL OVERVIEW

This section will present the methodology that will apply in the research. Figure 3.2 shows the flow chart of methodology process for Gr, CB, CNTs and PP composite for BPs in PEMFCs.

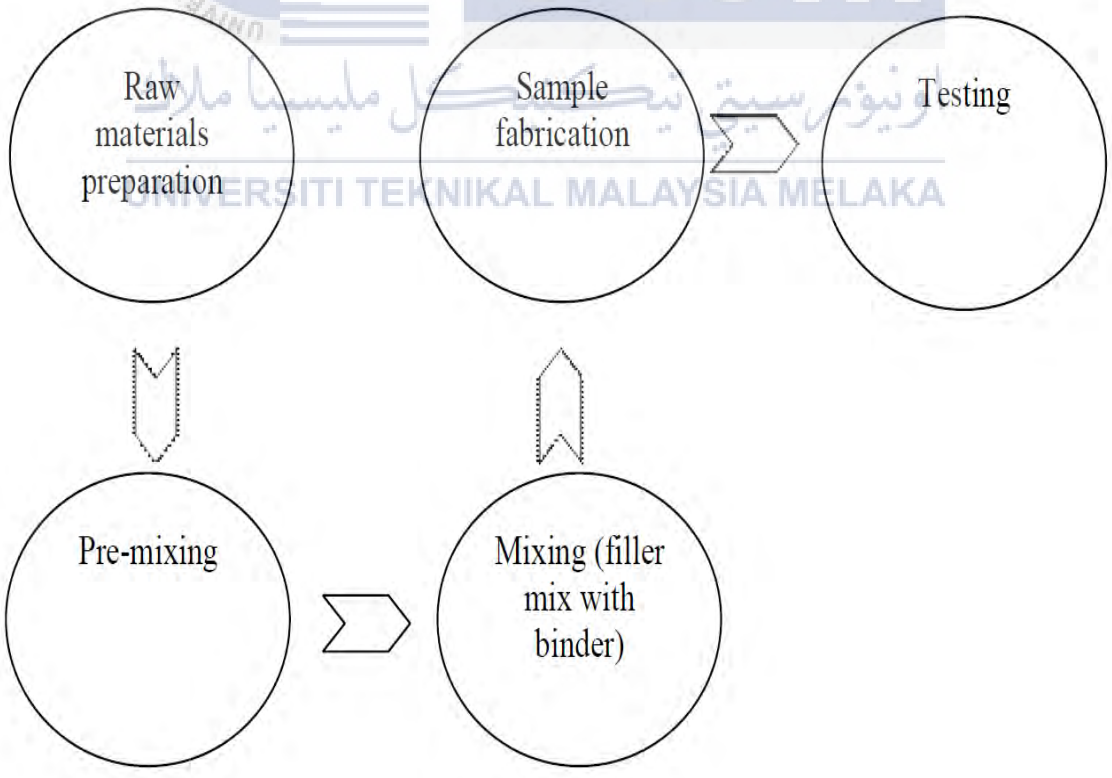


Figure 3.2: Flow chart of methodology process

3.3 RAW MATERIALS

In this study, the materials selected for composite development includes polymer matrix and conductive fillers. Therefore, the chosen materials that need in this research are Gr, CB, and CNTs as filler conductive. Meanwhile, PP was chosen to be a polymer matrix as a binder of bipolar plate for this research. Those materials were chosen instead of metals is due to corrosion resistance and less cost during fabrication. The Table 3.3 shows the material properties of G/CB/CNTs/PP.

Table 3.3: Material Properties of G/CB/CNTs/PP (Source: Selamat, et al.2015 [4])

Material	G	CB	CNTs	PP
Grade	3243	5303	NC 7000	Titan (600)
Density (g/cm^3)	1.74	1.7-1.9	1.0	0.91-0.92
Thermal stability (^oC)	350-400	3000	>700	180-220
Size	≤ 60 µm	≤ 5 µm	9.5 nm (diameter) 1.5 µm (length)	250 µm
Resistivity	1295 (10^{-8}Ωcm)	0.314Ωcm	-	1(1014Ω m)

3.4 FABRICATION METHOD

There are common type for fabrication method which is compression method. Before applying with this fabrication method, some steps need to be carried on like preparing raw materials according with its characterization then pre-mixing for those filler by ball mill machine and follow by using internal mixer machine to mix with the polymer. After this, compression moulding will be taking over, and a specimen of BPs will be form up.

