Polymeric bipolar plates for PEM fuel cells: experimental and modeling approach to assess factors influencing performance

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/7249

Publisher: © Paul S Greenwood

Please cite the published version.
This item was submitted to Loughborough’s Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/

by

Paul S Greenwood

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the award of Degree of Doctor of Philosophy of Loughborough University

1st June 2010

© by Paul S Greenwood 2010
“Anybody who has been seriously engaged in scientific work of any kind realizes that over the entrance to the gates of the temple of science are written the words: 'Ye must have faith.' It is a quality which the scientist cannot dispense with.”

- Max Planck (1932)
Abstract

Fuel cells are widely researched and have applications in residential, automotive, marine craft and space. Their efficiencies are typically 60% as a result of their electrochemical conversion and due to this they are considered beneficial to the reduction of CO₂ which accounts for 77% of all greenhouse gases. Polymer electrolyte membrane fuel cells are the most suited to automotive applications for their low operating temperatures, high power densities and fast start up times. Currently there are many problems still to be rectified before commercialisation takes place, one of which is the performance and manufacture of bipolar plates. The elimination of corrosion, reduction of mass and the improvement of mechanical, electrical and thermal conductivity properties are the main aims to progress bipolar plate technology. In addition, the large numbers of bipolar plates required in automotive fuel cell stacks is in the order of 400 plates and so mass production will be necessary to meet future demands as well as reduce costs through cheap production processes.

In order to meet these requirements polymeric based bipolar plates with conductive fillers have been pursued. The use of highly conductive, low density, low cost and corrosion resistant materials that can be utilised in production processes such as injection and compression moulding are ideal candidates for bipolar plates. However, balance of electrical/thermal conductivity and mechanical strength becomes the major task as highly conductive composites result in low mechanical strength. Therefore three conductive powders, a carbon black, graphite and magnetite (iron II,III oxide) were used as fillers in a polyethylene matrix to study the balance just mentioned for the two manufacturing processes stated above.

The composites were tested for their electrical and thermal conductivities and mechanical properties and compared to the US Department of Energy targets for 2015. The carbon black composites exhibited better electrical conductivity than the other fillers where at 65 wt% the conductivity was ~24 S/cm for through plane conductivity and had a flexural strength of ~32 MPa. Injection moulding produced composites with more material stability and greater mechanical strength than compression mouldings.
although compression mouldings produced composites with higher thermal conductivities where graphite displayed the highest thermal conductivity of \(~2\) \(\text{W/mK}\).

Modeling of the experimental results using Mamunya models for electrical and thermal conductivities and a modified Kerner’s equation for mechanical moduli were conducted. Models showed reasonable agreement with the experimental data where parameter tuning and deviations from the model were used to describe microstructural behaviour with regards to electrical tunnelling effects, link, node and blob structures and stress transfer at the filler-matrix interface.
Acknowledgements

I am thankful to my supervisors Prof Robert Thring and Prof Rui Chen for their guidance and patience during this journey.

I would like all the staff at Aeronautical & Automotive Engineering as well as the following people for their help throughout my work:

**MECHANICAL & MANUFACTURING ENGINEERING**
- Dr. Neil Hopkinson
- Richard Price
- Rod Springthorpe
- Bob Temple
- John Jones
- Bill Veitch

**ELECTRONIC & ELECTRICAL ENGINEERING**
- Dr. Robert Seager
- Peter Godfrey
- Chandrakant Mistry
- Peter Harrison

**CHEMISTRY**
- Prof. Stephen Fletcher
- Marion Dillon

**MATERIALS**
- Prof. Mo Song
- Dr. Bala Raghupathy
- David Hall
- Gary Critchlow
- John Bates
- Frank Page
- Ray Owens
- Andy Woolley

**CHEMICAL ENGINEERING**
- Dr. Klaus Hellgardt
- Tony Eyre
- Dave Smith
- Sean Creedon
- Graham Moody

**DESIGN SCHOOL**
- Craig Brown

Thank you to all my friends who have helped me during my time at Loughborough.
## Contents

Abstract ............................................................................................................................ i
Acknowledgements ........................................................................................................ iii
List of Tables ................................................................................................................ vii
List of Figures .............................................................................................................. viii
Nomenclature ............................................................................................................... xiii

### Chapter 1.0 - Introduction ............................................................................................... 1

1.1 What is a fuel cell ................................................................................................. 1
1.2 Types of fuel cell .................................................................................................. 2
1.3 Applications/Benefits ............................................................................................ 5
1.4 The PEM Fuel Cell ............................................................................................... 6
   1.4.1 The Electrolyte ............................................................................................... 7
   1.4.2 The Electrode/Catalyst Layer ........................................................................ 7
   1.4.3 The Membrane Electrode Assembly .............................................................. 8
   1.4.4 The Bipolar Plate ......................................................................................... 10

### Chapter 2.0 - The Thesis ............................................................................................... 12

2.1 Thesis Objectives / Rationale ............................................................................. 12
2.2 Layout of the Thesis ........................................................................................... 14

### Chapter 3.0 - Literature - Bipolar Plates ....................................................................... 15

3.1 Function .............................................................................................................. 15
3.2 Current Bipolar Plate Materials .......................................................................... 16
3.3 Materials in the literature .................................................................................... 19
   3.3.1 Metals ........................................................................................................... 19
   3.3.2 Graphite/Carbon-Polymer ............................................................................ 22
   3.3.3 Summary ...................................................................................................... 25
3.4 Materials Used In This Study ............................................................................. 28

### Chapter 4.0 - Methodology ........................................................................................... 30

4.1 Malvern Zetasizer & Mastersizer ....................................................................... 31
4.2 Density ................................................................................................................ 32
4.3 Two Roll Mill ..................................................................................................... 35
4.4 Ashing ................................................................................................................. 37
4.5 Injection Moulder ............................................................................................... 39
4.6 Compression Moulding ....................................................................................... 42
4.7 Laser Cutting ....................................................................................................... 45
4.8 Tensile & Flexural Strength / Modulus .............................................................. 46
4.9 FEGSEM ............................................................................................................. 49
4.10 Electrical Conductivity ..................................................................................... 51
4.11 Thermal Conductivity ....................................................................................... 53
Chapter 5.0 - Results

5.1 Powder Characterisation
  5.1.1 Carbon Black
  5.1.2 Graphite
  5.1.3 Magnetite
  5.1.4 Errors

5.2 Ashing
  5.2.1 Errors

5.3 Electrical Conductivity
  5.3.1 Carbon Black
  5.3.2 Graphite
  5.3.3 Magnetite
  5.3.4 Errors

5.4 Thermal Conductivity
  5.4.1 Carbon Black
  5.4.2 Graphite
  5.4.3 Magnetite
  5.4.1 Errors

5.5 Tensile & Flexural
  5.5.1 Carbon Black
  5.5.2 Graphite
  5.5.3 Magnetite
  5.5.4 Errors

5.6 Microstructure
  5.6.1 Carbon Black
  5.6.2 Graphite
  5.6.3 Magnetite
  5.6.4 Errors

Chapter 6.0 - Modeling

6.1 Theories
  6.1.1 Electrical / Thermal – Percolation Theory
  6.1.2 Mechanical - The rule of mixtures

6.2 Models
  6.2.1 Electrical conductivity
  6.2.2 Thermal conductivity
  6.2.3 Mechanical strength

6.3 Summary

6.4 Modeling of Experimental Data
  6.4.1 Electrical Conductivity Models
  6.4.2 Thermal Conductivity Models
  6.4.3 Mechanical Models

Chapter 7.0 - Discussion

Chapter 8.0 - Conclusions
Chapter 9.0 - Future Work ................................................................. 152

Appendix A .................................................................................... 154
Appendix B .................................................................................... 155
Appendix C .................................................................................... 156
Appendix D .................................................................................... 157
Appendix E .................................................................................... 158
Appendix F .................................................................................... 159
Appendix G .................................................................................... 160
Appendix H .................................................................................... 162
Appendix I .................................................................................... 165
Appendix J .................................................................................... 166
Appendix K .................................................................................... 167
Appendix L .................................................................................... 168

References ..................................................................................... 173
List of Tables

Table 1 - Comparison of operating temperatures, electrolyte materials, reaction processes, charge carriers, efficiencies and power output ranges for different types of fuel cell \(^\text{[1]}\) ........................................................................... 3

Table 2 - The US Department of Energy targets for 2015 for stack and bipolar plate characteristics. ................................................................. 13

Table 3 - Comparison of 316L stainless steel, aluminium and graphite with commercially available bipolar plate materials as well as specified materials investigated in the literature. The US DOE 2015 targets are also included........................................................................... 12

Table 4 - Injection moulding parameters used for the carbon, graphite and magnetite composites. ........................................................................ 40

Table 5 - Hot press parameters used for the carbon, graphite and magnetite composites up to 60/70 wt%. ........................................................................ 43

Table 6 - Ashing test results for carbon, graphite and magnetite powders showing a maximum increase of 6 % for the 50 wt% carbon and a maximum decrease in percentage of 3 % for the 60 wt% graphite. ......................... 63

Table 7 - Comparison of bipolar plate properties from table 3 with the best results gained from the polyethylene carbon, graphite and magnetite composites. All values are a maximum for the particular grade specified unless further information is specified in brackets. ...................... 146
List of Figures

Figure 1 - Schematic diagram of a typical fuel cell electrochemical conversion process. ................................................................. 1

Figure 2 - The electrochemical process in a PEM fuel cell showing major fuel cell components. ......................................................... 6

Figure 3 - Structure of a PEMFC membrane electrode assembly - electrode, catalyst layer and membrane. ............................................. 8

Figure 4 - Hexagonal graphite structure (as opposed to rhombohedral graphite which is considered thermodynamically unstable.) ...................... 17

Figure 5 - Major components of the Malvern Zetasizer and Matersizer used to measure particle size. ........................................................... 31

Figure 6 - Micromeritics Helium Pycnometer used to measure density of solids especially where agglomerations are present. .................. 32

Figure 7 - Two Roll Mill concept for mixing multiple components namely polymeric based materials. .............................................. 35

Figure 8 - Ashing test procedure used to determine the weight percentage of filler for each composite batch. .................................................. 37

Figure 9 - Injection moulding process (simplified) showing the metering and injection stages. ................................................................. 39

Figure 10 - Hot press equipment showing the heating stage prior to compression. An example of moulding plates is also shown. ................. 42

Figure 11 - Laser cutting process for the carbon, graphite and magnetite composites. ................................................................................. 45

Figure 12 - Tensile test jaw setup for the tensile strength tests conducted with a 2.5 kN load cell. ................................................................. 46

Figure 13 - 3 point bend test apparatus used for the flexural strength tests used with a 2.5 kN load cell. ......................................................... 47

Figure 14 - Major components of a Field Emission Gun Scanning Electron Microscope (FEGSEM). ................................................................. 49
Figure 15 - Sample holder for electrical conductivity measurements. The 4 connections (positive supply, negative supply and the two voltage probes) are connected to a Danbridge DB501 4-point probe. The white solid arrow indicates injection moulding flow direction and the dotted white arrow indicates the perpendicular direction.

Figure 16 - Working parts of the Cussons P5687 thermal conductivity apparatus showing sample preparation before clamping.

Figure 17 - Particle size distribution for Carbon powder. The peak particle count shown is at 145 nm. The D[4,3] (mean) particle size was 149 nm.

Figure 18 - Carbon powder FEGSEM micrographs showing secondary structures (Figs. 18a and b), and primary structures (Figs. 18c and d).

Figure 19 - Particle size distribution for Graphite powder. The peak particle count shown is at 443 µm. The D[4,3] (mean) particle size was 447 µm.

Figure 20 - Graphite powder FEGSEM micrographs showing mainly flat plate structures (Figs. 20a and b) amongst smaller shards of graphite (Fig. 20c).

Figure 21 - Particle size distribution for Magnetite powder. The peak particle count shown is at 63 µm. The D[4,3] (mean) particle size was 71 µm.

Figure 22 - Magnetite powder FEGSEM micrographs showing sharp edged boulder-like particles (Figs. 22a and b) of up to 40 µm in size with small fragments of approximately 1 to 3 µm (Fig. 22c).

Figure 23 - The electrical conductivity of the carbon composite showed two similar sets of results for through plane and in plane conductivities. Both sets of data showed an increase in conductivity with increasing carbon content.

Figure 24 - In plane graphite electrical conductivity showing an exponential increase with increasing graphite loading. Through plane conductivity is not shown due to no conductivity measured.

Figure 25 - Compression moulded graphite composite electrical conductivities for in plane and through plane directions both with exponential increases beyond 50 wt%.

Figure 26 - Thermal conductivity results for injection and compression moulded carbon composites up to 65wt% and 32wt% respectively.

Figure 27 - Thermal conductivity results for injection and compression moulded graphite composites up to 57 wt%.

Figure 28 - Thermal conductivity results for injection and compression moulded magnetite composites up to 71 wt%.
List of Figures

Figure 29 - Comparison of tensile strength for injection and compression moulded carbon composites with increasing carbon content. ................................. 76

Figure 30 - Elastic modulus of injection and compression moulded carbon composites................................................................................. 77

Figure 31 - Flexural strength variation with increasing carbon content for injection and compression moulded carbon composites......................... 78

Figure 32 - Flexural modulus of injection and compression moulded carbon composites.................................................................................. 79

Figure 33 - Tensile strength of injection and compression moulded graphite composites with increasing graphite content........................................ 80

Figure 34 - Elastic modulus of injection and compression moulded graphite composites..................................................................................... 81

Figure 35 - Comparison of injection and compression moulded graphite composite flexural strengths with increasing graphite content......................... 82

Figure 36 - Flexural modulus of injection and compression moulded graphite composites.................................................................................. 83

Figure 37 - Variation in tensile strength with increasing magnetite content for injection and compression moulded magnetite composites.................... 84

Figure 38 - Elastic modulus of injection and compression moulded magnetite composites................................................................................. 85

Figure 39 - FEGSEM micrographs of (a) 11 wt%, (b) 26 wt%, (c) 32 wt%, (d) 40 wt%, (e) 56 wt% and (f) 65 wt% injection moulded carbon in polyethylene................................................................. 88

Figure 40 - FEGSEM micrographs of (a) 11 wt%, (b) 26 wt% and (c) 32 wt% compression moulded carbon in polyethylene....................................... 89

Figure 41 - FEGSEM micrographs of (a) 14 wt%, (b) 23 wt%, (c) 29 wt%, (d) 39 wt%, (e) 50 wt% and (f) 57 wt% injection moulded graphite in polyethylene................................................................. 91

Figure 42 - FEGSEM micrographs of (a) 14 wt%, (b) 23 wt%, (c) 29 wt%, (d) 39 wt%, (e) 50 wt% and (f) 57 wt% compression moulded graphite in polyethylene................................................................. 92

Figure 43 - FEGSEM micrographs of (a) 9 wt%, (b) 20 wt%, (c) 32 wt%, (d) 40 wt%, (e) 51 wt%, (f) 60 wt% and (g) 71 wt% injection moulded magnetite in polyethylene................................................................. 94
Figure 44 - FEGSEM micrographs of (a) 9wt%, (b) 20wt%, (c) 32wt%, (d) 40wt%, (e) 51wt%, (f) 60wt% and (g) 71wt% compression moulded magnetite in polyethylene. ................................................................. 96

Figure 45 - Representation of percolation theory where increasing filler content from (a) to (c) eventually forms clusters, highlighted in green, that create conduction paths. .......................................................... 100

Figure 46 - Electrical conductivity profile for composites with increasing filler volume fraction displaying different cluster formations. ................. 101

Figure 47 - Averaged in plane and through plane conductivity plot for the electrical conductivity of the injection moulded carbon composites. The model fitting is shown with a solid line. .............................................. 118

Figure 48 - Balberg’s Structures [84] - (a) No structure, (b) low structure, (c) high structure. ......................................................................................................... 119

Figure 49 - Links Nodes and Blob structures [85] - (a) Nodes, (b) Links, (c) Blobs. ξ is a unit length. ...................................................................................... 120

Figure 50 - In plane electrical conductivity plot for graphite model. The model is represented by the solid line and fit to the experimental data points. .... 121

Figure 51 - Averaged data plot combining in plane and through plane electrical conductivities for compression moulded graphite composites. ........ 122

Figure 52 - Representation of a shell structure [68] where L is the polymer phase diameter and nd is the number of particles (n) multiplied by the particle diameter (d). ................................................................. 125

Figure 53 - Thermal conductivity models (solid lines) fitted to the injection and compression moulded carbon composite data. ....................... 126

Figure 54 - Results of the thermal conductivity models (solid lines) for injection and compression moulded graphite composites fitted to the experimental data. ......................................................... 127

Figure 55 - Injection and compression moulded thermal conductivity models, shown in solid lines, for the polyethylene magnetite composites. .......... 129

Figure 56 - Elastic modulus models for the injection and compression moulded carbon composites. ................................................................. 131

Figure 57 - Flexural modulus models for injection and compression moulded carbon composites. ................................................................. 132

Figure 58 - Elastic modulus models for injection and compression moulded graphite composites. ................................................................. 133
List of Figures

Figure 59 - Flexural modulus models for injection and compression moulded graphite composites. ................................................................. 134

Figure 60 - Elastic modulus models for injection and compression moulded magnetite composites ............................................................ 135

Figure 61 - Comparison of Mamunya’s model for electrical conductivity with experimental data obtained in this study for injection moulded carbon composites ................................................................. 168

Figure 62 - Extract from Mamunya et al [67] showing the electrical conductivity trends of modelled data and experimental data .................. 169

Figure 63 - Compressibility of polyethylene with increasing temperature conducted by Chung [90], the last data point is an extrapolation to 240 °C. .......... 170

Figure 64 - The volume percent change of polyethylene at 10 bar of pressure for increasing temperature .......................................................... 171

Figure 65 - The volume percent change of polyethylene at 160 °C with increasing pressure ................................................................. 172
Nomenclature

A - Sample cross-sectional area
b - Sample width
β - Compressibility
Cp - Heat capacity of water
d - Sample thickness
δP - Change in pressure
Δl - Change in length
Ec - Elastic modulus of the composite
Em - Elastic modulus of the matrix
Ef - Elastic modulus of the filler.
F - Force at proportional limit
F - Packing factor
f - Modeled data
KE - Einstein coefficient
K - Thermal conductivity (W/mK)
Km - Thermal conductivity of the composite
Kl - Thermal conductivity of the polymer
Kh - Thermal conductivity of the filler
l - Original length
L - Span length
m - Gradient of proportional section
M - Mass of water collected
Mcr - Empty crucible mass
M_{Cr+PE+F} - Crucible and PE-filler mass.
M_{Cr+F} - Crucible and burnt PE-filler mass.
Mp - Mass of powder.
M_{CUP} - Mass of cup.
N - Exponent
νm - Poisson’s ratio of the matrix
P1 - Prep Pressure
P₂ - Test Pressure
P - Maximum load
Pₚₘ - Thermal resistivity of the composite
Pₜₚ - Thermal resistivity of the filler
Pₜ₁ - Thermal resistivity of the polymer
ϕₜ - Critical volume fraction
ϕ - Filler volume fraction
Q - Heat conducted
σ - Conductivity (S/cm)
σₚₜ - Flexural stress
ρₜₚ - Density of the filler
ρₚₘ - Density of the matrix
ρₚₚ - Electrical resistivity of the composite
ρₜₚ - Electrical resistivity of the filler
ρₜ₁ - Electrical resistivity of the polymer
SSₕₚ - Sum of squares of the residuals
SSₜₒ₉₉ - Total sum of squares
Ω - Resistance (ohms)
σ - Electrical conductivity of the composite
σₜ - Electrical conductivity at the percolation threshold
σₚₚ - Electrical conductivity at the maximum packing factor
σ₁ - Electrical conductivity of the polymer
σₜₚ - Electrical conductivity of the filler
σ - Electrical conductivity of the composite
T₁ - Temperature of the lower stage
T₂ - Temperature of the upper stage
t - Time for water collection
t - Critical exponent
Vₐₕₜ - Empty volume of the sample chamber (with cup)
Vₐₚₑₓₚ - Expansion volume
Vₛₐₜ₉₉ - Volume of test sample
Vₜ - Volume fraction of filler.
Vₜ’ - Lowest filler volume fraction
(1-Vₙ) - Volume fraction of matrix.
Nomenclature

V - Initial volume
δV - Change in volume
Vol% - Volume percentage of the filler
wt% - Weight percentage of the filler
W₁ - Water inlet temperature
W₂ - Water outlet temperature
Wt%F - Weight percentage of filler.
x - Experimental data
\bar{x} - Mean of the experimental data
Chapter 1.0

Introduction

1.1 What is a fuel cell

Fuel cells are devices that electrochemically combine a fuel and oxidant to produce electrical energy. In terms of electron transfer, the process involves oxidation of reactants on one side of the fuel cell (e.g. $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$) and a reduction of reactant ions on the other side (e.g. $2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{H}_2\text{O}$) whilst electrons released from the reaction drive an external circuit. Below is a picture of a typical fuel cell depicting the process.