3.5 CHARACTERIZATION OF RAW MATERIALS

There is specific conductive filler which are Gr, BB and CNTs ratio and weight of percentage of PP as binder. The ratio of fillers and binder is set at 75:25. While CNTs is will add small amount set at 0, 5, 10, 15 wt% as a filler mix with Gr, CB to form 75 wt% of composites as shows at Table 1.1. It will give synergy effect on electrical conductivity and mechanical properties of PEMFCs.

3.6 Pre-Mixing

A process of pre-mixing for polymer Nano composite is using ball mill. The possibility of using ball mill to produce nano scale reinforcement has been verified instead of trying to discover low cost processes. In this research will study the effectiveness of conductivity of CNTs. Therefore, all materials as the composition of composite Gr, CB, and CNTs composites are mixed using ball mill for mixing process.

The materials were weighted based on the composition that has been specified as shown in Table 3.6. Therefore, a container with fill some of steel balls was filled with raw material in powder form which were weighted. The materials are poured slowly because those materials are too light. The machined was run with the time rate around one and half hours to ensure that the combination of fillers is well-mixed.

Figure 3.6: Ball Mill

Table 3.6: Composition of CNTs, G, and CB

CNTs		CB		Gr	
%	Gram	%	gram	%	Gram
5	6.67	25	33.33	45	60
10	13.33	25	33.33	40	53.33
15	20.00	25	33.33	35	46.67

3.7 INTERNAL MIXING PROCESS

In this step, Gr, CB and CNTs will be mix with PP according to its ratio between filler and binder by using lab blender for internal mixing process. The machines are cylindrical container and the material are deforming by rotating blades.

Figure 3.7: Blender

3.8 COMPRESSION MOULDING

Compression moulding method has been selected for this research to produce bipolar plate. This process is using Hot Press Machines. The mixer of composite is poured into mould carefully and immediately after par-mixing and internal mixing process is done. Figure 3.8 (a) shows the hot press machine and Figure 3.8 (b) shows 140mm x 60mm mould. Par heating time is 6 minutes, temperature at 80°C. While pressure is constant at 80 ton to compress mould in 30 minutes.

Figure 3.8 (a): Hot Press Machine

Figure 3.8 (b): 140mm x 60mm mould

3.9 TESTING METHOD

In this step, we carry out the properties of the bipolar plate by adding different amount of CNTs into mixer. The properties that we test which is electrical conductivity, bulk density, shore hardness and flexure strength.

3.9.1 Electrical Conductivity

Electrical conductivity of the sample was measured using Jandel Multi Four Point Probe technique at a constant current supply. It is measurement of resistivity of a sample. In this method, the outer probes apply current to the sample and the inner two probes measure the voltages. Based on F390-98 standard.

Figure 3.9.1: Jandel Multi

3.9.2 Flexural Strength

Flexural strength was measure by three-point method using the Instron Universal Testing Machine. Based on D790 standard.

3.9.3 Bulk Density

The composite bipolar plate was cut with Proxxon Table Saw as shown at figure 3.9.3 (b) to dimension to measure the bulk density by using Electronic Densimeter as shown figure 3.9.3 (a). Based on D1895 standard.

Figure 3.9.3 (a): Electronic Densimeter

Figure 3.9.3 (b): Proxxon Table Saw

3.9.4 Shore Hardness

For testing shore hardness of composite bipolar plate, we use stereoscopic tester as our apparatus. The hardness test of the composite also involved dropping a diamond tipped hammer, which fall inside a composite plate under the force of its own weight from a fixed height, onto the test specimen. Based on D2240 standard.

Figure 3.9.4: Shore Hardness

3.9.5 Scanning Electrical Microscopic

Scanning Electron Microscopy (SEM) can imaging and analysis a sample. The sample structure can be physically examined, and their elemental composition determined. Besides, it also produces many types of signal that can be used to obtain information about the surface topography and composition.

CHAPTER 4

RESULT AND ANALYSIS

4.1 FINAL COMPOSITION

In this research, the conductive filler used which are G, CB and CNTs while binder is EP. The ratio of filler (G/CB/CNTs) and binder (PP) is fixed at 80:20. By adding different weight of CNTs this composite, it will give different effect and result based on DOE target. Table 4.1 shown the weight of each G, CB, CNT and PP in gram based on Rule of Mixer.

Table 4.1: Weight of G, CB, CNT and PP

Sample	Filler (80%)			Binder (20%)
	G (g)	CNT (g)	CB (g)	PP (g)
1	22	0	10	8
2	21.6	0.4	10	8
3	21.2	0.8	10	8
4	20.8	1.2	10	8

4.2 Electrical Conductivity

Jandel Multi Height Four Probe is the device to carry out the electrical conductivity testing in determining the ability of the CPC bipolar plate to conduct electricity. 18 reading was taken, 9 from the top surface and the other 9 from the bottom surface. The reading is calculated using the below formula to get conductivity in Siemens per Centimeter (S/cm).

$$\mathbf{S\ cm^{-1}} = \frac{\mathbf{1}}{\mathbf{2\pi S\ (data\ average)(0.6336)}}$$

Where: S = 0.1cm (distance of Jandel Multi Height Four Point Probe)

0.6336 = factor of thickness per diameter per specimen

Table 4.2 shows the electrical conductivity result of each specimen based on different percentages of CNT. While figure 4.1 shows the plotted graph of electrical conductivity against percentage of CNT.

Table 4.2: Conductivity of G/CNT/CB/ PP bipolar plate

Carbon Black content (wt %)	Conductivity (S/cm)
0	99.5070
1	90.5548
2	124.7544
3	120.5711

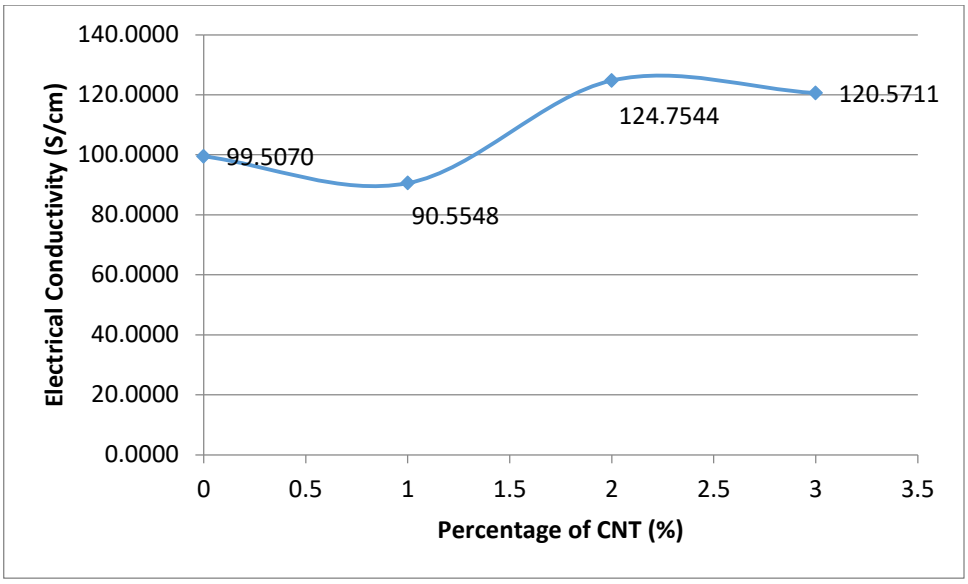


Figure 4.2 Graph of electrical conductivity against percentage of CNT

Based on threshold percolation theory, the increasing of filler content will increase the electrical conductivity of the bipolar plate due to the continuous conductive network that is form between the filler. However, there is a limit for the CNT content in that filler. Based on the result in Table 4.2 and Figure 4.2, there are show the trend of each composites with different content of CNT. CNTs as reinforcement introduced into polymer composite, which shows outstanding electrical and mechanical properties. CNT of 1wt%, the electrical conductivity has below than 0wt%. However, CNT of 2wt% increase and its drop until 3wt% but still higher than 1wt% and 0wt%. The highest electrical conductivity is equal to 124.7544 S/cm which contain 2wt% of CNTs.