Figure 1 - Schematic diagram of a typical fuel cell electrochemical conversion process.
All fuel cells contain electrodes, an anode where oxidation (loss of electrons) occurs and a cathode where reduction (gain of electrons) takes place. Sandwiched between the two electrodes is an electrolyte, most fuel cell electrolytes are solid however some are liquid. Most fuel cells utilise catalyst layers (which can be considered part of the electrode) between the electrode and electrolyte and are where the actual electrochemical reactions take place.

Catalyst layers contain a transition element(s) that induces electrochemical reactions on its surface, as found by William Grove back in 1839 where the recombination of hydrogen and oxygen into water took place in two half cells made with platinum electrodes.

Once the fuel on the anode splits and the electrons move through the external circuit, the reactant ions travel though the electrolyte that has been specifically designed to allow the reactant species to pass through to the cathode. This in a way helps to prevent non reactants i.e. pollutants crossing over and facilitates the crossover of the reactant ions for recombination with other reactant species on the cathode.

At the cathode, the oxidant (oxygen) combines with the incoming anode reactant species and the returning electrons from the external circuit to complete the reaction resulting in the production of water. As well as water production, beneficial heat is produced that can be used to keep low temperature fuel cells at their optimum operating temperatures.

Unlike batteries where there are fixed amounts of reactants limiting the output of electrical energy, fuel cells can sustain their electrical output as long as there is a constant supply of reactants and are operating within preferred temperature limits.

1.2 Types of fuel cell

There are many types of fuel cell each operating at different temperatures, utilising different fuels with different electrolyte structures/materials. The main types of fuel
cell are Direct Methanol (DMFC), Polymer Electrolyte Membrane (PEMFC), Alkaline (AFC), Phosphoric Acid (PAFC), Molten Carbonate (MCFC) and Solid Oxide fuel cells (SOFC). Below in table 1 is a fuel cell comparison showing the differences in operating temperatures, electrolyte materials, reaction processes, charge carriers, efficiencies and power ranges of the various fuel cells.

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Operating Temperature</th>
<th>Electrolyte Material</th>
<th>Overall Reaction Process</th>
<th>Charge Carrier</th>
<th>Efficiency (Typical)</th>
<th>Power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMFC</td>
<td>50-90°C</td>
<td>Sulphonated PTFE</td>
<td>CH₃OH + 3/2 O₂ → 2H₂O + CO₂</td>
<td>H⁺</td>
<td>40%</td>
<td>0.5-1</td>
</tr>
<tr>
<td>PEMFC</td>
<td>80°C</td>
<td>Sulphonated PTFE</td>
<td>H₂ + 3/2 O₂ → H₂O</td>
<td>H⁺</td>
<td>40-50%</td>
<td>0.001-1000</td>
</tr>
<tr>
<td>AFC</td>
<td>60-220°C</td>
<td>Potassium Hydroxide</td>
<td>H₂ + 3/2 O₂ → H₂O</td>
<td>OH⁻</td>
<td>50%</td>
<td>1-100</td>
</tr>
<tr>
<td>PAFC</td>
<td>200°C</td>
<td>Concentrated Phosphoric Acid</td>
<td>H₂ + 3/2 O₂ → H₂O</td>
<td>H⁺</td>
<td>40%</td>
<td>50-1000</td>
</tr>
<tr>
<td>MCFC</td>
<td>650°C</td>
<td>Molten Carbonate</td>
<td>H₂ + 3/2 O₂ → H₂O</td>
<td>CO₃²⁻</td>
<td>45-55%</td>
<td>100-100,000</td>
</tr>
<tr>
<td>SOFC</td>
<td>600-1000°C</td>
<td>Yttrium-stabilised Zirkondioxide</td>
<td>H₂ + 3/2 O₂ → H₂O</td>
<td>O⁻</td>
<td>50-60%</td>
<td>10-100,000</td>
</tr>
</tbody>
</table>

Table 1 - Comparison of operating temperatures, electrolyte materials, reaction processes, charge carriers, efficiencies and power output ranges for different types of fuel cell [1].

Fuel cells can be categorised into low temperature fuel cells such as direct methanol, polymer electrolyte membrane and alkaline fuel cells; medium temperature fuel cells such as the phosphoric acid fuel cell and high temperature fuel cells such as the molten carbonate and solid oxide fuel cells.

**Direct Methanol**

Direct methanol fuel cells operate on liquid methanol where methanol and water from a 1 molar solution react at the anode producing carbon dioxide and hydrogen ions (H⁺).
The hydrogen ions pass through a polymer membrane to combine with oxygen at the cathode to produce water, both electrodes incorporate platinum catalysts. \[2\]

**Polymer Electrolyte Membrane**

Polymer electrolyte membrane fuel cells utilise hydrogen gas at the anode forming water at the cathode when the hydrogen ions are combined with oxygen, they also use a polymer membrane as an electrolyte and a platinum catalyst. \[2\]

**Alkaline**

Alkaline fuel cells using platinum catalysts oxidise hydrogen gas at the anode with hydroxyl ions (OH\(^-\)) from the liquid potassium hydroxide electrolyte. Water produced from the reaction remains in the electrolyte and the electrons released reduce oxygen at the cathode in the presence of water to produce hydroxyl ions that are added to the electrolyte. \[2\]

**Phosphoric Acid**

Phosphoric acid fuel cells use liquid phosphoric acid as an electrolyte to facilitate the passage of hydrogen ions toward the cathode. The hydrogen ions are produced from hydrogen gas at the anode in the same way as DMFCs and PEMFCs. \[2\]

**Molten Carbonate**

Molten carbonate fuel cells incorporate a porous ceramic electrolyte filled with a molten carbonate salt mixture. Carbonate ions (CO\(_3^{2-}\)) in the electrolyte react with hydrogen gas at the anode catalyst (non precious metals used) to form water and carbon dioxide. Electrons released reduce oxygen in the presence of carbon dioxide (which is fed back from the anode) at the cathode to produce carbonate ions that pass into the electrolyte. The high temperature of the fuel cell means that various hydrocarbons can be used as a fuel, as internal reforming enables hydrogen extraction from such fuels. \[2\]
Solid oxide fuel cells split hydrogen, from various light hydrocarbons, at the anode releasing electrons to react with oxygen at the cathode to produce oxygen ions (O$_2^-$), the ions then travel thorough a solid ceramic electrolyte made of Yttria stabilised zirconia (YSZ). The oxygen ions are combined at the anode with hydrogen ions to produce water. Like MCFCs, internal reforming can be accomplished due to the high operating temperatures. [2]

1.3 Applications/Benefits

Fuel cells are used in a variety of applications from residential (SOFCs, PAFCs and MCFCs), terrestrial and marine vehicles (PEMFCs) to space (AFCs) [3]. Fuel cells utilise more energy from fuel due to the higher efficiencies of electrochemical conversion, typically 60%, compared to combustion engines of around 25 % [4] in laboratory tests. Fuel cells are silent with only water and heat being the main products if not the only products for most types of fuel cell. Stack and system design can be tailored to specific applications with particular space requirements, as there are no moving parts in a fuel cell this adds to the simplicity of the system and reduces maintenance costs.

The main benefit of fuel cells is to reduce global carbon dioxide (CO$_2$) levels when using renewable hydrogen, e.g. hydrogen obtained from the electrolysis of water using energy from renewable power sources. Road transport accounts for 10.5 % of global CO$_2$ emissions where CO$_2$ itself is attributable to 77 % of all greenhouse gasses [3].

PEM fuel cells have a faster start up time than other fuel cells, are capable of high power densities and operate at relatively low temperatures. Sealing and assembly are less complex with no need for corrosive acids or bases as in other fuel cells [5]. This makes them attractive for use in automotive applications and is the type of fuel cell discussed in this thesis.
The structure of PEM fuel cells along with current difficulties in optimizing performance are detailed in the next section.

1.4 The PEM Fuel Cell

![Diagram of a PEM fuel cell]

Figure 2 - The electrochemical process in a PEM fuel cell showing major fuel cell components.

Above is a diagram of a PEM fuel cell. They convert hydrogen into $\text{H}^+$ ions and electrons at the anode which are then recombined with oxygen at the cathode. Below are the reactions at each electrode.

Anode: $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$

Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

The electrons produced at the anode flow around an external circuit to the cathode and provide the electricity, however current flows in the opposite direction from cathode to anode.

The fuel cell system contains many cells connected together to form a stack, each cell typically contributes approximately 0.7 V to the overall stack voltage and so the number of cells used is governed by the desired voltage output. Just like batteries connected in
series, many cells provide a higher potential. Typical laboratory efficiencies of PEM fuel cells are 60% but can be as much as 80% for combined heat and power sources (CHP) where the heat generated from a stack provides a useful source of energy.

Each cell in the stack is made up of a solid polymer electrolyte and porous electrodes (incorporating the gas diffusion layers and catalyst layers). In a stack the cells are connected alternately in series with bipolar plates that also serve to deliver reactant gases, remove exhaust gases and liquid water and provide cooling if required.

1.4.1 The Electrolyte

The most common electrolyte is Nafion which is essentially sulfonated polytetrafluoroethylene (PTFE).

The strong bonds between the fluorine and the carbon make it durable and resistant to chemical attack, the material can be made into thin films of about 50 μm thick due to its mechanically strong nature. The material is hydrophobic but the ionically bonded HSO₃ groups (forming SO₃⁻ ions on the side chains) are hydrophilic which cluster together, thus creating hydrophilic regions within a hydrophobic substance. Water is absorbed into the structure where the H⁺ ions (that are weakly attracted to the SO₃⁻ groups) can freely move between the hydrophilic clusters and create a dilute acid. The H⁺ ions can move along the structure but the hydrated regions must be as large as possible for this to happen and so the protonic conductivity of the electrolyte is linked to water content. Typically in a well hydrated electrolyte there will be about 20 water molecules for each SO₃⁻ side chain [2].

1.4.2 The Electrode/Catalyst Layer

Platinum (Pt) is the best catalyst for the anodic and cathodic reactions although they can be rendered inactive/poisoned by low levels (>50 ppm [1]) of carbon monoxide (CO) in a contaminated fuel supply. Small Pt particles are embedded on the surface of larger carbon particles to form a carbon-supported catalyst (Pt/C). This means that there will be a very high surface area of Pt in contact with the reactants. The carbon-supported
catalyst is usually fixed to a carbon cloth/paper and often PTFE is added to expel water to the surface from where it can evaporate. The carbon cloth provides some mechanical strength for the electrode and forms the electrical contact between the catalyst and bipolar plate; it also helps to diffuse the gas onto the catalyst and so is called the gas diffusion layer. The electrode is then fixed to each side of the polymer electrolyte to form a membrane electrode assembly (MEA).

1.4.3 The Membrane Electrode Assembly

Figure 3 shows the arrangement of the membrane and electrode in a MEA.

![Figure 3 - Structure of a PEMFC membrane electrode assembly - electrode, catalyst layer and membrane.](image)

In order for a fuel cell to function, the Pt particles have to be in contact with their carbon support to provide an electron conduction path away from the catalyst layer to the external circuit. The Pt particles also have to be accessible to the hydrogen gas flowing through the porous structure of the electrode and catalyst layer. Finally the Pt particles have to be in sufficient contact with the electrolyte to allow the H⁺ ions to
traverse the membrane to the cathode. This situation gives rise to a number of optimisation / balancing problems.

Although conductivity in the electrolyte increases with increasing water content, too much water can block the pores within the electrodes and gas diffusion layers hindering gas flow. As water is produced at the cathode, air is fed through the cell at a faster rate than necessary which provides more than the stoichiometric amount of oxygen. The air flowing over the cathode is used to remove product water.

A reduction in gas flow and/or concentration is called a mass transport loss or concentration overvoltage. This is not only due to water blockage as mentioned above but also the oxygen content in the air as oxygen is used up as it passes over the MEA leaving a higher concentration of nitrogen towards the end of its flow cycle. This results in a voltage drop where the degree of oxygen depletion is dependent on the amount of current being drawn and current density would be lowest where the oxygen concentration is lowest [2].

During operation, protons moving from anode to cathode typically pull water molecules with them, called electro-osmotic drag. This can produce a drying effect at the anode side of the electrolyte even when the cathode is well hydrated, especially at high current densities. As the membranes are very thin they are prone to drying out and low relative humidities of the gasses add to the drying effect. At approximately 60 °C gas flow will dry out the electrodes (mainly the anode) faster than the water is produced and so external humidification is necessary. Typically the relative humidity is above 80 % to prevent drying out of the membrane and less than 100 % to prevent water build up in the electrodes [2].

Other losses that occur within the PEM fuel cell are activation overvoltage, fuel crossover and ohmic overvoltage. Activation overvoltage is caused by losses in driving the chemical reaction that transfer electrons to and from the electrodes. Where the electrode and electrolyte come into contact there is a build up of charge where the electrons from the electrode and the protons from the electrolyte meet at the cathode, called the charge double layer. The build up of charge means that there will be a
voltage produced (activation overvoltage) and so the more charge built up the bigger 
the activation overvoltage. The catalyst increases the probability of the cathodic 
reaction without a large build up of charge. Ways of decreasing activation 
overpotential include using more effective catalysts, increasing electrode roughness (i.e. 
surface area), increasing reactant concentration, increasing the pressure and increasing 
temperature [2].

Fuel crossover (or Internal Currents) occurs when small numbers of electrons are 
conducted through the electrolyte and do not contribute to the electrical power of the 
fuel cell. Small amounts of reactant (H\textsubscript{2}) may also cross over the electrolyte and react 
with the oxygen at the cathode and so will also not contribute to any electrical 
generation.

Resistance losses (ohmic overvoltage) stem from a resistance to the conductance of 
electrons and protons in the electrodes and electrolyte respectively. There can be higher 
than normal resistances if the electrodes and electrolyte or the electrodes and bi-polar 
plates do not have sufficient contact for efficient conduction. The resistances can be 
decreased by the use of thin electrolytes, although some thickness is required to prevent 
short circuits, high conductivity electrode and bipolar plate materials and efficient 
design of fuel cell components to reduce contact resistance [2].

1.4.4 The Bipolar Plate

Bipolar plates connect MEAs together in series between each electrode. The end plates 
(monopolar plates) conduct electrons to and from the external circuit whilst clamping 
the whole fuel cell structure together. The bipolar plates also house distribution 
channels (flow fields) for the reactant gases to flow over each MEA. There are many 
designs for bipolar plate flow fields all with the aim to prevent/minimise blockages due 
to water build up and enable suitable gas flow to remove unwanted/waste products.

The most common flow field design is the serpentine design. The channels, usually 
1mm x 1mm cross section, should be large enough to allow the passage of water 
droplets and gas through the fuel cell. Also the system design should allow for the
length of the channels which cause large pressure drops from inlet to outlet. Without this, a region of the electrode would be left without any reactants and so a performance decrease would occur.

With two flow fields on each side and a central spine to separate them, the bipolar plates become very thick when compared to the MEA and so account for ~ 80 % of the overall mass of the fuel cell [6]. The cost and complexity of bipolar plates increase when there is a need for stack cooling. As fuel cells increase in size there is a greater need to remove unwanted heat from the stack and it becomes harder to ensure that all parts of the fuel cell are cooled to same or similar temperatures. Usually another set of channels are cut into the bipolar plate or alternatively separate cooling plates are added through which air or water is passed. Typically fuel cells below 2kW are air cooled and larger fuel cells are water cooled where the water can be used for CHP production [2].