4.3 Flexural Strength

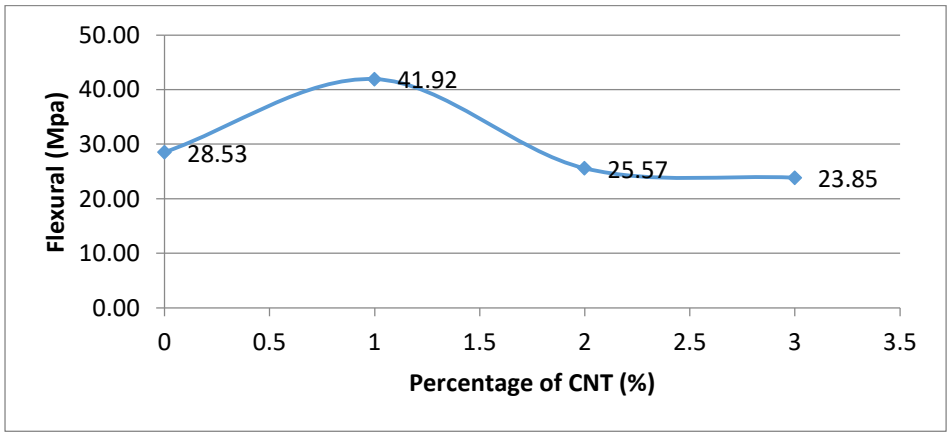


Figure 4.3 Graph of flexural stress (MPa) against percentage of CNT

The graph of flexural strength against weight percentage of CNT in the composite has been plotted as shown in Figure 4.3. At 0 wt% of CNT, the flexural strength is equal to 23.85 MPa and it is the lowest flexural strength compare with another composite which contain CNT material as reinforcement. By increase the volume fraction of CNT to 1 wt%, flexural strength has shown the highest value, 41.92 MPa. When CNT content equal to 2wt%, the flexural strength decrease until 25.57 MPa. Moreover, flexural strength increase to 28.53 MPa when CNT equal to 3wt%.. This result does not meets the standard set by the US-DOE which is 25 MPa or exceed.

4.4 Density

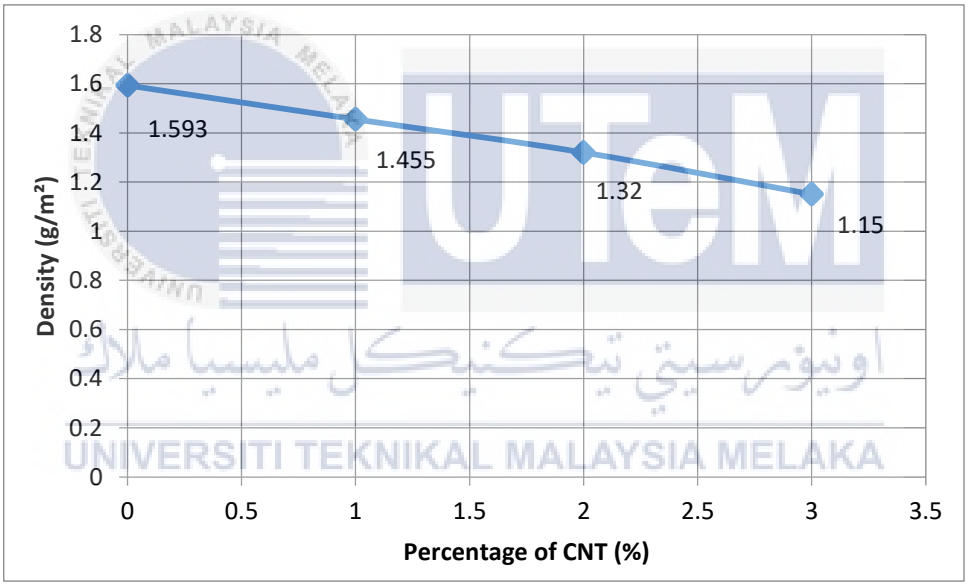


Figure 4.4 Graph of density (g/cm^3) against percentage of CNT

The graph of density against percentage of CNT above shows the specimen that have the highest density value is specimen without content of CNT, 1.593 g/cm^2. The density of the G/CB/CNT/PP bipolar plate decrease significantly when the content of CNT increase. All the specimen meets the US-DOE requirement for the bipolar plate which is less than 5 g/cm^2.

4.5 Hardness

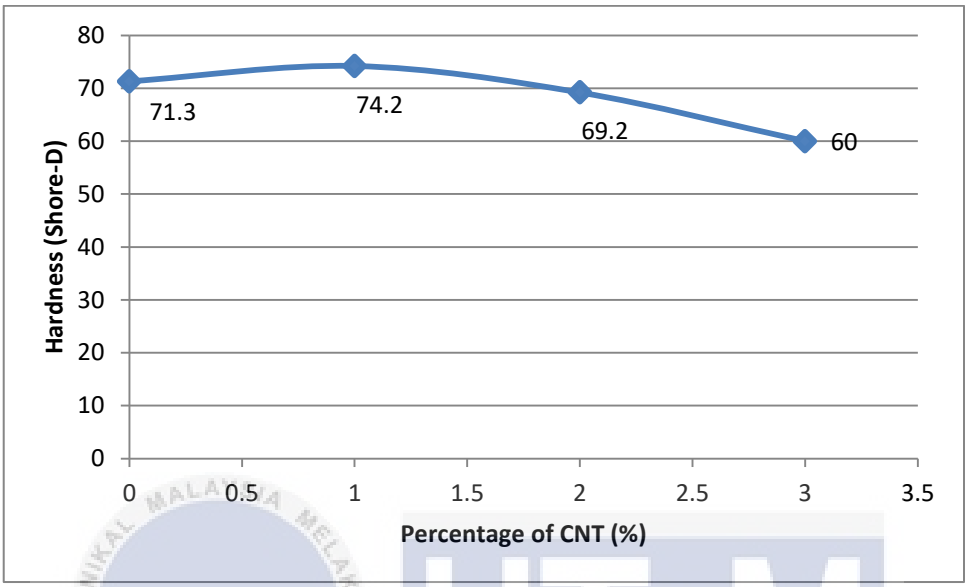
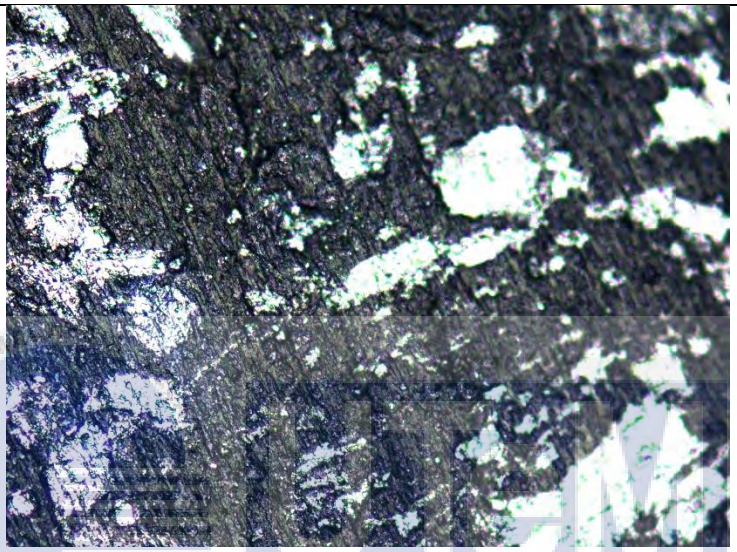
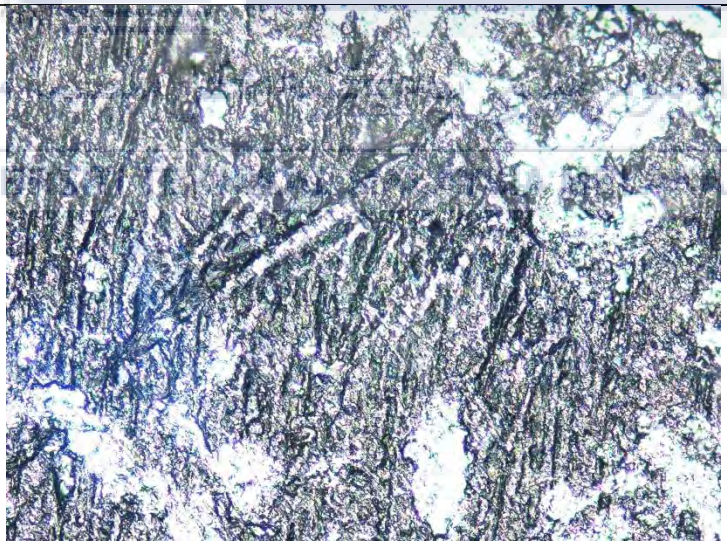