Bipolar plates have a higher cost compared to the other fuel cell components due to lengthy production cycles for machining and surface treatment as most bipolar plates are made from graphite or stainless steel. Graphite is a good conductor, better than stainless steel, and can withstand a corrosive environment. However it is very brittle and plates manufactured using graphite need to be of a minimum thickness in order to provide sufficient mechanical strength when inserted into a fuel cell. Once in operation, the bipolar plates are subjected to membrane expansion forces and vibrational forces, especially in automotive applications, as well as the weak acid environment within the membrane. Stainless steel can better handle the mechanical requirements of a fuel cell at lower thicknesses but does not do well with respect to corrosion resistance and electrical conductivity when compared to graphite. Poor electrical conductivity of bipolar plates will add to the overall resistance losses of the fuel cell and is magnified when large numbers of plates (depending on voltage requirements) are incorporated into a fuel cell. These disadvantages and materials discussions will be elaborated on further in the next chapter.
Chapter 2.0

The Thesis

2.1 Thesis Objectives / Rationale

There are many problems that hinder fuel cell technology from being fully commercialised; these are mainly due to the reasons described previously in section 1.4. These were, the potential poisoning of the catalyst, membrane hydration and porous layer and flow field blockages leading to gas flow problems. These factors can lead to, over time, membrane wear and tear and reduced fuel cell performance. Due to this, fuel cells are not completely reliable or durable and have operating lifetimes of around 2000 hours \(^7\) compared to 10,000 hours for modern internal combustion engines \(^8\).

There has been considerable attention paid to bipolar plate research, metals have been extensively researched in order to reduce / eliminate their corruption tendencies as they can be made thin with good mechanical strength. However, in addition to the reduction in bipolar plate performance over time due to corrosion, membrane contamination by metal ions also occurs. Due to this, research has been conducted into alternative corrosion resistant polymeric based bipolar plates. It has been demonstrated that polymers filled with conductive fillers could provide some level of conductivity whilst retaining the benefits of corrosion resistance and fast manufacture. By using highly conductive, low density, corrosion resistant fillers together with a polymeric matrix, the issues of electrical and thermal conductivity of the composite become the main hurdles to overcome. When investigating polymeric bipolar plate materials, there is a balancing act between the electrical / thermal properties and the mechanical properties.

The main aims of any bipolar plate research is to decrease bipolar plate mass and cost and to increase mechanical strength whilst providing sufficient electrical and thermal
conductivity. The US Department of Energy has stated targets for various bipolar plate requirements for 2015 as can be seen in table 2 below and is a good guide for current progress. Graphite plates alone cannot fully meet the mechanical requirements of a fuel cell, however, mixed with a polymeric binder its mechanical properties are improved but at the loss of electrical conductivity.

Table 2 below details the US department of Energy’s targets for 2015 \(^9\) for automotive PEM fuel cells.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Cell Stack</td>
<td></td>
</tr>
<tr>
<td>Lifetime</td>
<td>5,000 hours</td>
</tr>
<tr>
<td>Power density</td>
<td>650 W/kg</td>
</tr>
<tr>
<td>Cost per kW</td>
<td>$30/kW</td>
</tr>
<tr>
<td>Bipolar Plate</td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>&gt; 100 S/cm</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>&gt; 20 W/mK</td>
</tr>
<tr>
<td>Gas Permeability</td>
<td>&lt; 2x10(^{-6}) cm(^3)/s cm(^2)</td>
</tr>
<tr>
<td>Corrosion (current)</td>
<td>&lt; 1 µA/cm(^2)</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>&gt; 25 MPa</td>
</tr>
</tbody>
</table>

Table 2 - The US Department of Energy targets for 2015 for stack and bipolar plate characteristics.

In order to increase power density and lower the cost per kW of fuel cells, polymeric plates offer lower densities with cheaper material costs. Cost is further improved by employing mass production techniques such as injection and compression moulding that take advantage of polymeric materials. Injection moulding would be able to supply the mass production demands for fuel cells, where for automotive use there could be over 400 bipolar plates employed for a 300 V system. Production cycle times for injection moulding have been reported as low as 10 seconds per plate whilst projected costs have been calculated at €1.4 per plate \(^{10}\).

Due to the mechanical insufficiencies of graphite and the corrosion problems inherent to metallic materials as well as the complexities of production for such materials;
injection mouldable materials with highly conductive, corrosion resistant properties would be ideal. The aim of the thesis is to mix different conductive powders with a thermoplastic polymer to create a cost effective composite material that exhibits such properties mentioned previously using common polymer processing techniques. Details of the injection and compression moulding techniques and how they work are detailed in chapter 4. The materials were tested for flexural, tensile, thermal and electrical properties and used to verify/improve current models that describe such behaviour in composite materials.

Current models used to explain electrical, thermal and mechanical composite behaviour will be looked at and one model per property chosen and applied to this study. As the processing of these materials can influence these properties, the models, where applicable, will be adapted to take into account such variations in processing plus any behaviour that would arise from the experimental results.

2.2 Layout of the Thesis

The thesis looks at the current materials and production methods used in bipolar plate manufacture together with experimental results from various sources in the literature and recommended targets set by the DOE will be used to gauge material suitability. The methods used to carry out the experimental work are given in chapter 4 describing techniques employed from material manufacture to sample testing. Results and discussions on the polymeric bipolar plate materials will be presented in chapter 5 and current models used to model behaviour of such materials will be described in chapter 6. Further discussions will be presented in chapter 7 comparing the suitability of materials from this study to those in the literature as well as the DOE targets and finally, chapters 8 and 9 will conclude the study and recommendations will be made for future work.
Chapter 3.0

Literature - Bipolar Plates

Bipolar plates account for significant portions of the overall mass and cost of PEM fuel cells. Woodman et al [11] stated that for a 33 kW stack 88% of its mass could be attributed to graphitic plates or 81% if metallic plates were used. Tsuchiya et al [12] apportioned 45% of the overall stack cost to the bipolar plates. By applying a learning curve they found that stack costs could be reduced to the same level as that of internal combustion engines. The key factors for this were the power density improvement and mass production processing of bipolar plates and electrodes enabling a cost of 38 $/kW with a volume production of 5,000,000 stacks [12].

3.1 Function

Bipolar plates have many functions; Cooper [13] listed 51 bipolar plate requirements and design rules, however only factors related to this thesis will be mentioned here, they are:

- Delivery of reactant gasses over the whole MEA surface.
- Enable the removal of reaction / unwanted products.
- Prevent leakage of gasses and coolant together with the gasket.
- Form an electrical contact between neighbouring cells.
- Remove unwanted heat from the active area.
- Provide some structural support for the mechanically weak MEAs.

With these requirements in mind, bipolar plate materials and associated production processes have to produce bipolar plates that:
• Accommodate small narrow channels with complex flow field designs in order to maximise the spread and control of reactant gases over the MEA surface.
• Allow flow field designs that facilitate reactant and waste species throughput to prevent build up of oxygen depleted air (nitrogen) and liquid water.
• Enable sufficient sealing with the gasket material in order to retain appropriate gas flow and pressures.
• Minimise electrical resistance to maximise electrical efficiency as poor plate performance is magnified by the number of plates within the stack.
• Are thermally conductive to create optimal fuel cell operating conditions i.e. by removing excess heat and maintaining optimal operating temperatures to aid membrane performance and gas humidification.
• Are mechanically strong enough to withstand forces during stack compaction whilst being as thin as possible to reduce overall stack mass and volume.

3.2 Current Bipolar Plate Materials

Graphite

Graphite plates are usually manufactured by the compression moulding of a phenolic resin (thermoset polymer) binder with as high a graphite loading as possible \(^{[14]}\). For example, the filler content in plates manufactured by Schunk are in the region of 70-95 wt\% \(^{[15]}\). The plate is moulded into a flat sheet of the required bipolar plate thickness and then flow fields and other features such as bolt holes are later machined into the plate. Graphite plates tend to be heavy as they can have a density of 2.26 g/cm\(^3\) \(^{[16]}\) and their high costs result from intensive labour processes and manufacturing by milling which is a very expensive process \(^{[17]}\).

Graphite is one allotrope of carbon. Unlike the ground state of free carbon where there are two valence electrons, graphite has a valence state of four. This arises when one of the two electrons from the s-orbital is promoted to a higher orbital, a 2p orbital, where the 2s-orbital and two 2p-orbitals become hybridized to form a sp\(^2\) orbital. A delocalised 2p orbital is also formed resulting in a valence of 4 electrons for bonding to other atoms. Each sp\(^2\) orbital bonds with another sp\(^2\) orbital to form a hexagonal
structure in a parallel plane (basal plane). The delocalised 2p orbital which is perpendicular to the plane bonds to other delocalised orbitals of different planes to form the graphite structure \[^{[18]}\] as shown in figure 4.

![Figure 4 - Hexagonal graphite structure (as opposed to rhombohedral graphite which is considered thermodynamically unstable.)](image)

The electrical and thermal conductivities of graphite are greatest in the basal plane and fairly poor between planes giving rise to anisotropic properties. This is due to the strong covalent bonds within the basal plane compared to the weak Van der Waals bonds between the basal planes that are longer in bond length. The structure of graphite is also weakest and prone to shearing between the planes and will always contain imperfections such as vacancies, stacking faults, disclination, screw dislocations and edge dislocations. All of these imperfections will have a negative effect on the thermal, electrical and mechanical properties of the material.

Pure graphite is very chemically inert, although impurities are usually present that slightly degrade its inertness. Any chemical activity can take place at the sites of impurity, at imperfections mentioned previously and at the end of the basal planes. However with such a variety of reactions sites, graphite still remains highly inert and is able to withstand the corrosive environment (pH 2-3 \[^{[19]}\]) of a fuel cell.

**Stainless Steel**

Stainless steel (316/316L) containing 0.03-0.08 % carbon, 16-18 % chromium, 10-14 % nickel, 2 % magnesium and 2-3 % Molybdenum as well as iron is considered the stainless steel grade with the best corrosion resistance. It is an austenitic stainless steel
as opposed to ferritic or martensitic stainless steels. Austenitic steels are formed by the heat treatment of ferritic steel between 900 °C and 1400 °C when the material undergoes a phase transition from body centred cubic to face centred cubic and then quenched to retain its microstructure. The transition to face centred cubic gives the steel toughness, ductility and excellent cold working ability \[20\].

Stainless steel has superior mechanical properties to graphite, bipolar plates can be made thinner, 0.2-1mm thick \[21\], whilst retaining the same level of gas impermeability, stiffness and strength as a graphite plate (~3mm) \[2\]. They typically require stamping processes to create flow field designs on their surface.

Although stainless steel has good mechanical and electrical conductivity properties, its corrosion resistance in a fuel cell environment is a severe problem affecting performance and lifetime of a fuel cell \[22\]. Corrosion occurs due to pitting corrosion \[23\], where localised areas of depleted oxygen create an anode and an area of excess oxygen become cathodic generating galvanic corrosion. Metal oxides formed on the surface of the stainless steel increase the passivation layer and therefore reduces the conductivity of the bipolar plate. Also metal ions from corrosion easily leech into and poison the membrane where the dissolved metal ions lower its ionic conductivity \[24\].

The current use of stainless steel for bipolar plates is not purely based on the bare material; stainless steel undergoes proprietary surface treatments to enhance corrosion resistance that are not detailed here. However treatments found in the literature will be detailed in the next section.
3.3 Materials in the literature

3.3.1 Metals

Numerous methods have been employed to reduce corrosion in metallic bipolar plates. This section details research on stainless Steel (SS316L), nickel alloys, aluminium, titanium and copper.

**Stainless Steel**

Gold coatings on stainless steel were found to perform the same as graphite and improved corrosion resistance by preventing oxygen from diffusing through the coating. However gold is expensive and so alternative low cost coatings were developed (materials not specified) it was reported that stainless steel covered with thin layers of the coatings performed the same as graphite bipolar plates when conducting cell voltage vs. operation time tests \[25\].

M2-48 (polyacetylene) was deposited on SS316L and pyrolysed to produce a carbon layer was used as a top layer of a three-layer coating. The first and second layer was a commercial graphite spray; the total thickness of the combined layers was 70-100 µm. The coating was able to protect the stainless steel against corrosion, however further work was required to assess the long term stability (>1000 h) of the coating \[26\].

Physical vapour deposition (PVD) coating of YZU001 like-diamond film was applied to SS316L and the corrosion rate was reduced (0.1 µm per year) compared to that of graphite material (15 µm per year). However it was stated that this was for applications in low voltage, low power density and short operating time \[22\], hence this coating was considered unstable and Lee et al proposed longer duration tests to be conducted. Lee et al did not specify the electrical conductivity of such a coating, only saying that it had good electrical conductivity.

Stainless steel substrates coated with a carbon nanotube (CNT) / polytetrafluoroethylene (PTFE) coating have been investigated by Show et al \[27\]. The
film (75% CNT) with an electrical conductivity of 12 S/cm decreased the contact resistance of the plate from 46 mΩ/cm² to 12 mΩ/cm² and therefore increased fuel cell output power by 1.6 times. This study was done to improve on the costs associated with bipolar plates with regards to previous work by Show et al. [28] mentioned later in this section under “Titanium”.

Plasma nitriding of SS316L conducted by Tian et al. [29] showed a surface formation of a dense γ\textsubscript{N} phase of 5-8µm thick where no nitrides (CrN or Cr\textsubscript{2}N) precipitated in the nitrided layer which improved surface performance. Corrosion resistance through corrosion current tests was improved slightly and interfacial contact resistance was reduced. Tian et al considered plasma nitriding of SS316L to be a promising approach; however it was unclear as to whether the slight improvement in performance outweighed the cost of the surface treatment.

Kim et al. [30] investigated the application of titanium oxynitride (TiN\textsubscript{y}O\textsubscript{x}) films on SS316L with varying oxygen content by inductively coupled plasma assisted reactive sputtering. At an oxygen content of approximately <12 at%, the corrosion resistance is enhanced whilst the interfacial contact resistance remains unchanged. The corrosion current density decreased from 8 µA/cm² to 2.7 µA/cm² and it was postulated that the oxygen atoms locate at the column and grain boundaries preventing corrosive media from penetrating into the substrate.

**Nickel alloys**

According to the work of Brady et al. [31], thermally nitrided Niobium-Titanium-Tungsten (Nb-Ti-W or Tribocor) alloys have excellent corrosion resistance and good conductivity but are costly which make them an unlikely candidate for bipolar plates. Due to this cost, relatively inexpensive thermally nitrided Ni-X base alloys forming Cr\textsubscript{2}N, CrN, NbN, TiN or VN surface layers have shown corrosion resistances nearly equal to nitrided Nb-30Ti-20W in corrosion current tests [31].

Preferential thermal nitridation was used to form a pin-hole defect free CrN/Cr\textsubscript{2}N surface on a Nickel-Chromium (Ni-Cr) alloy. Excellent corrosion resistance and a
negligible contact resistance increase was observed over a 4100 h exposure in 80ºC sulfuric acid and over a 1000 h proton exchange membrane test. Future work was aimed at reducing levels of Cr and using less expensive Ni(iron) or iron based substrates to meet bipolar plate cost goals [32].

**Aluminium**

Physical vapor deposition coating of YZU001 like-diamond film was applied to 5052 aluminum alloy in the same way as the stainless steel mentioned previously. The metallic PVD coated 5052 aluminum bipolar plates performed better than the original aluminium material however the corrosion rate (0.247 μm per year) was higher than the stainless steel but still lower than that of graphite material. Again this was for low voltage, low power and short operating times [22].

In the work of El-Khatib et al [33], it was stated that bare aluminium metal and its alloys are precluded from being used as a lightweight bipolar plate because of their low corrosion resistance. Therefore aluminium substrates were coated with SS316L stainless steel using high velocity oxy-fuel (HVOF) spray and were found to significantly lower the corrosion current of the aluminium substrate by more than one order of magnitude. Multiple layers of 100-200μm thick were sprayed showing a decrease in corrosion rate with increases in coating thickness. However, the corrosion currents obtained were still higher than the acceptable level for fuel cell use due to the eventual contamination of the membrane by corrosion contaminants.

**Titanium**

Show [28] studied bare titanium (Ti) plates as well as Ti plates coated with an amorphous carbon film by radio frequency plasma enhanced chemical vapour deposition (RF-PECVD). The output power of a fuel cell was 1.4 times higher than with bare Ti and had a low contact resistance of 20 mΩ compared to 60 mΩ for Ti. The performance of the film was stable and did not delaminate after an operating time of 200 h. It was unclear as to why an expensive material like Ti would be used for bipolar
plates; in addition it required etching with hydrofluoric (HF) acid before the RF-PECVD process both of which would add to production costs.

**Copper**

Copper-beryllium alloy (C-17200) tested in a single cell for 100 hours at a constant load of 1 A showed good performance with a cell resistance of 0.0836Ω which was comparable to SS316L. At 70°C after corrosion testing, the C-17200 showed a maximum resistivity of 27.65 µΩcm compared to SS316L at 92.79 µΩcm. There was some sacrificial dissolution or corrosion of copper rather than the beryllium where mainly cuprous oxide (Cu₂O) was found on the surface. Future work was to develop a more beneficial, highly corrosion resistant surface treatment.  

**3.3.2 Graphite/Carbon-Polymer**

Besmann et al [35] fabricated a phenolic resin / chopped carbon fibre perform sealed with chemically vapour-infiltrated carbon to produce plates that had conductivities of 200-300 S/cm. The proprietary slurry process incorporated 400 µm long fibres in a phenolic resin and cured to form a preform. This preform was then infiltrated with carbon using a chemical vapour infiltration technique to seal the surface of the preform. The material had a low density of 0.96 g/cm³ due to the trapped porosity and had a flexural strength of 175 MPa ±26 MPa. Flow field patterns in the plate were embossed into the preform prior to infiltration.

Besmann et al stated the cost should not be a barrier due to the process lending itself well to economies of scale; however the labour intensiveness/cost of this technique was not mentioned. According to Middelman et al [10] carbon-carbon composites are not expected to achieve ambitious cost price targets especially with expensive chemical vapour infiltration processes.

Thermosetting resins, polyester (POE) and phenolic modified alkyd (PhA) containing graphite powder were studied by Bhlapibul et al [36]. 66 wt% (saturation) of graphite powder in the resins was mixed and compression moulded. The POE mixture was
found to be better than the phenolic resin mixture with a conductivity of 4.5 S/cm, flexural strength of 5.96 MPa and a density of 1.69 g/cm³. Carbon fibre (of unspecified dimension) was later added to improve on these properties and resulted in increased electrical and mechanical properties. However with an addition of 10%PhA to the mix the properties were slightly improved again and resulted in an electrical conductivity of 16.6 S/cm, flexural strength of 17.6 MPa and a density of 1.68 g/cm³.

Wu et al [37, 38] studied carbon nanotube (CNT) filled polyethylene terephthalate (PET)/polyvinylidene fluoride (PVDF) blends. By making a triple continuous network containing 6 vol% CNT and PET/PVDF in a 1:1 ratio via a PET-CNT pre-mixture and then secondary mixing with PVDF. The material was injection mouldable and exhibited a 2500% improvement in electrical conductivity; however it was still only 0.059 S/cm. It was reported that the CNT-filled PET phase offered an electrical short circuit for the composite while the clean PVDF phase provided the mechanical strength.

Other PET-CNT blends incorporating polypropylene, high density polyethylene and nylon 6,6 were conducted but did not produce any improvement. Only the addition of a further 6vol% CNT improved conductivity to 0.25 S/cm.

One of the main aims of pursuing the concept of polymers filled with conductive fillers is to reduce costs via low cost materials and/or low production costs whilst retaining sufficient properties for use in fuel cells. As mentioned previously in chapter 2 injection moulding has the potential to reduce bipolar plate costs considerably due to reduced production times/costs.

It has been reported that injection moulding can take 30-60 s per plate (material unspecified) according to Heinzel et al [39] where plates of 2.4-4 mm thick have been produced ranging from 5-150 S/cm in electrical conductivity. Other improvements in characteristics include a density of 1.6g/cm³ with material costs from 2-10 €/kg. The carbon compounds used in the study were not elaborated on.

Injection moulding cycle times of less than 10s have been obtained by Middelman et al [10] for plates of less than 3 mm. The plates had high thermal conductivity 28-40 W/mK, flexural strengths of 40-45 MPa, electrical conductivities of 167-217 S/cm and
densities from 1.6-2 g/cm³. The materials referred to in this research were termed Conduplate LT-X, MT-X and HT-X from Nedstack BV.

Commercially available materials based on graphite [40] had high conductivities and flexural strengths but had the penalty of higher densities ≥1.85 g/cm³. SGL Carbon’s Sigracet research, now sold to Eisenhuth GmbH, has 3 grades of bipolar plate material. PPG86 – a polypropylene/graphite material, BMA5 – a polyvinylidene fluoride (PVDF)/graphite material and BBP4 – a phenolic resin/graphite material.

All grades were suitable for compression and injection moulding except for the BMA5 grade which was only suitable for compression moulding [Appendix E]. The BMA5 grade had up to 80 wt%[41] of graphite content with an electrical conductivity of 100 S/cm, thermal conductivity of 20 W/mK, flexural strength of 40 MPa and a density of 2.1 g/cm³. The BBP4 grade had an electrical conductivity of 200 S/cm, thermal conductivity of 20 W/mK, a flexural strength of 40 MPa and a density of 1.97 g/cm³. The PPG86 grade had an electrical conductivity of 55.6 S/cm, thermal conductivity of 14 W/mK, a flexural strength of 40 MPa and a density of 1.85 g/cm³.

Another manufacturer, Schunk GmbH, have bipolar plates made from carbon/graphite in the range of 70–95 wt% and formed by compression moulding [15]. Two grades are produced, FU4369 for low temperature PEM fuel cell applications and FU4369HT for high temperature PEM fuel cells. The FU4369/FU4369HT grades have an electrical conductivity of 111 S/cm, a flexural strength of 40 MPa, a thermal conductivity of 55 W/mK and a density of 1.9 g/cm³; the two grades only differ in heat deflection temperature and glass transition temperature.

Bulk Moulding Compounds Inc produce a thermosetting BMC 940 grade for bipolar plates by compression moulding and post baking at 177° C for 15 minutes. It has an electrical conductivity of 70 S/cm, flexural strength of 38 MPa, a thermal conductivity of 13.4 W/mK and a density of 1.89 g/cm³ [Appendix G].

The materials characteristics detailed above can be seen clearly in the comparison table, table 3.
3.3.3 Summary

From the literature it can be seen that a lot of attention has been paid to metallic bipolar plates whether it be surface treatment or coatings of different materials. Although corrosion currents and corrosion rates have decreased, albeit at the expense of cost, metals still have a tendency to corrode. It has been found that metal ion dissolution into the MEA reduces membrane performance where the anode-side flow plate is the main source of the contaminants and direct contact enhances the contamination level [21]. Also any passive films such as oxide layers in aluminium or stainless steel protect the metal from corrosion but also act as an electrical insulator [42] therefore increasing contact resistance. For these reasons metals are not a straightforward choice for bipolar plates.

As mentioned previously, graphite bipolar plates can be heavy and expensive. Carbon-polymer bipolar plates can potentially offer corrosion resistant, high conductivity bipolar plates at a low cost. Three companies, Schunk, Eisenhuth and BMC were mentioned in the previous section to have commercially available bipolar plate materials. Some of these materials have injection moulding capability and most have compression moulding capability all with the aim of high volume, mass production.

Although these materials show promise and are suitable for current commercial use, they still fall short of US DOE targets with regards to electrical conductivity as the important through plane conductivities are lower than the in-plane conductivities. On the next page is a table (table 3) summarising the properties of the materials in the literature, both commercial and non-commercial. A recommendation is given by the author for density in table 3. Although it is possible to have high density materials with superior power to weight ratios with regards to stack output as is the case for stainless steel, the value of < 2.0 g/cm$^3$ would mainly apply to polymeric based bipolar plates. Most polymeric bipolar plate materials commercially available and in the literature are around 2 g/cm$^3$ in density, however this property is likely to increase with improved electrical properties. Therefore it is crucial to keep densities lower than 2 g/cm$^3$ in order to meet/maintain stack power density requirements.
<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Conductivity (S/cm)</th>
<th>Flexural Strength (MPa)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Corrosion Current / Rate</th>
<th>Tensile Strength (MPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US Dept Of Energy Targets 2015 / Author’s Recommendation</td>
<td>&gt; 100</td>
<td>&gt; 25</td>
<td>&gt; 20</td>
<td>&lt; 1 μA/cm²</td>
<td>-</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>316L Stainless Steel</td>
<td>51 [25]</td>
<td>-</td>
<td>16.27 [43]</td>
<td>384 μA/cm² (H₂) 586 μA/cm² (Air)</td>
<td>485 [44]</td>
<td>8.0 [44]</td>
</tr>
<tr>
<td>SS316L - YZU001 Coating [22]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1 μm per year</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SS316L - CNT/PTFE Coating [27]</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SS316L - TiNₓOᵧ Coating [30]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7 μA/cm²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium - YZU001 Coating [22]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.247 μm per year</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>POE-PhA / Graphite / C-Fibre [36]</td>
<td>16.6</td>
<td>17.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.68</td>
</tr>
<tr>
<td>CNT-PET / PVDF 6Vol%</td>
<td>0.059† / 0.011‡ [38]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>34 [13]</td>
<td>-</td>
</tr>
<tr>
<td>CNT-PET 12Vol%</td>
<td>0.25 [37]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chopped Fibre / Carbon powder [35]</td>
<td>200-300</td>
<td>175 MPa (±26 MPa)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>Schunk FU4369/HT [Appendix C]</td>
<td>111† / 52.6‡ *</td>
<td>40</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
</tr>
<tr>
<td>Eisenhuth PPG 86 [Appendix D]</td>
<td>55.6† / 18.2‡ *</td>
<td>40</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>1.85</td>
</tr>
<tr>
<td>Eisenhuth BMA 5 [Appendix E]</td>
<td>100† / 20‡ *</td>
<td>40</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
</tr>
<tr>
<td>Eisenhuth BBP 4 [Appendix F]</td>
<td>200† / 41.7‡ *</td>
<td>40</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>1.97</td>
</tr>
<tr>
<td>BMC 940 [Appendix G]</td>
<td>70</td>
<td>38</td>
<td>13.4</td>
<td>-</td>
<td>-</td>
<td>1.89</td>
</tr>
</tbody>
</table>

† In-plane conductivity. ‡ Through-plane conductivity. * Conductivity converted from resistivity. Author’s recommendation (not DOE target).

Table 3 - Comparison of 316L stainless steel, aluminium and graphite with commercially available bipolar plate materials as well as specified materials investigated in the literature. The US DOE 2015 targets are also included.
Table 3 shows a general trend of low conductivity compared to the DOE target with regards to through plane conductivity. The through plane value is considered the more useful value as current flow through the plate will be in this direction rather than parallel to the flat faces of the bipolar plate (in-plane direction). Where only one conductivity value is denoted, it is unknown as to whether these are through plane or in-plane conductivities. In comparison to the other values it is likely that they are in-plane conductivities and so the through plane conductivities would therefore be significantly lower according to the trend.

All of the materials satisfy or come close to the DOE flexural strength requirement of >25 MPa except for pure graphite where, understandably, one of the main aims of this as well as many other studies is born.

Many of the polymer based materials are compression and/or injection mouldable. Although the potential of these materials to be rapidly processed is high, the reality, especially for compression moulding, is that cycle times can be long particularly if more than one processing step is required. Longer processing means higher costs per plate, therefore stacks containing in the region of 400 plates will incur significant costs. The most promising material from the literature is the Conduplate range from Nedstack and the unspecified material from Heinzel et al [39] where both have stated very fast injection moulding times, <10s and 30s-60s respectfully. However due to the ambiguity of the conductivity values (through plane or in-plane?), a conclusion cannot be made about their potential for fuel cell use.

Middleman et al [10] gave a cost breakdown of the Nedstack material and processing and predicted that for a production run of 1,000,000 plates per year the cost of each plate would be €1.4. This cost per plate would be ideal if put into practice as the bipolar plate cost is considered a major bottleneck for fuel cell commercialisation [22].

As stated in the work of Besmann et al [35] chopped fibres played a crucial role in the high electrical conductivity, high flexural strength as well as the low density attained. Their two filler system required some lengthy processing and cannot be translated into a fast compression or injection moulding process. The modelling and experimental work
outlined in this thesis will focus on single component, mono dispersed systems for fast production methods. Therefore carbon fibres, although they are injection mouldable, are not easily aligned through injection moulding in the through plane direction and would create anisotropic properties in favour of the in-plane direction.

3.4 Materials Used In This Study

The filler materials used in this study were not typical filler grades as those found in the literature; the material properties such as electrical conductivity could not be verified or guaranteed by the manufacturers as this would vary with processing. Therefore the filler materials were chosen based on ease of availability and low cost in keeping with the aim of low cost bipolar plate materials. The fillers are all in the powdered form for ease of processing in a thermoplastic matrix.

**Carbon Black**

Carbon blacks are well known for their electrical conductivity, the carbon black used in this study was a Monarch 800 grade from Cabot Corporation (Ellesmere Port, Cheshire, UK). Its physical and chemical properties can be seen in appendix A and is an amorphous carbon with an average density of 1.8 g/cm³. The characterisation of the powder can be seen in section 5.1.1, the density value of 1.82 g/cm³ used for this study was the value obtained by the helium pycnometer method shown in section 4.2. The powder is known for its use in pigmentation and is advertised with a possible use in leather colourants [48]. Reference to the carbon black filler and its composites will be referred to as “carbon” throughout this thesis.

**Graphite**

Graphite is also well known for its electrical properties, the graphite powder used was an unspecified grade from Erodex Ltd (Halesowen, West Midlands, UK). It was an industrial grade graphite from the graphitisation of an oil/polymer mixture [49]. The powder characterisation can be seen in section 5.1.2 and has a density of 2.24 g/cm³.
Various Erodex graphite grade applications include high temperature mechanical applications, seals and tooling.

**Magnetite**

Magnetite or iron(II,III)oxide is well known for its magnetic properties but not for its electrical conductivity, as it is already oxidised iron it does not oxidise further. Magnetite contains two valence states of Fe$^{2+}$ and Fe$^{3+}$, electrical conductivity/electron hoping occurs from Fe$^{2+}$ to Fe$^{3+}$ where the states change to Fe$^{3+}$ and Fe$^{2+}$ accordingly [50]. The magnetite powder, MagniF10 with a density of 5.02 g/cm$^3$, was obtained from Minelco Ltd (Flixborough, North Lincolnshire, UK); the characterisation of the powder can be seen in section 5.1.3.

**Polyethylene**

The matrix for the composites needed to be applicable mainly to injection moulding where high flow rate/low viscosity was required when heavily loaded with filler as this would also be sufficient for compression moulding. With this in mind, a high density polyethylene (HDPE) with a melting point higher than fuel cell operating temperatures (80 °C) and a high melt flow rate was used. The polymer chosen was the ExxonMobil HMA018 HDPE injection moulding grade with a melting point of 129 °C and melt flow index of 30 g/10min [Appendix B].
Chapter 4.0

Methodology

This chapter describes the methods used in the characterisation of the powders, the manufacture and testing of the composites. The powders were characterised with respect to particle size, density and morphology. Malvern particle analysers for nano and micron scale powders were used to assess the average particles sizes and electron microscopy employed to assess morphology in order to better understand behaviour observed during testing as well as to form assumptions for the modeling in chapter 6. Density measurements were used to calculate the overall composite densities and to convert between volume percentage and weight percentage as is described in chapter 5; a pycnometer was used as simple technique to obtain the measurements.

The manufacture of the composites incorporated mixing of the constituents by the two roll mill process where only low volumes were required and material wastage was kept to a minimum compared to the widely used compounding method that incurs greater material wastage. The fast manufacturing processes mentioned previously in chapter 2 were employed, the injection moulding technique and its parameters are detailed here as well as the compression moulding technique with details of the laser cutting technique utilised as part of the compression moulding process.

Testing of the composites in order to assess bipolar plate properties described in the literature as well as the DOE criteria were done for tensile and flexural mechanical properties and electrical and thermal conductivities. The testing of the materials was conducted with an Instron tensometer fitted with tensile jaws for tensile tests and 3pt bending apparatus for flexural tests. Electrical conductivity was tested using the well known 4 point probe technique and the thermal conductivity tested using a Cussons P5687 thermal conductivity device.
4.1 Malvern Zetasizer & Mastersizer

The Malvern Zetasizer and Mastersizer, schematic shown in figure 5, measures particle sizes in the nanometre and micron ranges respectively. Particles of less than a few microns are measured by observing the Doppler shift of the incident light due to the Brownian motion of the suspended particles. Light will be scattered from the particles and its frequency will be shifted, the speed of the particles determines how much the frequency is shifted. By knowing the incident light frequency and measuring the scattered light frequency to determine the shift, particle size can be calculated.

During testing of the fillers in the Mastersizer it was found that the carbon filler particle size was in the nanometer range therefore the Zetasizer was used. Although both pieces of equipment use the same method to determine particle size, there was a difference in sample preparation. For the Zetasizer, 1.5 mg of carbon was placed in a glass sample tube with 30 ml of de-ionised water and 2 drops of Coulter Laboratory Reagent. The sample tube was shaken and then placed in an ultrasonic bath for 1 hour. The mixture of carbon and water was further diluted by putting 3.5 ml of de-ionised water in a 4 ml cuvette along with 6 drops (0.375 ml) of the carbon-water mixture from a pipette. The cuvette was then shaken and placed in the Zetasizer. The Zetasizer was set to take an
average particle size from 10 runs. This process was repeated twice more with a fresh cuvette filled with the same solution from the sample tube. The computer recording the readings then produced a plot of the particle size distribution.

The Mastersizer required less sample preparation. The sample holder system incorporated a mechanical stirrer within a container of de-ionised water that circulated the particulates through the light chamber. The system was flushed numerous times by draining and filling the sample chamber repeatedly before use and after use until all residual material had been removed. A small amount of dry powder (1.5 mg) was added to the sample chamber where it would be dispersed in the de-ionised water and the rotation speed of the stirrer was set to 2000 rpm. The Mastersizer took measurements in the same way as the Zetasizer and an average plot was given of the particle size distribution.

4.2 Density

The unknown densities of the graphite and magnetite powders as well as the known carbon powder were found using a Micromeritics Helium Pycnometer 1305 shown in figure 6.

Figure 6 - Micromeritics Helium Pycnometer used to measure density of solids especially where agglomerations are present.
Methodology

A 5 cm\(^3\) sample chamber was inserted into the sample chamber holder and the cap screwed firmly on. Before testing, the pycnometer was set to the prep position with the fill valve open, the vent valve closed, the < 35 selector knob set at < 35 and the < 5 selector knob set at < 5. The helium supply to the pycnometer was regulated to 1.6 bar and the fill rate control knob was turned so that a reasonable fill rate (pressure increase) was observed on the LCD panel so that when the fill valve is closed an accurate pressure can be obtained due to a lag in pressure reading. The fill valve was then closed, the vent valve was opened and the vent rate control knob was set so that the measured rate of pressure decrease would be approximately 3 psi/s.

A sample cup was weighed empty (M\(_{\text{cup}}\)) and then weighed again when half filled with powder (M\(_{\text{cup}} + M_p\)). The mass of the powder was then calculated by subtracting the mass of the empty cup from the total mass of the cup and powder. The sample cup with the powder was then placed into the sample chamber and the chamber cap screwed on firmly. With the prep/test valve set to prep, the vent valve was closed and the fill valve was opened and then closed to obtain a pressure of 16 to 18 psi (prep pressure). The prep/test valve was then set to test and the new pressure reading (test pressure) was left to stabilise for 30 seconds and then the vent valve was opened. This filling and evacuating of the test chamber was repeated 10 times to drive off any trapped gases or moisture in the powder or the pycnometer. When the helium had been vented the pressure reading should be zero, otherwise the zeroing knob was used to set the pressure reader zero point.

For testing, the same filling and evacuating procedure was followed however the fill pressure obtained was 19.5 psi ±0.2 psi. Tests on the same sample were run 10 times and the prep pressure (P\(_1\)) as well as the test pressure (P\(_2\)) were recorded and used in equation 1.

\[
V_{\text{SAMP}} = V_{\text{CELL}} - \frac{V_{\text{EXP}}}{[(P_1 / P_2) - 1]}
\]  

(Equ 1.)

Where:  
- \(V_{\text{SAMP}}\) - Volume of test sample (cm\(^3\))  
- \(V_{\text{CELL}}\) - Empty volume of the sample chamber (with cup)  
- \(V_{\text{EXP}}\) - Expansion volume  
- P\(_1\) - Prep Pressure  
- P\(_2\) - Test Pressure
Methodology

$V_{\text{CELL}}$ and $V_{\text{EXP}}$ are constants given by the manufacturer/calibrator and were 7.713738 and 6.144719 cm$^3$ respectively.