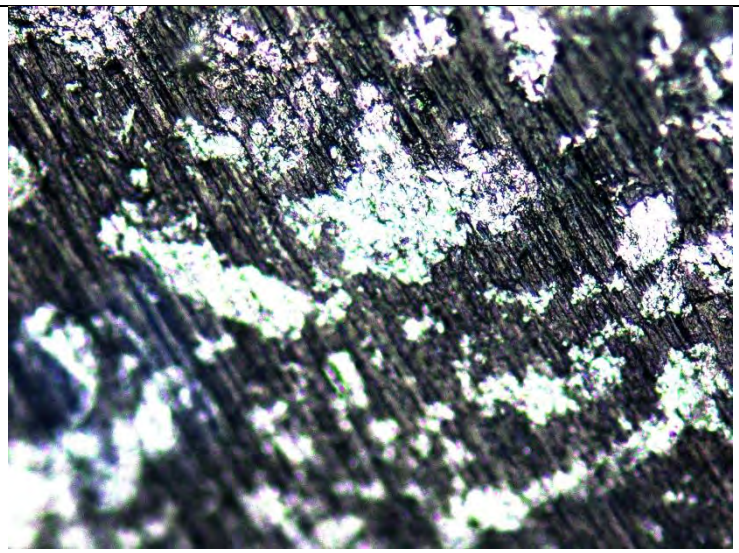
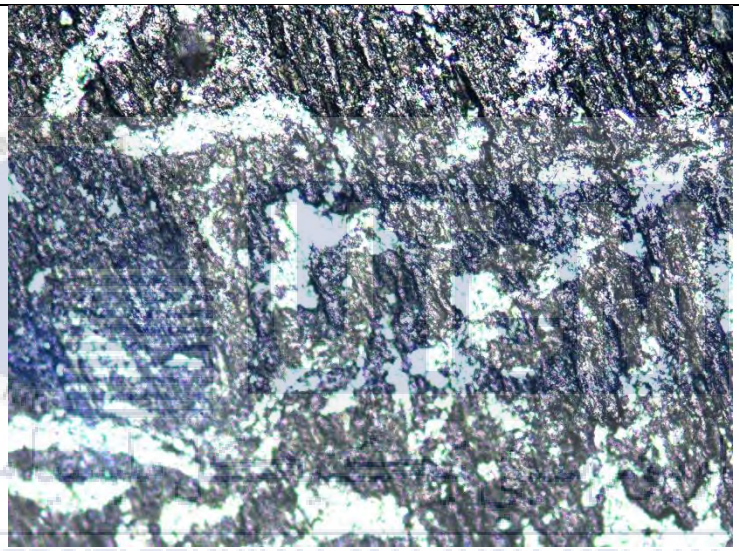
Figure 4.5 Graph of hardness (Shore-D) against percentage of CB

The Figure 4.5 shows the result of shore hardness (type D) against CNT (wt%) result. The graph shows that the highest hardness is equal to 74.2 when composite has 1wt% of CNT. While 3wt% of CNT shows the lowest hardness of result, 71.3. Besides, the 0 wt% and 2wt% of CNT have the result 71.3 and 69.2 respectively. Due to the value of hardness of CNT 2wt% and 3wt% are below 0wt%, this result is not meet the US-DOE requirement for bipolar plate.

4.6 Microstructure Analysis

Table 4.6: Dispersion of CNTs on surface composite

CNTs (wt%)	Dispersion of CNTs
0	
1	

2	
3	

The table 4.6 shows the microstructure of each specimen. The hardness of 2 wt% and 3wt% of CNT become fracture due to void that occur on the specimen surface. This is because of the unsuitable of compress pressure and time during hot press.