An average volume for each sample was obtained and three different samples of each powder were run using this method. The densities of each were calculated by dividing the mass of the powder found earlier by $V_{\text{SAMP}}$ and the three densities were averaged for each powder.

Observations

A low venting rate was chosen so that the powder was not disturbed in the sample chamber which would then lead to powder particles exiting the sample chamber. The mass of each sample after testing was measured to monitor any changes in mass as a result of the testing.
4.3 Two Roll Mill

A two roll mill was used to mix the conductive fillers with the polyethylene. The mill churns molten polymer between two heated rollers where the separation distance between the rollers can be used to form sheets of material as it peels off the rollers. As the material cannot be lost within the moving parts of the equipment, there is very little wastage of material. The process requires a fair amount of manual labour therefore the user, to a certain extent, can determine the level of homogeneity within the mixture. Below is a diagram of the process.

![Diagram of Two Roll Mill concept for mixing multiple components namely polymeric based materials.](image_url)

Figure 7 - Two Roll Mill concept for mixing multiple components namely polymeric based materials.
Methodology

Polymer was added to the two roll mill pre-heated to temperatures of 128 °C and 123 °C on the rear and front rollers respectively. Once completely melted, filler powder was added slowly using a spatula and the two constituents left to churn whilst a mill knife was used to spread the mixture around. The separation between the two rollers was gradually widened to accommodate more material. After sufficient mixing the heaters were turned off and left to cool by approximately 5 °C, the resulting thick sheet was cut away from the front roller as it turned. The solidified composite sheet was then pelletized in a pelletizer. The process was repeated for 10, 20, 30, 40, 50 and 60 wt% filler loaded batches; 5 batches at each loading were produced with each batch totalling 300 g.

Observations

On melting, the polyethylene goes from white to clear and is fairly sticky. When the rollers are separated to accommodate more material, the mixture will stick to the cooler roller (front roller). This makes it easier to spread with the mill knife.

At higher loadings it becomes increasingly difficult to add filler and so filler has to be added gradually with intermittent periods of mixing. Filler that falls through the rollers can be gathered from the collection tray and put back into the mix. This may be repeated as many as 15 times in order to achieve a complete mixture and therefore some batches require more processing time than others.

In addition to spreading with the mill knife, it was useful to squeeze the mixture once in a while by closing the roller separation to return some of the mixture adhered to the front roller back to the churning mass between the rollers. This also helped with removing any material adhered to the rear roller where if left on the rear roller will not contribute to the overall mixture. The mill knife was also used to remove stubborn stray lumps on the rear roller.

The filler loading at or close to the maximum achievable by this process was gauged by observing the filler consistency during churning. The mixture would become more
brittle rather than fluid and fissures would open up in the churning mass. All fillers were taken to this point where the magnetite was able to be mixed up to 70 wt%.

Due to the stickiness of the polyethylene it was difficult to peel the sheet off the roller without the aid of the mill knife to scrape it off. However with increasing filler content, the mixture became less sticky and was easier to peel off the roller.

4.4 Ashing

Below, figure 8 shows the Ashing test procedure used to determine the carbon contents in weight percent (wt%) of each batch of composite.

1 - An empty crucible is weighed (M_Cr).

2 - Crucible and PE-filler is weighed (M_Cr+PE+F).

3 - Crucible and PE-filler burnt in an oven.

4 - Crucible and burnt PE-filler is weighed (M_Cr+F).

5 - Weight percentage of filler (Wt%F) is calculated using:

\[
Wt\%F = \frac{(M_{Cr+F} - M_{Cr})}{(M_{Cr+PE+F} - M_{Cr})} \times 100
\]

(Equ 2.)

Figure 8 - Ashing test procedure used to determine the weight percentage of filler for each composite batch.
An empty crucible was weighed and the same crucible with a small amount of composite pellet was weighed again. It was then placed in an oven and after burning out the polymer at 500 °C for approximately 75 minutes (including the ramping to and from 500 °C) the crucible containing plain filler was weighed again. From the difference in masses of the composite and plain filler after having subtracted the empty crucible mass, the percentage of filler in the original pellets was calculated.

This was repeated again for each sample to gauge accuracy of the results.

**Observations**

Smoke was seen rising out of the furnace as the polymer burnt. This was used as a sign of when the composite had been fully burned out, i.e. when no more smoke was observed. This took approximately 60 minutes, for higher weight percentages of composite the time until no observed smoke was reduced due to lower polymer content however a 75 minute burnout time was still applied.
4.5 Injection Moulder

Injection moulders melt polymers through multiple heating stages and inject the melt into a cavity under high pressure, the mould cavity opens and the part is then ejected using pins that emerge from the face of the cavity. The process can be set up to run continuously with each injection + ejection cycle completing in less than a minute. This process is shown below in figure 9.

Figure 9 - Injection moulding process (simplified) showing the metering and injection stages.
The pellets of varying weight percentages were each weighed out to equal volumes of 150 cm³, the weights equivalent to 150 cm³ were calculated using the results from the density and ashing tests. Each batch of pellets were fed into the hopper of a Negri-bossi NB62 injection moulder where they were forced towards the nozzle by the rotation of the screw. As they moved along the screw the pellets were melted by the heating coils within the barrel to 200 °C. The screw moved back as more material was taken in (metering) and when the required metering size had been reached the injection unit was ready for injection. The metering size for each test sample was 50 mm and the shot was injected at a pressure of 100 bar. The test samples conformed to ASTM 638 Type I test bars.

Before injection the two halves of the mould came together and the injection unit with its nozzle was pressed up against the heated sprue. During injection the screw acted as a plunger and forced the molten material through the nozzle and sprue and into the mould under high pressure. Afterwards the injection unit retracted, the two halves of the mould opened after 30s of cooling and ejector pins located on the movable half of the mould helped to free the part from the mechanism. Below is a table summarising the injection moulding parameters.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sprue</th>
<th>250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle</td>
<td>200 °C</td>
<td></td>
</tr>
<tr>
<td>Zone 1</td>
<td>190 °C</td>
<td></td>
</tr>
<tr>
<td>Zone 2</td>
<td>180 °C</td>
<td></td>
</tr>
<tr>
<td>Zone 3</td>
<td>170 °C</td>
<td></td>
</tr>
<tr>
<td>Mould</td>
<td>30 °C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Injection</th>
<th>Pressure</th>
<th>100 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metering Size</td>
<td>50 mm</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>0.5 s</td>
<td></td>
</tr>
</tbody>
</table>

| Screw Diameter | 30 mm |
| Holding pressure | 10 bar |
| Cooling time   | 30 s  |
| Clamping force | 40 tonnes |

Table 4 - Injection moulding parameters used for the carbon, graphite and magnetite composites.
Methodology

The test sample mould had a channel in the mould directing the shot flow from the centrally placed sprue into the top of the test sample cavity. The longest length of the cavity was orientated along the vertical axis producing a flow direction parallel to the length of the test sample. Only one test sample was created per shot cycle and the part of the solidified shot formed by the channel was sufficiently thin to be snapped off after ejection from the mould. The shape of the test samples can be seen in figure 11 on page 45.

Observations

As the filler content increased, the injection moulder found it increasingly difficult to push the shot through the sprue as the sprue had started to build up a layer of filler within it thus narrowing the sprue. In order to keep the injection moulder flowing to prevent blockages, the various batches (i.e. 0 wt% to 60+ wt%) of composites of the same filler were fed into the hopper one after the other. This produced pure, white, polyethylene samples at first that would eventually turn black. The number of completely white test specimens (0 wt%) to come out of the injection moulder were counted, usually 15 test samples. In the transition from 0 wt% to 10 wt%, i.e. from white to black, there were a number of grey test samples produced, five test samples. This number of five test samples together with the number of white (successful) test samples were used as a guide to knowing when one batch had completely cleared the injection moulder and when the next batch was reliable. Therefore after counting the number of successful test samples and scrapping the five intermediate test samples along with 3 more from the next batch; 12 samples were produced per batch with no cross contamination between batches.
4.6 Compression Moulding

Compression moulding was conducted using a square mould measuring 300 mm x 300 mm with a 250 mm x 250 mm x 3 mm cavity in the pattern plate as can been seen in figure 10 below.

![Diagram of compression moulding process](image)

Figure 10 - Hot press equipment showing the heating stage prior to compression. An example of moulding plates is also shown.

Two hot presses were used, one for heating and one for cooling. The table on the next page summarises the hot press parameters used for the composites.
### Methodology

<table>
<thead>
<tr>
<th>Material / Grade</th>
<th>Melting Time (Before Compression)</th>
<th>Hot Press Temperature</th>
<th>Compression Force / Time</th>
<th>Cooling Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>20 mins</td>
<td>160 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (10 wt%)</td>
<td>30 mins</td>
<td>170 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (20 wt%)</td>
<td>30 mins</td>
<td>175 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (30 wt%)</td>
<td>30 mins</td>
<td>185 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (40 wt%)</td>
<td>30 mins</td>
<td>200 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (50 wt%)</td>
<td>30 mins</td>
<td>220 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Carbon (60 wt%)</td>
<td>30 mins</td>
<td>240 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Graphite (10, 20 wt%)</td>
<td>30 mins</td>
<td>170 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Graphite (30 wt%)</td>
<td>30 mins</td>
<td>175 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Graphite (40 wt%)</td>
<td>30 mins</td>
<td>190 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Graphite (50 wt%)</td>
<td>30 mins</td>
<td>210 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Graphite (60 wt%)</td>
<td>30 mins</td>
<td>230 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Magnetite (10 – 30 wt%)</td>
<td>30 mins</td>
<td>160 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
<tr>
<td>PE-Magnetite (40 – 70 wt%)</td>
<td>30 mins</td>
<td>170 °C</td>
<td>20t / 10 mins</td>
<td>10 mins</td>
</tr>
</tbody>
</table>

Table 5 - Hot press parameters used for the carbon, graphite and magnetite composites up to 60/70 wt%.

First the base plate was sprayed with a silicon mould release agent and the pattern plate placed on top. A sufficient amount of pellets of the various materials were placed in the cavity of the pattern plate such that when the top plate was placed on top of the pellets it rose 6 to 8 mm above the pattern plate. The top plate was sprayed with mould release agent before being placed on top.

The mould was then placed into the heated press without any applied pressure. The hot press was closed to a point where the top of the mould was touching or in close proximity to the upper heating element of the heated press. The material in the mould was then left to melt under the weight of the top plate. The top plate would eventually touch and lie flat on the face of the pattern plate, as this occurred the hot press was closed to keep the top plate in close proximity to the upper heating element. This melting process would take approximately 30 minutes, after which the hot press was manually pumped to a pressure of 20 tons and held for 10 minutes. As the mould was compressed, excess material overflowing from the mould had to be scraped off to prevent fouling of the hot press surfaces.
The cooling press had been pre-cooled to approximately 12 °C with circulating tap water. When released from the heated press the mould was put into the cooling press and the same 20 tons of force applied for 10 minutes. After cooling the mould was removed from the press and prised open to extract the flat composite plate.

Two plates of each composite grade were moulded using this technique.

Observations

As the filler content increased, the hot press temperature needed to be increased. Mould release agent was used instead of non-stick plastic sheeting between the mould layers to aid in the heat conduction to the composite pellets. As such the non-stick sheeting made compression moulding impossible for the higher content composite grades processed at above 200 °C.

Plastic non-stick sheeting was better for compression mould release but it allowed air to be trapped on the surface of the composite sheet whereby large impressions were observed. The silicone mould release did not trap air but it allowed more adhesion of the material to the mould resulting in difficult mould releases. There was also no difference between silicone or teflon mould release sprays.

The release of the top plate of the mouldings of the polyethylene carbon composite grades above 30 wt% revealed fractured pieces of the composite sheet approximately 10 mm by 10 mm. The cooling rate was reduced by leaving the mould in the heated press overnight to cool down along with the heating elements; however this resulted in the same fractured composite sheets.
4.7 Laser Cutting

ASTM 368 Type I test bars were cut from the compression moulded composite plates by laser. A 150 W coherent diamond carbon dioxide pulsed laser with a wavelength of 10.6 µm was used. Air was forced onto the cut to blow away melted material; the air pressure was set to 5.5 bar. The laser setting was set for plastics and so the beam width was set to 1mm and travel rate set to 10 mm/s. Eight test bars were cut from each plate along with three circular (20 mm diameter) samples for thermal conductivity tests. Figure 11 below illustrates the process.

Figure 11 - Laser cutting process for the carbon, graphite and magnetite composites.
4.8 Tensile & Flexural Strength / Modulus

An Instron tensile test machine was used to pull the test specimens apart under a constant preset velocity. When fitted with 3 point bending apparatus the machine will bend test samples under a constant velocity. Figures 12 and 13 show the test setup.

Figure 12 - Tensile test jaw setup for the tensile strength tests conducted with a 2.5 kN load cell.
Methodology

Figure 13 - 3 point bend test apparatus used for the flexural strength tests used with a 2.5 kN load cell.

Five samples of each composite loading were tested, each test sample was measured in width and thickness at three different locations and averaged for tensile stress calculations (i.e. Tensile stress = Tensile force / Sample cross sectional area). The test samples were then loaded into a tensile machine fitted with a 2.5 kN load cell and were lined up along the central axis and clamped into the lower jaw and then clamped with the upper jaw. Any slack in the system was removed, the crosshead speed was set to 50 mm/min (ASTM D638) and the test was started; the results were recorded by computer.

When fitted with the 3 point bending apparatus the midpoint of each sample was placed in line with the midpoint of the apparatus and any gap between the sample and the three contact points was zeroed. The middle point would push the midpoint of the sample downwards while the two outer points would act as pivot points on the sample. The forces measured by the same 2.5 kN load cell were then logged on a computer.

The apparatus was set to a span of 50 mm, the crosshead speed set to 2 mm/min according to ASTM D790 and each sample’s width and thickness was measured in...
three different locations and then averaged. Five samples for each composite loading were measured and the flexural stress was given by the equation below.

$$\sigma_F = \frac{3PL}{2bh^2} \quad \text{(Equ 3.)}$$

Where:  
\(\sigma_F\) - Flexural stress  
P - Maximum load  
L - Span Length  
b - Sample width  
h - Sample thickness

From the results, elastic and flexural moduli were gained from the following two equations.

Elastic modulus = Tensile Stress / Tensile Strain:

$$E_m = \frac{F}{A} \frac{l}{\Delta l} \quad \text{(Equ 4.)}$$

Where:  
\(E_m\) - Elastic modulus  
F - Force at proportional limit  
A - Sample cross-sectional area  
\(\Delta l\) - Change in length  
l - Original length

Flexural modulus = Flexural Stress / Flexural Strain or:

$$E_F = \frac{L^3m}{4bd^3} \quad \text{(Equ 5.)}$$

Where:  
\(E_F\) - Flexural Modulus  
L - Span length  
m - Gradient of proportional section  
b - Sample width  
d - Sample thickness
Observations

Polyethylene graphite test samples greater than 39 wt% and 71 wt% magnetite samples were not tensile tested as they slipped through the jaws during testing even though different jaw types were applied with more clamping force.

Flexural samples that did not fracture were not used in this study as a comparison with fractured samples would be inaccurate.

4.9 FEGSEM

Figure 14 - Major components of a Field Emission Gun Scanning Electron Microscope (FEGSEM).
The FEGSEM (Field Emission Gun Scanning Electron Microscope) shown in Figure 14 differs from a normal SEM by using field emission to generate the electron beam instead of thermionic emission. It uses a finely tipped tungsten crystal; electrons are drawn from the filament tip by a potential field set up by the first anode below the tip of the filament. The electrons then travel down the column aided by the second anode. The electron beam passes through the first condenser lens and coarse adjustments to the beam can be made. The second condenser lens forms the beam into a thin and tightly packed beam and it is where the fine control over the beam can be made. The beam is then made to scan in a grid like fashion by the scanning coils to produce an image on a television monitor. The beam passes through the objective lens to focus the beam onto the desired part of the sample. The beam then hits the sample and any primary and/or secondary electrons are detected at the detector and then fed to the computer. The FEGSEM enables a narrower beam with spot sizes less than 2.0 nm, thus higher resolutions are obtained.

The composite samples along with the bare filler powders were gold coated and placed on the sample stage in a vacuum environment. A beam energy of 5 kV was used at 750,000X magnification.
4.10 Electrical Conductivity

Figure 15 - Sample holder for electrical conductivity measurements. The 4 connections (positive supply, negative supply and the two voltage probes) are connected to a Danbridge DB501 4-point probe. The white solid arrow indicates injection moulding flow direction and the dotted white arrow indicates the perpendicular direction.

The electrical resistance of each sample was measured with a Danbridge DB501 4-point probe. As shown in figure 15, two probes supply a current through the sample and the other two probes measure a potential difference. The use of 4 probes eliminates the effects of contact resistance that would otherwise obscure readings in samples of very low conductivity.

A sample of 20 x 20 mm square with a thickness of 3 mm was cut from the ASTM D638 test bars. In-plane measurements in-line with the injection moulding flow direction and through-plane measurements perpendicular to the flow were obtained by placing two 1mm needle probes spaced 10 mm apart on each side of the sample. When changing samples, the contact pressures of the probes on each sample were made as equal as possible by using an adjustable stage with spacers to create repeatable
Methodology

adjustments for all samples. Then a resistance reading was noted from the readout on
the display and converted to conductivity using equation 6 below.

\[
\sigma = \left( \frac{2}{\Omega \cdot \frac{A}{L}} \right)^{-1}
\]

(Equ 6.)

Where:
- \( \sigma \) - Conductivity (S/cm)
- \( \Omega \) - Resistance (ohms)
- \( A \) - Cross sectional area between 2 test probes (1 x 0.3 cm).
- \( L \) - Length of the sample

Observations

The resistance readings required time to settle and stabilise, in most cases this took 1 to
2 minutes.
4.11 Thermal Conductivity

A P5687 thermal conductivity apparatus was used to determine the thermal conductivity of the composites. Below figure 16 shows the working parts of the equipment.

The lower stage moves up and down into the equipment housing using the clamping lever. The calorimeter with water in and out connections are contained inside the equipment housing along with the heater controls and displays.

The thermometer / thermocouple connections protrude out of the housing near the sample stage.

Firstly, samples of the composites were polished on polishing wheels down to 1 μm abrasive grade and then cleaned in an ultrasonic bath. After drying, the samples were then clamped one at a time between the heated upper stage and the lower stage with a thin layer of thermal paste on each sample face. The thermal paste used was Artic Silver 5 and a small bead was applied to the centre of the sample faces. When clamped using the clamping lever, the paste was spread radially to the outer edges of the samples so that the top and bottom faces were covered without excess overspill.
The Dewar was then placed over the system for insulation and the water system was turned on and left to overflow at an approximate rate of 0.5 cm³ per second. The heating element was set to 95 °C (± 0.1 °C) by tuning the current setting to a position that stabilised the temperature reading at the upper stage as well as the temperature reading at the lower stage. Once the heating element had been stabilised at 95 °C and the lower stage had reached a stable temperature somewhat lower than the upper stage, readings were taken.

Five samples for each composite were tested, the thermocouple readings of the water in and water out as well as the mass of water collected within 10 seconds were taken, also measurements from thermocouples placed as close as possible to the sample faces were done. Water collection was done in a beaker with the mass of the dry beaker known, then weighed after collection and dried for the next collection.

The measurements were taken at two minute intervals for ten minutes per sample and then averaged. The following equations [51] were used to determine the thermal conductivity (K) of the samples.

\[ Q = C_p \cdot \frac{M}{t} \cdot (W_2 - W_1) \]
\[ K = \frac{Q \cdot L}{A \cdot (T_2 - T_1)} \]  
(Equ 7.)

Where:  
K - Thermal conductivity  
Q - Heat conducted  
L - Sample thickness  
A - Sample cross sectional area  
T₁ - Temperature of the lower stage  
T₂ - Temperature of the upper stage  
Cₚ - Heat capacity of water  
M - Mass of water collected  
t - Time for water collection  
W₁ - Water inlet temperature  
W₂ - Water outlet temperature
Observations

Polishing of the samples produced an even flat surface where the previous processing stages had not. This obviously reduced each sample by a few microns in thickness.

Current settings were not the same, although they were closely related for samples within the same batch; the current setting for the first sample was used as a guide for the other four samples in the batch saving test time.

Residual thermal paste would build up if the upper and lower stage were not cleaned of paste before each test.
Chapter 5.0

Results

The results detailed in this chapter show the output from the experimental methods discussed in the last chapter. Powder and composite characterisation through particle size analysis and microscopy is given, electrical and thermal conductivities of the composites are also detailed. Tensile and flexural properties from the tensile and 3 point bending tests are given as well as the microscopy of the composites post fracture.

5.1 Powder Characterisation

The following sections detail the particle size, density and physical appearance of the carbon, graphite and magnetite powders from Cabot Corporation, Erodex Ltd and Minelco Ltd respectively as described earlier in chapter 3.

5.1.1 Carbon Black

Figure 17 shows the particle size distribution of the carbon powder measured by the Malvern Zetasizer. The mean particle size was 149 nm in a range of 35 nm to 500 nm. The micrographs of the powder shown in figures 18a and 18b show that the powder was highly agglomerated ranging from 2 μm to 25 μm in agglomerate size. These secondary agglomerates were made up of smaller agglomerates (primary agglomerates) of a similar size to that measured by the Zetasizer shown in figures 18c and 18d. Furthermore these primary agglomerates were made up of carbon particles of 20 nm in size as can be seen in figure 18d.
Figure 17 - Particle size distribution for Carbon powder. The peak particle count shown is at 145 nm. The D[4,3] (mean) particle size was 149 nm.

Figure 18 - Carbon powder FEGSEM micrographs showing secondary structures (Figs. 18a and b), and primary structures (Figs. 18c and d).
When comparing the Zetasizer measurement to the FEGSEM micrographs it was obvious that the sample preparation technique was able to break up the secondary agglomerates but not the primary agglomerates and therefore the true particle size was not obtained by the zetasizer. It is very possible that these small agglomerations were not broken up by the shear forces in the two roll mill the implications of which are discussed in chapter 7.

The manufacturer’s value for density of the carbon powder was verified using the helium pycnometer technique. Therefore the manufacturer’s value of 1.8 g/cm$^3$ in appendix A (found by gas absorption) was similar to the value of 1.82 g/cm$^3$ found by and used in this study.

5.1.2 Graphite

![Graphite Particle Size Distribution](image)

Figure 19 - Particle size distribution for Graphite powder. The peak particle count shown is at 443 µm. The D[4,3] (mean) particle size was 447 µm.
Figure 20 - Graphite powder FEGSEM micrographs showing mainly flat plate structures (Figs. 20a and b) amongst smaller shards of graphite (Fig. 20c).

Figure 19 shows the particle size distribution for the graphite powder. The mean particle size was 447 µm in a range of 150 µm to 800 µm. The micrographs in figure 20 show a difference in particle size from the mastersizer measurements. Sizes of approximately 10 µm to 100 µm with small graphite shards of approximately 2 µm can be seen. The particle shape and sizes were not uniform, particles were either flat plates with sharp irregular edges or large and boulder-like. It is highly likely that the mastersizer measurements may have measured the large boulder-like particles or agglomerates of them due to poor dispersion as the largest particle dimension observed in the micrographs was 115 µm in size.

The graphite density was measured at 2.24 g/cm³ which is close to a typical value of 2.26 g/cm³[^16] for graphite.
5.1.3 Magnetite

Figure 21 - Particle size distribution for Magnetite powder. The peak particle count shown is at 63 µm. The D[4,3] (mean) particle size was 71 µm.

The Malvern mastersizer result in figure 21 gave a mean particle size of 71 µm in the range of 15 to 150 µm. On the other hand the magnetite micrographs in figure 22 showed particles sizes of up to 40 µm and small dust-like fragments as low as 1µm, however it is possible that only smaller particles were shown in the micrographs. Just like the graphite, particle size and shape varied, all particles were of a boulder-like shape with numerous flat faces.

The density of the magnetite was found to be 5.02 g/cm$^3$ and was considerably higher than the other fillers. This would create composites with higher densities than the carbon and graphite and would create large differences between weight percentage and volume percentage conversions as discussed later in this chapter.
Figure 22 - Magnetite powder FEGSEM micrographs showing sharp edged boulder-like particles (Figs. 22a and b) of up to 40 µm in size with small fragments of approximately 1 to 3 µm (Fig. 22c).

5.1.4 Errors

The Malvern zetasizer and mastersizer measurements could have been skewed due to unbroken agglomerates and poor dispersion. The mastersizer preparation method, more than the zetasizer preparation method, was reliant on the physical agitation of the test liquid and may not have been sufficient to break up agglomerates. However the use of FEGSEM to further analyse the size and shape of the fillers was beneficial to gain detailed representations of the fillers.

The helium pycnometer, although suited to agglomerated powders such as the ones used in this study, gave errors in the density readings as follows:
Results

Carbon error: - 0.03 g/cm\(^3\) to + 0.04 g/cm\(^3\).
Graphite error: - 0.04 g/cm\(^3\) / + 0.04 g/cm\(^3\).
Magnetite error: - 0.03 g/cm\(^3\) / + 0.03 g/cm\(^3\).

The spread of data was very even around the average and was taken from a set of 30 tests done over three samples per powder. There was no observed loss in mass when measuring the powder samples post test where the weighing balance used before and after test was accurate to 1 mg. The source of error could be attributable to closed cavities within the agglomerates where the helium could not penetrate therefore affecting the volume measurements. Another source could be the presence of other gases or moisture trapped in the powder where the numerous filling and evacuations of the test chamber before each test was not enough to remove these.
5.2 Ashing

The table below shows the results of the ashing tests.

<table>
<thead>
<tr>
<th>Intended Carbon Content (wt%)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual Carbon Content (wt%)</td>
<td>11</td>
<td>26</td>
<td>32</td>
<td>40</td>
<td>56</td>
<td>65</td>
</tr>
<tr>
<td>Volume Percent ($\rho = 1.82$ g/cm$^3$)</td>
<td>6.15</td>
<td>15.70</td>
<td>19.96</td>
<td>26.11</td>
<td>40.28</td>
<td>49.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intended Graphite Content (wt%)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual Graphite Content (wt%)</td>
<td>14</td>
<td>23</td>
<td>29</td>
<td>39</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>Volume Percent ($\rho = 2.24$ g/cm$^3$)</td>
<td>10.82</td>
<td>18.21</td>
<td>23.34</td>
<td>32.27</td>
<td>42.70</td>
<td>49.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intended Magnetite Content (wt%)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual Magnetite Content (wt%)</td>
<td>9</td>
<td>20</td>
<td>32</td>
<td>40</td>
<td>51</td>
<td>60</td>
<td>71</td>
</tr>
<tr>
<td>Volume Percent ($\rho = 5.02$ g/cm$^3$)</td>
<td>1.77</td>
<td>4.35</td>
<td>7.88</td>
<td>10.81</td>
<td>15.90</td>
<td>21.42</td>
<td>30.79</td>
</tr>
</tbody>
</table>

Table 6 - Ashing test results for carbon, graphite and magnetite powders showing a maximum increase of 6 % for the 50 wt% carbon and a maximum decrease in percentage of 3 % for the 60 wt% graphite.

The actual content by weight percent of the carbon, graphite and magnetite mixtures varied between 0 % to 6 %, -3 % to 4 % and -1 % to 2 % respectively compared to their intended weight percent loadings. All values are an average of two tests rounded to the nearest whole percent.

The tests showed that the carbon and graphite composites varied quite a lot from their intended percentage filler loadings and the magnetite grades only varied slightly from their intended percentages. The increases and decreases in weight percent could be attributable to the loss of material in the two roll mill where material trapped in small inaccessible regions of the rollers did not contribute to the overall material composition.
As a comparison, the weight percentages have been converted to volume percentages using the following equation.

\[
Vol\% = \left[ \frac{wt\% / \rho_F}{(wt\% / \rho_F) + ((100 - wt\%) / \rho_M)} \right] \times 100
\]  

(Equ 8.)

Where:

- Vol\% - Volume percentage of the filler
- wt\% - Weight percentage of the filler
- \(\rho_F\) - Density of the filler
- \(\rho_M\) - Density of the matrix

5.2.1 Errors

During mixing using the two roll mill there was some material wastage on the rollers as the first material to be put in (the polyethylene) spread out over the front roller into awkward/inaccessible areas of the machine. This could have led to a decrease in polyethylene content. Also there was no way of creating a homogenous mixture of the two materials, only by spreading the mixture over the roller and re-churning it created the mixing action. Therefore there was no way of guaranteeing a homogeneous mixture or gauging how evenly the blend was mixed so the technique involved user judgment.

When burning out the polymer it was possible that the carbon contained within the polyethylene could have contributed to the filler loading measured. At the same time the burning of the polymer produced sooty flames and thus would have reduced the carbon content measured, therefore these contributions to the error were considered negligible.

All the inaccuracies mentioned above were considered unquantifiable. The final ashing test values were then rounded to the nearest whole percent giving an inaccuracy of ±0.5 % but due to the spread of the data i.e. 0 wt% to 60+ wt%, a ±0.5 % error was negligible. Therefore the ashing test measurements were considered accurate representations of the filler content.
5.3 Electrical Conductivity

5.3.1 Carbon Black

Figure 23 - The electrical conductivity of the carbon composite showed two similar sets of results for through plane and in plane conductivities. Both sets of data showed an increase in conductivity with increasing carbon content.

Figure 23 shows the plot of through plane and in plane electrical conductivity for the injection moulded carbon composite between 40 wt% and 65 wt% carbon loadings. The through plane conductivity started higher than the in plane conductivity with an exponential increase with increasing carbon loading. The in plane conductivity started lower than the through plane conductivity but overtook the through plane conductivity at 65 wt% exhibiting a greater increase. Both conductivity plots showed an increase in material instability as shown by the increase in the range of the scatter bars with increasing carbon loading. No samples below 40 wt% conducted and so 40 wt% can be considered the percolation threshold for the injection moulded carbon composites.

The minimum through plane conductivity was 7.17 S/cm at 40 wt% increasing to 13.31 and 23.88 S/cm for 56 wt% and 65 wt% respectively. The in plane conductivities for
increasing carbon loading were 2.59 S/cm, 9.14 S/cm and 26.58 S/cm at 40, 56 and 65 wt% respectively. Scatter ranges for both sets of data collected increased with increasing carbon loading showing increasing material instability.

Data for the compression moulded carbon composites was limited and not sufficient for a graphical plot. Electrical conduction for through plane conductivity started at 0.242 S/cm at 26 wt% and increased to 0.367 S/cm at 32 wt%. There was only one value obtained for in plane conductivity and was 0.183 S/cm at 32 wt%. There were also a limited number of conductive samples per data point, i.e. two out of five conductive samples for 26 wt% through plane conductivity and three out of five conductive samples for 32 wt% thorough plane and in plane conductivities. Due to this, there was little consistency in the data and the small range of 26 wt% to 32 wt% was not enough for a comparison with the injection moulded data but was good as an indication of conductivity levels and percolation threshold.
5.3.2 Graphite

The injection moulded graphite composites gave one set of data for in plane electrical conductivity, readings below 39wt% (percolation threshold) were unobtainable. The in plane conductivity increased exponentially from 39 wt% to 57 wt% with increasing material instability as shown by the scatter bars. The electrical conductivity at 39 wt% was 0.012 S/cm increasing to 0.049 S/cm at 50 wt% and further increasing to 0.203 S/cm at 57 wt%. The data exhibited minimal material instability until 57 wt% where the scatter range increased rapidly to +0.107/-0.040 S/cm. Although this range was fairly low in terms of electrical conductivity it was considerably greater than the previous scatter ranges at 39wt% (+0.003/-0.002 S/cm) and 50 wt% (+0.004/-0.005 S/cm).

One data point of 0.315 S/cm was measured for the through plane conductivity at 57 wt% with a scatter of +0.065/-0.071 S/cm. The lack of readings for through plane conductivity up to 57 wt% would suggest some orientation of the filler during injection
moulding in favour of the in plane conductive direction, however the sudden conductivity at 57 wt% would suggest otherwise. As shown later in this chapter, the FEGSEM micrographs showed no obvious alignment in such a direction and it is highly likely that the data is the result of a poor filler with anisotropic conductivity.

Figure 25 - Compression moulded graphite composite electrical conductivities for in plane and through plane directions both with exponential increases beyond 50 wt%.

The electrical conductivities for the compression moulded graphite composites were similar and initially increased at a similar rate for both in plane and through plane conductivities until 57 wt%. At 57 wt% the through plane conductivity increased to more than double that of the in plane conductivity with a far greater material instability than that of the in plane measurements. Again, samples below 39wt% did not conduct and can be considered the percolation threshold.

The in plane conductivity increased from 0.002 S/cm to 0.033 S/cm to 0.409 S/cm at 39 wt%, 50 wt% and 57 wt% respectively. The through plane conductivity increased from 0.001 S/cm to 0.022 to 0.850 S/cm for 39 wt%, 50 wt% and 57 wt% respectively.
The scatter ranges for in plane and through plane conductivity were very narrow at 39 wt% and 50 wt%. At 57 wt% the scatter ranges increased considerably to $+0.071/-0.214$ S/cm and $+0.489/-0.427$ S/cm for in plane and through plane conductivities respectively.

The through plane conductivity was more than double that of the in plane conductivity with an scatter range greater than its conductivity value. It was expected that there was no orientation during compression moulding and this again shows poor filler properties and increased randomness due to the anisotropic conductivity of the filler.

The higher conductivity at 57 wt% of the compression moulded samples than the injection moulded samples could be due to the increase in processing pressure allowing better particle to particle contact. However the increase in processing pressure should have presented higher conductivities at 39 wt% and 50 wt% for compression moulding than injection moulding but was not the case. Due to the random orientation and irregular particles sizes and geometry it can be concluded that the two sets of data could vary widely irrespective of the processing technique employed. This can be shown with the 57 wt% injection and compression moulded graphite data where if both data sets were plotted on the same graph their scatter ranges would overlap.

5.3.3 Magnetite

The data gained for the magnetite composites were limited due to poor electrical conductivity across the range of samples and thus were not suitable for graphical plots. However, like the compression moulded carbon composites; it was a good indicator of conductivity levels and percolation thresholds.

One injection moulded sample at 71 wt% had an in plane conductivity of $1 \ \mu$S/cm and through plane conductivity of $0.03 \ \mu$S/cm.

For the compression moulded samples, only one sample at 60 wt% conducted with a value of $6.65 \ \mu$S/cm for through plane conductivity but no values were gained for in plane conductivity. At 71 wt% the in plane conductivity was $0.0014$ S/cm and the
through plane conductivity was 1.26 µS/cm with scatter ranges of +0.76/-1.0 µS/cm for in plane and +0.5/-0.7 mS/cm for through plane conductivities.

5.3.4 Errors

The readings for each sample required some time to stabilise. Some samples increased in conductivity to a stable point and some decreased in conductivity to a stable point. In doing so it was difficult to recognise the absolute point at which the readings were stable as the rate of change of the readings decreased as it approached the stable point. The error in any potential readings not taken at the stable point was considered negligible due to changes in the readings only occurring to the nearest 3\textsuperscript{rd} decimal place.

The variation in the contact force between the samples and the probes was minimised by using end stops beyond which the adjustable stage width would not decrease further. This should have ensured contact forces were the same for each sample and any minute variations would have been negligible.

All but one data point in figures 23 to 25 were averages of five samples where the scatter bars represent the spread of five results for each data point. The data point for compression moulded graphite at 57 wt\% through plane conductivity was an average of four samples where one sample had failed to conduct.

Other data points with less than five conductive samples were the compression moulded carbon composite data points and the magnetite composite data points where graphical plots could not be produced. For the compression moulded carbon composite at 26 wt\% only two samples for through plane conductivity conducted and at 32 wt\% three samples were conductive for both in plane and through plane conductivities.

As stated previously, one sample at 71 wt\% conducted for the in plane and through plane measurement of the injection moulded magnetite composite. For the compression moulded magnetite composite, one sample conducted at 60 wt\% for through plane
conductivity only and one out of five samples failed to conduct at 71 wt% for in plane conductivity whilst all five samples conducted for through plane conductivity.