CHAPTER 5

DISCUSSION

All the four have been carried out and based on it, the result was analyzed and determined to state whether the properties if the G/CB/CNT/PP bipolar plate meets the standard set by US-DOE for a bipolar plate. From all the test, there are 2 out of four of the result does not successfully meet the requirements needed by US-DOE which is the electrical conductivity and the flexural strength. While the other properties the hardness and density is managed meet the requirement.

5.1 Electrical Conductivity Test

The test of electrical conductivity is the most important properties in bipolar plate. In this study, loading of CNTs has affected the electrical conductivity of composite. The ratio of fillers and binder is fixed at 80:20. CB and PP were fixed at 25% and 20% respectively while G and CNTs were fixed at 55%. When the weight of CNTs increase, the electrical conductivity increase based on the result shown at Figure 4.1. But at CNTs 1 wt%, the electrical conductivity of the composite drop to 9 10 S/m. There are two critical problem for CNTs use as reinforcement in polymer composite. First, CNTs has strong intrinsic Van der Waals force cause aggregate into bundles. It will affect the dispersion of CNTs in composite. Secondly, lack of interfacial bonding of CNTs and smooth surface will show weak interfacial adhesion between matrix and CNTs [15, 18]. These two problems will limit the improvement of electrical properties in polymer composite [15]. Therefore 1 wt% of CNTs composite result in electrical conductivity decrease.

5.2 Flexural Strength Test

Based on the result obtained from the flexural strength test, the highest value of flexural stress is 41.92 MPa and meets the standard requirements set by US-DOE which is higher than 25 MPa. However, the trend of the line is also not constant or shows the certain pattern. The trend of the line inconstant due to the bonding of G, CB and CNT particles are not strongly enough because of the lacking of PP content. The results of flexural strength had not achieved the DOE target for 3 wt% of CNT which is 23.85MPa below 25MPa. This also because on the mod of fracture occurs either ductile or brittle failure. There are two type of brittle failure which is transgranular and intergranular fracture.

5.3 Density Test

The density value of all specimen does meet the standard requirement of the US-DOE which is less than 5 g/cm^3. The density test shows that the percentage of CNT is inversely proportional with the density value. The maximum density obtain is 1.593 g/cm^3 with the CNT content 0%.

5.4 Hardness Test

Based on the result obtain from hardness test, the hardness increase at weight loading 1 wt% and start decrease to 3 wt%. When increase of CNT loading, the increase of hardness. While continuous decrease the loading of CNT from 2wt% to 3 wt% with their value below of CNT 0 wt%. The hardness result is not constantly. Bases on the result, the best loading of CNT is 1 wt% for hardness.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

There are two main objective of this research. Firstly, to study the effect of CNTs on the properties of Gr/CB/PP and to determine the critical loading of CNTs in Gr/CB/PP. Therefore, by this research was study the effect of CNT loading on the electrical and mechanical properties of Gr/CNT/CB as a filler and PP as a binder. In order to determine the effect of CNTs content in Gr/CB/CNT/PP composite, the testing such as electrical conductivity, flexure testing, density testing, hardness and microstructure analysis has been done. All four (4) specimens are successfully fabricated and tested through this study. Based on the experiment and the result obtained, it shown that at 1% weight of CNTs had the best achieved requirement of US DOE target on hardness and density. The flexure strength and the electrical conductivity are not achieved the target based on the factor that need to study further and need to improve in future.

The first process fabrication of the specimen was mixing. Mixing process is the important part of the fabrication composite. It is because composite is the combination of two or more material that contain matric and reinforcement. Therefore, in the mixing process, the material must mix ideally to produce a material with characteristic or properties needed. Other than that, the important in fabrication composite of bipolar plate are compression. Compression moulding is known that the step to develop the composite specimen. Therefore, the important parameters that needs to be consider in the compression process that control the fabrication process are temperature and pressure.

6.2 Recommendations

In this study, bipolar plate that containing the CNTs is under development process. Therefore, have several technique or process that need to be improve to achieve the mechanical and electrical properties. There are possible recommendation for the future that need to improve.