5.4 Thermal Conductivity

Unlike the electrical conductivity data, the thermal conductivity data yielded measurable values for all composite grades explored giving enough data for trend lines to be determined.

5.4.1 Carbon Black

Figure 26 - Thermal conductivity results for injection and compression moulded carbon composites up to 65wt% and 32wt% respectively.

The thermal conductivity for the injection and compression moulded carbon composites in figure 26 showed exponential increases with compression moulded samples increasing at a higher rate than injection moulded samples. The exponential curve fit and 2\textsuperscript{nd} order polynomial fit for the compression and injection moulded composites respectively showed a good fit with R\textsuperscript{2} values greater than 0.96.
The maximum thermal conductivity for the compression moulded carbon composite was 0.61 W/mK at 32 wt% and 1.09 W/mK for the injection moulded carbon composite at 65 wt%. The minimum conductivities at 0 wt% were 0.36 W/mK and 0.35 W/mK for the compression and injection moulded samples respectively. The compression moulded samples showed a noticeable increase immediately after 0 wt%; however the injection moulded samples only began to increase at 26 wt%.

Although the highest carbon content had the largest scatter range of +0.054/-0.083 W/mK, the scatter ranges showed no trend in increasing material instability with increasing carbon content and were generally narrow in range.

As before, there was no carbon composite material available for test above 32 wt%.

5.4.2 Graphite

Figure 27 - Thermal conductivity results for injection and compression moulded graphite composites up to 57 wt%.
Results

Injection and compression moulded thermal conductivity results for the graphite composite shown in figure 27 showed consistent increases with compression moulded samples increasing at a slightly greater rate than the injection moulded samples. Both data sets showed noticeable increases after 0wt% and both curve fits to the data were 2\textsuperscript{nd} order polynomials with $R^2$ values close to 1.

The maximum and minimum conductivities for the compression moulded samples were 2.17 and 0.36 W/mK respectively. The maximum and minimum conductivities for the injection moulded samples were 1.77 and 0.35 W/mK respectively. Both exhibited maximums at 57 wt%, the highest graphite content.

Again, the scatter ranges were consistently narrow and showed no trend in material instability with increasing graphite content.

5.4.3 Magnetite

![Thermal Conductivity for Injection and Compression Moulded Magnetite Composites](image)

Figure 28 - Thermal conductivity results for injection and compression moulded magnetite composites up to 71 wt%.
The thermal conductivity results shown in figure 28 for the compression and injection moulded magnetite composites showed a similar trend to each other. Both data sets were almost identical and increased exponentially with increasing magnetite content. The curve fit for compression moulded samples started slightly lower in thermal conductivity than the injection moulded samples but then increased more rapidly to a maximum conductivity of 1.05 W/mK at 71 wt%. The maximum conductivity for the injection moulded samples was 0.89 W/mK. The minimum conductivities remained at 0.35 W/mK and 0.36 W/mK for injection and compression moulded samples respectively.

Both curve fits were 2nd order polynomials with $R^2$ values of 0.97 and 0.92 for the compression and injection moulded data respectively. Although the scatter bar ranges at 71wt% for both data sets were larger on average, there was still no general trend shown for material instability across the data sets.

The trend line $R^2$ values were lower than those for the carbon and graphite therefore showing a wider spread of data. The largest scatter range from the data was $+0.068/-0.050$ W/mK at 71 wt% (injection moulded).

5.4.1 Errors

The readings gained from the P5687 thermal conductivity apparatus were very sensitive to the temperature measurements taken for the water in and water out of the apparatus. The errors were minimised by the use of thermocouples and thermocouple readers accurate to one hundredth of a degree centigrade. A temperature change of 0.01 °C between the water in and water out readings would result in an approximately 0.02 W/mK change. The use of thermometers as was described by the manufacturer would have incurred errors of $\pm0.5$ of a degree centigrade resulting in far larger errors.

To a lesser extent, the sample thickness measured would also have introduced errors however the micrometer used was accurate to one hundredth of a millimetre and so would have reduced such errors to a negligible level.
The surface roughness of the samples would have also affected the thermal conductivity readings. Although the samples were polished, surface roughness on the micron scale would have remained but would have been minimised by the use of thermal paste. The use of thermal paste itself was prone to error if too much was applied creating a thick layer between the sample and the equipment contacts as its intended use was to fill gaps in surface roughness only. Only small amounts of paste were used, enough to cover the surface of the samples when clamped but not enough to incur large excess overspills.

The error associated with the paste was unquantifiable as there was no way of assessing whether the correct amount of thermal paste was applied on a microscopic level. However, it was considered small as the thermal paste was a better thermal conductor (8.7 W/mK) than the composites. This means that the rate of thermal conduction was not hindered by the paste, although, if sufficiently thick it would have presented two solid interfaces for thermal conductance.

5.5 Tensile & Flexural

5.5.1 Carbon Black

Figure 29 on the next page shows the tensile strength comparison between injection and compression moulded samples with increasing carbon content. The initial addition of carbon (11 wt%) to form the composite increased the tensile strength of the injection moulded pure polyethylene considerably from 11.19 MPa to 23.32 MPa and reached a maximum of 23.97 MPa at 26 wt%. The tensile strength thereafter decreased to 23.55, 22.18, 20.17 and 16.20 MPa at 32, 40, 56 and 65 wt% respectively for the injection moulded samples. The reduction in tensile strength is due to the reduction in filler-matrix interfaces and the increase of filler-filler interfaces with increasing filler content thus changing the failure mechanism.
The compression moulded samples displayed less tensile strength than the pure polyethylene compression moulded samples with a decreasing trend with increasing carbon content. The compression moulded pure polyethylene had a higher tensile strength of 17.92 MPa compared to the injection moulded samples but after the addition of carbon decreased to 16.67, 15.29 and 10.11 MPa at 11, 26 and 32 wt% respectively. The increased strength of the compression moulded pure polyethylene was due to the increase in processing pressure of an additional 12 bar resulting in a densely packed polymer microstructure with greater polymer chain interlocking.

On the whole, the compression moulded samples exhibited a greater degree of material instability than the injection moulded samples as is shown by the length of the scatter bars where the scatter ranges remained fairly consistent with increasing carbon content.
The elastic modulus of the injection and compression moulded carbon composites are shown in figure 30. The injection moulded composite increased somewhat linearly with increasing carbon content displaying increasing brittleness up to 453 MPa, a linear trend line was fitted to the data with an $R^2$ value of 0.9796. The scatter bars of the composite remain fairly narrow until 57 wt% and 65 wt% where the maximum scatter was $+26 / -75$ MPa illustrating large variations / material instability in the data set at high loadings.

The compression moulded composite showed increasing brittleness with increasing carbon content with a peak of 227 MPa at 32 wt%, the scatter ranges in the data remained consistently high throughout the data set. As stated previously, samples with loadings above 32 wt% were unobtainable due to poor processing. A linear least squares fit to the data gave a reasonable fit with an $R^2$ value of 0.813 and the largest scatter range was $+91/-37$ MPa.
Figure 31 - Flexural strength variation with increasing carbon content for injection and compression moulded carbon composites.

Figure 31 shows the flexural results for the injection and compression moulded carbon composites with increasing carbon content. Injection moulded samples fractured at and above 26 wt% exhibiting a maximum flexural strength of 35.07 MPa at 40 wt%. The plot shows flexural strengths of 26.85, 32.18, 35.07, 33.64 and 32.34 MPa at 26, 32, 40, 56 and 65 wt% respectively and shows greater material instability with increasing carbon content.

The compression moulded carbon composite samples fractured at 11, 26 and 32 wt% where the maximum and minimum flexural strengths of 21.89 MPa and 13.40 MPa were at 26 and 32 wt% respectively. The material showed a consistent degree of material stability throughout the content range and the injection moulded grades showed less material stability with increasing carbon content than the compression moulded samples.
Fig. 32 - Flexural modulus of injection and compression moulded carbon composites.

The flexural modulus results for the carbon injection and compression moulded composites are displayed above in figure 32. Both sets of data showed increasing flexural modulus and thus increasing brittleness with increasing carbon content peaking at 3.5 GPa and 0.93 GPa for injection and compression mouldings respectively. The injection moulded samples exhibited a higher modulus with a greater exponential increase than the compression moulded samples.

The data sets showed no trend in material instability as the scatter ranges remained low and fairly consistent except at 32 wt% for the compression moulded samples where the scatter range of +0.37 / -0.12 GPa was the greatest. Both sets of data were fitted with exponential curve fits and displayed $R^2$ values greater than 0.95, samples below the minimum carbon contents shown did not fracture.

Summary

Generally the compression moulded samples displayed lower tensile and flexural properties than the injection moulded samples and displayed the lowest tensile and flexural strengths in the data sets at the highest carbon content (32 wt%). It is easy to
see from the data that if any compression moulded material above 32 wt% was processed its mechanical properties would have been greatly insufficient as proven by the extreme difficulty in their processing where fractured sheets of the material were produced on de-moulding.

The elastic modulus of all carbon grades showed increasing brittleness with increasing filler content with injection moulded samples exhibiting higher modulus than the compression mouldings. This can be seen in the example data plot presented in appendix I representing a limited selection of data. The points at which the tensile and flexural strengths decrease (40 wt% and 26 wt% for flexural injection and compression moulded samples respectively and at 11 wt% for tensile injection moulded samples) coupled with increasing moduli shows that the filler has a negative effect on the mechanical properties where the brittleness becomes too great. The compression moulded tensile data showed no benefit in the addition of the carbon filler and just like reduction in strength observed in all the carbon composite data, the failure mechanism had moved from a filler-matrix interface to an increasing filler-filler interface.

5.5.2 Graphite

![Graph of Tensile Strength of Injection and Compression Moulded Graphite Composites](image)

Figure 33 - Tensile strength of injection and compression moulded graphite composites with increasing graphite content.
Results

Figure 33 shows the tensile strength with increasing graphite content of the injection and compression moulded composites. The injection moulded grades increased greatly from the pure polyethylene result of 11.19 MPa to 22.65 MPa at 14 wt% and then steadily increased to a maximum of 27 MPa at 57 wt%. The scatter bars associated with the data set were extremely narrow and showed little variation in the materials’ property.

The compression moulded graphite samples performed somewhat similar to the pure polyethylene compression moulded samples displaying a relatively flat plot with the minimum at only 1.58 MPa less than the pure polyethylene at 17.92 MPa. The only exception to this was the maximum tensile strength of 21.41 MPa at 23 wt%. The scatter ranges were fairly large representing a reasonable degree of material instability except for the measurements at 23 wt% where the data was very compact (+0.37/-0.4 MPa).

No data was gained for the compression moulded samples above 39 wt% as the samples slipped through the grips of the test machine. This is discussed further in section 5.5.4.

Figure 34 - Elastic modulus of injection and compression moulded graphite composites.
The elastic moduli shown in figure 34 for the injection and compression moulded graphite composites showed increasing brittleness with increasing graphite content with injection moulded data displaying greater modulus than the compression moulded data. The increase in brittleness of such composites can also be inferred from the example data plots shown in appendix J where the plots represent a limited selection of data. Curve fitting to the data showed good agreement and gave $R^2$ values greater than 0.91 for the exponential and linear fits for the injection and compression data respectively. The highest modulus values for injection and compression mouldings were 410 MPa and 187 MPa respectively.

The scatter for the compression moulded data decreased slightly with increasing graphite content with the largest scatter range being $+50/-38$ MPa. As before, data above 39 wt% was not obtained as the samples slipped through the grips of the test machine. The scatter ranges for the injection moulded samples remained small until 50 wt% and 57 wt% where the largest scatter range was $+29/-19$ MPa.

The injection and compression moulded flexural strengths of the graphite composites shown in figure 35 showed an upward trend with increasing graphite content. The
Results

Injection moulded samples exhibited higher strengths with minimum and maximum flexural strengths of 28.79 and 37.66 MPa at 39 wt% and 57 wt% respectively. The minimum and maximum flexural strengths for the compression moulded samples were 21.88 and 29.77 MPa at 29 wt% and 57 wt% respectively. The test samples did not fracture below the minimum weight percentages mentioned.

Again, the injection moulded samples showed more material stability than the compression moulded samples as the scatter bar ranges were extremely narrow with the largest scatter range being +0.42/-0.65 MPa at 57 wt%. The relatively large scatter of the compression moulded samples, the largest scatter range being +2.36/-2.13 MPa at 50 wt%, showed that some material instability was present.

![Flexural Modulus of Injection and Compression Moulded Graphite Composites](image)

Figure 36 - Flexural modulus of injection and compression moulded graphite composites.

Figure 36 shows the flexural modulus results for the injection and compression moulded graphite composites with maximum moduli of 2.54 GPa and 1.77 GPa for injection and compression mouldings respectively. Both data sets showed similar increases in modulus with increasing graphite content with similar degrees of scatter across the range except for the injection moulded samples at 57 wt% where the scatter
range was +0.71/-0.53 GPa representing more material instability. The exponential curve fits to the data gave $R^2$ values greater than 0.96 with injection moulded data exhibiting greater modulus than the compression moulded data. As stated previously, samples below the minimum weight percentages shown did not fracture.

**Summary**

As with the carbon composites, the graphite injection moulded samples showed higher tensile and flexural strengths than the compression moulded samples with the injection moulded samples showing more material stability. The elastic and flexural moduli increased with increasing graphite content and therefore increased in brittleness. However unlike the carbon, the continuous increase in tensile and flexural properties with no peak except for the tensile properties of the compression moulded samples showed that there was no point at which the graphite filler became a negative influence. The point at which the graphite becomes a negative influence in the tensile compression moulded data was at 23 wt%.

5.5.3 Magnetite

![Graph showing tensile strength of injection and compression moulded magnetite composites.](image)

Figure 37 - Variation in tensile strength with increasing magnetite content for injection and compression moulded magnetite composites.
The plots shown in figure 37 show the variation in tensile strength with increasing magnetite content for injection and compression moulded magnetite composites. Aside from the pure polyethylene results of 11.19 MPa and 17.92 MPa for injection and compression moulded samples respectively, the differences in the two data sets were minimal. Both plots had maximums at 9 wt% of 18.66 MPa and 20.38 MPa for injection and compression moulded samples respectively. Both plots followed similar downward trends with increasing magnetite content with the largest separation between plots being 3.25 MPa at 32 wt%.

The compression moulded samples exhibited higher tensile strengths than the injection moulded samples but the injection moulded samples showed greater material stability with narrower scatter bar ranges.

Data for the compression moulded 71 wt% samples could not be obtained as the samples slipped through the grips of the test machine. Flexural test results for the injection and compression moulded magnetite composites were not obtained as the samples did not fracture during testing.

![Elastic Modulus of Injection and Compression Moulded Magnetite Composites](image)

**Figure 38** - Elastic modulus of injection and compression moulded magnetite composites.
The elastic moduli shown in figure 38 for the magnetite injection and compression moulded composites showed somewhat linear trends with $R^2$ values of approximately 0.88 and 0.77 respectively to the linear curve fittings. Injection moulded samples displayed greater modulus than the compression moulded samples and both showed increasing modulus with increasing magnetite content, the maximum moduli for injection and compression mouldings was 344 MPa and 245 MPa respectively.

There was no general trend in material instability with increasing magnetite content although the latter two samples in the compression moulded data set and predominantly the latter half of the injection moulded data set showed increased scatter between the samples. The largest scatter ranges in the data were +54/-19 MPa at 40 wt% for injection moulded samples and +37/-18 MPa at 60 wt% for compression moulded samples.

Although with less correlation than the carbon and graphite fillers the trends remain in good agreement with the data. The peak at 9 wt% for the tensile and flexural data shows the maximum benefit of the magnetite filler beyond which negative effects occur. As flexural tests for the injection and compression moulded magnetite did not give any results, no flexural modulus data was gained.

5.5.4 Errors

All sample thicknesses varied from sample to sample to within half of a millimetre as well as varied along the length of the same sample to within five hundredths of a millimetre. This was unavoidable due to uncontrollable processing tolerances, i.e. mould imperfections and shrinkage variations. The variations in thickness along the length of the sample were averaged and therefore errors due to this were minimised and considered negligible. The variations in thickness from sample to sample were accounted for in the tensile and flexural calculations and did not generate any errors.

The flexural test samples were loaded onto the test stage with any lateral movement minimised by reducing the gap between the 3 points on the 3 point bending apparatus to
hold the samples steady. This would have ensured that there was no slack in the system and that the variations in sample thickness were accounted for.

Data unobtained from sample slippage through the tensometer grips was not seen as a limitation as trends from the available data were already visible. Any results gained for the graphite compression moulded samples above 39 wt% and magnetite compression moulded samples above 60 wt% would only have completed the data set. However as graphite is a lubricant it was expected that at high graphite loading gripping of the samples would create a problem and that too great a grip pressure would fracture the samples. The slippage of the highest loaded magnetite grade was not expected and could be attributed to the filler surface morphology where smooth flat particle faces may have left no rough texture for surface friction.

5.6 Microstructure

The post-test flexural samples used for the micrographs fractured cleanly exhibiting brittle fractures throughout all grades. Samples of 11 wt% injection moulded carbon, 14, 23 and 29 wt% injection moulded graphite and all magnetite composites were initiated by scoring and fractured by hand; these fractures also showed similar degrees of brittleness.
5.6.1 Carbon Black

Figure 39 - FEGSEM micrographs of (a) 11 wt%, (b) 26 wt%, (c) 32 wt%, (d) 40 wt%, (e) 56 wt% and (f) 65 wt% injection moulded carbon in polyethylene.

The FEGSEM micrographs in figure 39 show the change in microstructure with increasing carbon content from 11 wt% to 65 wt% for the injection moulded composites. At 11 wt% (fig. 39a) there is a large polyethylene network that is highly interconnected...
Results

with only small clusters of agglomerates visible. With increasing carbon content the polyethylene network reduces in size and becomes less pronounced. With increasing carbon content there is visibly more and more carbon present until 65 wt% (fig. 39f) where the surface is mainly made up of carbon particles and only a small network of polyethylene strands.

![Image of micrographs](a) (b) (c)

Figure 40 - FEGSEM micrographs of (a) 11 wt%, (b) 26 wt% and (c) 32 wt% compression moulded carbon in polyethylene.