6.2.1 Change the ratio of filler and binder

Filler and resin are two main component that are important to fabricate the composites bipolar plate. The percentage of these components is 80% for filler and 20% for binder. Based on the percolation theory, increasing the amount of filler content will increase the electrical conductivity properties of the composites bipolar plate. It can see that the percentage for the PP act as the binder is not enough to hold and bind the filler content. Therefore, for the recommendation the quantity of the PP need to be increased more than 20% from the total weightage composition. Based on the result of fracture obtained, maybe at the compression process the temperature and pressure is not the best. Because when the difference of temperature change the result is fractuated by increasing the weight content of CNTs. Other than that, by consider the CNTs content. Maybe should use 0-10%wt CNTs.

6.2.2 Method for mixing process

The G/CB/CNT is mixing with PP by using ball mill machine. This equipment is not the best tool to mixing well the mixer. It can affect the properties of the composite. Therefore, a recommended to obtain a suitable time to use this equipment or change to another equipment which can good in mixing.

6.2.3 Change the compress temperature, time and pressure

Compression is one of the factors that affect the properties of composite. Based on the image captured by microscopic, there are might be having a void on the specimen surface. A recommendation is increase the pressure (MPa) or increase the compression time while the temperature can be fixed at 180°C due to the previous research.

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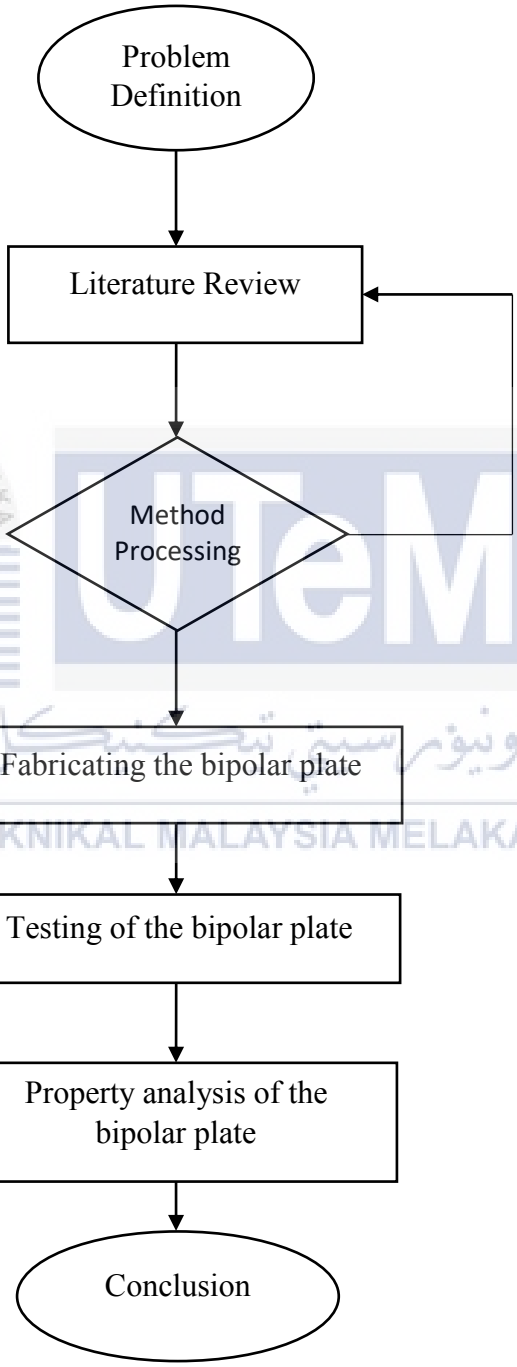
APPENDIXS

Flowchart of the research.



Gantt chart for Final Year Project 1.

Activity	2018			
	September	October	November	December
Selection and confirmation of project title				
Prepare the introduction of FYP 1 1. Objectives 2. Problems statement 3. Scope				
Study the literature review and methodology				
Sample preparation				
Report preparation				

Gantt chart for Final Year Project 2.

Activity	2018				
	January	March	April	May	June
Sample preparation					
Fabrication of bipolar plate					
Testing of bipolar plate					
Properties analysis					
Result and discussion					
Report preparation					