As only three grades of compression moulded carbon composite samples were able to be moulded, figure 40 shows the microstructure of the three carbon composites. The 11 wt% grade (fig. 40a) showed a dense network of polyethylene strands with few carbon agglomerates and loose particles adhered to the polyethylene structure just like the 11 wt% injection moulded grade. 26 wt% and 32 wt% microstructures in figures 40b and 40c respectively showed similar structures although the 32 wt% grade showed slightly less pronounced polyethylene strands. Both grades showed densely packed carbon
particles within the polyethylene structure and were equivalent to the 40 wt% injection moulded micrograph.

At the higher loaded carbon grades, i.e. above 40 wt% and 26 wt% for the injection and compression moulded grades respectively, the microstructure showed tightly packed carbon particles held together by the polyethylene network. As the carbon particles were of a similar size to the polyethylene microstructure the network of polyethylene appears to act as a reinforcing structure threaded throughout the carbon phase.
5.6.2 Graphite

Figure 41 shows the microstructures for the injection moulded graphite composites with increasing graphite content. At 14wt% (fig. 41a) there is mainly polyethylene with graphite sparsely distributed throughout the structure with no apparent contact between
Results

dgraphite particles. The visible graphite content increases with increasing graphite loading however there is no apparent contact between particles up to 39 wt% (fig. 41d) but at 50 wt% and 57 wt% (figs. 41e and 41f) there is some degree of particle contact visible. Throughout all the micrographs the graphite orientation appears to be random and shows no influence of injection moulding on flow direction.

Figure 42 - FEGSEM micrographs of (a) 14 wt%, (b) 23 wt%, (c) 29 wt%, (d) 39 wt%, (e) 50 wt% and (f) 57 wt% compression moulded graphite in polyethylene.
The compression moulded graphite composite micrographs shown in figure 42 show an increasing number of graphite particles with increasing graphite content with all graphite particles appearing randomly orientated. Again, apparent particle contact was visible at and above 50 wt% (figs. 42e and 42f) whilst at 39 wt% (fig. 42d) the graphite content appeared evenly dispersed. Below 39 wt% (figs. 42a, b and c) the composites were sparsely populated with graphite particles.
5.6.3 Magnetite

Figure 43 - FEGSEM micrographs of (a) 9 wt%, (b) 20 wt%, (c) 32 wt%, (d) 40 wt%, (e) 51 wt%, (f) 60 wt% and (g) 71 wt% injection moulded magnetite in polyethylene.
The micrographs shown in figure 43 showed a clear increase in magnetite content with increasing magnetite loading for the injection moulded samples. The particles remained randomly dispersed with no apparent particle contact before 71 wt% (fig. 43g). Surrounding each particle appears to be narrow crevices or air gaps where there has been some incompatibility and poor wetting between the polymer and the magnetite. For the same reason, large cavities/impressions can be seen where loose particles have dropped out of the surface during fracture.

Figure 44 shows the microstructures for the compression moulded magnetite composites with increasing magnetite content. The micrographs appeared the same as the injection moulded composites in that there were randomly dispersed particles in increasing numbers with increasing magnetite loading and no apparent particle contact before 71 wt%. The polymer phase at 71 wt% (fig. 44g) and partially at 20 wt% (fig. 44b) exhibited a more plastic deformation than the other grades shown by the long extrusions.
Figure 44 - FEGSEM micrographs of (a) 9wt%, (b) 20wt%, (c) 32wt%, (d) 40wt%, (e) 51wt%, (f) 60wt% and (g) 71wt% compression moulded magnetite in polyethylene.
5.6.4 Errors

All micrographs were taken of fracture surfaces from the flexural strength tests. As not all composites grades fractured, some samples were scored with a knife to initiate crack propagation and then bent in a similar flexural way. The composites fractured in this way were the injection moulded carbon at 11 wt%, the injection moulded graphite at 14, 23, and 29 wt% and all the samples for the injection and compression moulded grades of the magnetite composite.

Although the micrographs taken of the fracture surfaces gave a good indication of the microstructure of the composites, there would have been some distortion in the polyethylene phase and networks due to the fracture. This would be especially true for less brittle fractures i.e. composite grades where samples had to be scored with a knife to initiate the fracture. Filler particles would also have been dislodged due to the fracture; however impressions on the surface of the material gave indications of particle locations. Despite these errors, the microstructures were considered significantly intact to give an accurate depiction of the composite structures.

The micrograph of the compression moulded graphite at 50 wt% (fig 42e) revealed two spherical particles of iron oxide as found by EDX (Energy dispersive X-ray spectroscopy). A similar particle of iron oxide was found in the 20 wt% injection moulded magnetite composite (fig 43b). The spherical iron oxide particles were considered foreign to the native filler but were not considered influential in affecting material properties due to their rare occurrence.

The source of the contamination is unknown, however it is highly likely that any foreign materials found in the mixtures would have originated from the two roll mill. The use of materials from previous mixes trapped in the equipment and extractor hood could have been dislodged due to vibrations and physical contact with the composites. The spherical form of the iron oxide was obviously not naturally occurring due to the perfectly spherical shape and would not have come from a source of equipment rust which is normally flaky in form.
Due to the higher density of the magnetite compared to the carbon and graphite fillers, the maximum 71 wt% mixture obtained was far less in volume percent compared to the other fillers. This meant that there was far less magnetite filler present in the matrix, however the mixtures were taken to their highest processable loading and so this did not affect the set of data for the magnetite. A conversion between weight percent and volume percent can be seen in table 6 on page 63.
Chapter 6.0

Modeling

The modelling theories described in this thesis will focus on the electrical and thermal conductivities and the elastic and flexural moduli of the composite materials. To understand these properties of the composites and the mechanisms that contribute to them, theories have been developed to model the behaviour of the materials with varying filler content. In this way the models can help tailor / optimise the composite design in order to better fit the application and reduce costs.

The following parameters as stated by Lux \cite{52} that should be taken into account in all electrical conductivity models are:

- Size and geometry of the filler.
- Quantity and distribution of the filler.
- Interaction between conductive and insulating components.
- Preparation method of the mixtures.

This would also be true for thermal conductivity models due to the similar physical conduction requirements as electrical conductivity and also true for mechanical models where the above factors would affect fracture behaviour.

The size and geometry of the filler would affect contact surface area between particles and at the filler-matrix interfaces therefore determining the level of conduction for electrical and thermal properties and adhesion for mechanical properties. For spherical particles, lower percolation threshold is obtained with smaller particle size \cite{53, 54}. Similarly the quantity and distribution of the filler would increase or decrease the probability of such contact between particles. The interaction between filler and matrix would affect the degree of contact between filler particles where the interaction (i.e.
surface energy) would determine the level of wetting \[^{[55]}\]. Therefore an increase in the level of polymer coating on each particle would hinder electrical and thermal conduction but improve mechanical strength. The preparation of the mixtures such as mixing technique, pressure and temperature would affect both the distribution of the filler and its interaction in the matrix where ideally homogeneous mixtures are desired for predictable properties.

There are many models in the literature that model electrical, thermal and mechanical properties. Only a few are discussed in the next sections where comparisons in the literature have been made between models that have been applied to similar composites such as the ones in this thesis. Due to the spherical particle shape of the carbon filler and the boulder-like graphite and magnetite filler shapes coupled with the random orientation observed from both magnetite and graphite micrographs as shown in chapter 5, a spherical mono dispersed filler phase is assumed for all models.

6.1 Theories

6.1.1 Electrical / Thermal – Percolation Theory

As electrical and thermal conductive properties require sufficient particle to particle contact, theories based on this have been developed. The main theory, called percolation theory, has been used to describe the electrical and thermal properties of many materials and has been applied many times to composites like those studied here. By visualising a grid/lattice pattern representing the matrix with dots filling each square in the grid (where filler particles reside), a pattern shown in figure 45 is achieved.

![Figure 45 - Representation of percolation theory where increasing filler content from (a) to (c) eventually forms clusters, highlighted in green, that create conduction paths.](image-url)
Adjacent dots form clusters, highlighted in green in figure 45c. When these clusters extend throughout the lattice i.e. from top to bottom and left to right, they form a conduction path and therefore the composite becomes conductive. Since the filler particles are randomly distributed there is a probability \( p \) that a lattice square will be occupied, therefore the probability that a lattice square is unoccupied will be \( 1-p \). When \( p=1 \), every lattice square would be occupied.

Monte Carlo simulations were done using large lattices with increasing probability from 10 % to 90 %, Stauffer [56] gave examples of 60x60 lattices where near 60 % a critical point was found, called the percolation threshold. This is the point at which the composite becomes conductive due to the clusters forming a large continuous network. The percolation threshold in relation to filler content as a volume fraction is illustrated in figure 46 below.

![Figure 46](image)

Figure 46 - Electrical conductivity profile for composites with increasing filler volume fraction displaying different cluster formations.

Figure 46 illustrates the conductivity level of a composite with increasing filler content. The composite remains non conductive up to the percolation threshold, at the percolation threshold a conductive network is formed and the volume fraction at that
point can be considered the critical volume fraction. The conductivity of the composite increases rapidly as the conductive network grows with increasing volume fraction and then starts to level off as the further growth of clusters has little effect on the overall conductivity.

Different fillers have different degrees of conductivity; however within the same material the physical properties of the filler such as size and shape can affect the percolation threshold \(^{57}\). Fillers that are non-spherical are subject to orientation during processing such as injection moulding and to some extent compression moulding that tend to produce materials with anisotropic conductivity \(^{58,59}\).

Chemical properties such as the surface energies of the matrix and filler have a role to play in electrical/thermal conductivity. Filler dispersion within the matrix increases as the difference between filler and matrix surface energy decreases. This has an effect of increasing percolation threshold but improves overall conductivity \(^{54}\).

Electrical and thermal conductivity models are further described in sections 6.2.1 and 6.2.2.

6.1.2 Mechanical - The rule of mixtures

There are many theories / computational techniques that are applicable to mechanical property modelling such as mean-field theory, shear lag theory, finite element methods (FEM) and the rule of mixtures.

Mean field theory (or self consistent field theory) aims to reduce a many-body system that is generally very difficult to solve with all its interactions to a one-body problem with an average or effective interaction.

Shear-lag theory explains the transfer of load into a fibre from the surrounding matrix and therefore is useful for fibre loaded materials.
FEM is a computational technique for finding approximate solutions of partial differential equations by either eliminating or approximating the partial differential equations into ordinary differential equations to simplify calculations.

The rule of mixtures is a simplified model that estimates mechanical behaviour reasonably well. Compared to the other models / theories mentioned, the rule of mixtures is very basic in its approach and is the foundation for further models described in section 6.2.3 that improve upon its predictive abilities. The rule of mixtures and subsequent models is the theory chosen for this study due to its simplicity.

The rule of mixtures can be used to predict the elastic modulus of composites from the elastic moduli and volume fractions of the filler particles and the matrix \[60\]. It states that the modulus of a unidirectional fibre composite is proportional to the volume fractions of the materials in the composite. Elastic modulus of the composite is estimated by the sum of the two products derived by multiplying the elastic modulus of the reinforcement material and the matrix material by their respective volume fractions \[60\] and is given by:

\[
E_c = E_f V_f + E_m (1 - V_f)
\]

(Equ 9.)

Where:
- \(E_c\) - Elastic modulus of the composite.
- \(E_f\) - Elastic modulus of the filler.
- \(V_f\) - Volume fraction of filler.
- \(E_m\) - Elastic modulus of the matrix.
- \((1-V_f)\) - Volume fraction of matrix.

The above equation is known as the Voigt model, also called the upper bound of the rule of mixtures. Later, Reuss and Angew \[61\] described a uniform stress model, referred to as the lower bound of the rule of mixtures, given by:

\[
E_c = \left[\frac{V_f}{E_f} + (1 - V_f) E_m\right]^{-1}
\]

(Equ 10.)
The rule of mixtures can be useful to estimate elastic modulus but it is not an accurate numerical method for modeling. Models/theories similar to the rule of mixtures that are more accurate predictors of mechanical behaviour are explained in section 6.2.3.

6.2 Models

It is beyond the scope of this thesis to describe fully all models in the literature; a derivation of chosen models used in this thesis is given in section 6.4.

6.2.1 Electrical conductivity

Three models presented are, statistical, thermodynamic and structure oriented models that have been compared by Clingerman et al [62]. All the models take into account the volume fraction of the filler, however not all require known conductivities of the filler or polymer. The volume fraction should be known to account for dispersion levels and the proximity between filler particles to gauge the degree of contact between them. Geometrical percolation models that can be used to predict conductivity will not be mentioned here as they model sintered particle structures from dry mixtures of polymer and filler particles. Therefore the composites formed are of a different microstructure to the composites formed by regular mixing processes such as compounding.
Statistical – McLachlan’s Model

McLachlan’s model proposed for conductive particles in an insulating matrix takes into account the resistivities of the constituents, volume fraction, the percolation threshold and a critical exponent. The equation is shown below.

\[
\frac{(1 - \phi)(\rho_m^{1/t} - \rho_h^{1/t})}{\rho_m^{1/t} + \left(\frac{1 - \phi_c}{\phi_c}\right)\rho_h^{1/t}} + \frac{\phi(\rho_m^{1/t} - \rho_l^{1/t})}{\rho_m^{1/t} + \left(\frac{1 - \phi_c}{\phi_c}\right)\rho_l^{1/t}} = 0
\]

(Equ 11.)

Where:

\(\phi\) - Filler volume fraction

\(\rho_m\) - Electrical resistivity of the composite

\(\rho_h\) - Electrical resistivity of the filler

\(t\) - Critical exponent

\(\phi_c\) - Critical volume fraction

\(\rho_l\) - Electrical resistivity of the polymer

The critical exponent can be found by calculation and is a function of the demagnetization or depolarization coefficients of the low and high resistivity materials or it can be found by curve fitting [62].
Thermodynamic – Mamunya Model

The Mamunya model takes into account the interactions between the polymer and filler using interfacial tension and surface energies in addition to the size and quantity of material where \( F \) denotes packing factor of the filler and thus takes into account filler morphology. Conductivity above the percolation threshold is given by:

\[
\log \sigma = \log \sigma_c + (\log \sigma_m - \log \sigma_c) \left( \frac{\phi - \phi_c}{F - \phi_c} \right)^k
\]

(Equ 12.)

\[
k = \frac{K \cdot \phi_c}{(\phi - \phi_c)^{0.75}} \quad K = A - B \cdot \gamma_{pf} \quad F = \frac{V_f}{V_f + V_p}
\]

\[
\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p \cdot \gamma_f)^{0.5} - 2(\gamma_p^p \cdot \gamma_f^p)^{0.5}
\]

Where:

\( \sigma \) - Electrical conductivity of the composite

\( \sigma_c \) - Electrical conductivity at the percolation threshold

\( \sigma_m \) - Electrical conductivity at the maximum packing factor

\( \phi \) - Filler volume fraction

\( F \) - Packing factor

\( V_f \) - Volume occupied by filler

\( V_p \) - Volume occupied by polymer

\( \phi_c \) - Percolation threshold

A & B - Constants

\( \gamma_{pf} \) - Interfacial tension

\( \gamma_p \) - Surface energy of the polymer (\( \gamma_p^{pd} \) - Polar/dispersive contribution)

\( \gamma_f \) - Surface energy of the filler (\( \gamma_f^{pd} \) - Polar/dispersive contribution)
Structure Oriented Percolation Models – Lewis-Neilsen Model

This model relates the conductivity to the aspect ratio and the co-ordination number of the filler. The constant A is equal to 2 for spherical particles [63]. The conductivity is given by:

\[
\sigma_m = \sigma_l \left(1 + \frac{AB\phi}{1 - B\Psi\phi}\right)
\]  
(Equ 13.)

\[
B = \frac{\sigma_h / \sigma_l - 1}{\sigma_h / \sigma_l + A} \quad \Psi' \approx 1 + \left(\frac{1 - F}{F^2}\right)\phi
\]

Where:

- \(\sigma_m\) - Electrical conductivity of the composite
- \(\sigma_l\) - Electrical conductivity of the polymer
- A - Function of aspect ratio and orientation
- B - is equal to 1 for polymer systems
- \(\phi\) - Filler volume fraction
- \(\sigma_h\) - Electrical conductivity of the filler
- F - Packing factor

Chosen Model

Each of the models described in the previous section have their limitations. Mclachlan’s model, although considered an accurate statistical model, can be difficult to calculate (for the critical exponent) if the demagnetization and depolarization coefficients are unknown. The critical exponent would then have to be found by curve fitting which was found unsuccessful according to Clingerman et al [62].

Mamunya’s model provided the best fit to experimental data [62, 64]. Surface energy that is incorporated into the model was a significant factor regarding electrical conductivity
[64, 54] however in the studies of Clingerman et al; the high surface energy of nickel caused a breakdown in the model [62]. The surface energy of nickel is 2.34 J/m$^2$ [65].

Structure orientated models including the Lewis-Nielsen model do not take into account or predict surface energy interactions between the filler and matrix which has been considered a major limitation with this classification of models [64]. Also the model requires the conductivity of the filler which could not be obtained in this investigation.

From the three models shown, the Mamunya model was thought to offer the most accurate prediction of electrical conductivity with little input from experimental data as well as the fact that the electrical conductivity of the fillers could not be obtained. The Mamunya model however predicts the rapid increase in conductivity (i.e. the linear portion of the conductivity profile) to the levelled off portion of the conductivity profile near to the maximum filler conductivity as can be seen in figure 46. An example of the model in comparison to the experimental results can be seen in Appendix L.

Therefore, another model by Mamunya [66, 67] will be used that predicts the electrical conductivity from the percolation threshold up to the somewhat linear portion of the conductivity profile. The electrical conductivity is given by the equation:

$$
\sigma = \sigma_c + (\sigma_m - \sigma_c) \cdot \left( F - \phi_c \right)^t 
$$

Where:
- $\sigma$ - Electrical conductivity of the composite
- $\sigma_c$ - Electrical conductivity at the percolation threshold
- $\sigma_m$ - Electrical conductivity at the maximum packing factor
- $\phi$ - Filler volume fraction
- $F$ - Packing factor
- $V_f$ - Volume occupied by filler
- $V_p$ - Volume occupied by polymer
- $\phi_c$ - Percolation threshold
- $t$ - Critical exponent

(Equ 14.)
Although this equation does not take into account the surface energy interaction of the filler and matrix it can be used to model electrical conductivity behaviour based on the critical exponent, \( t \).

### 6.2.2 Thermal conductivity

As the thermal requirements for conductivity are similar for electrical conductivity, many equations from the previous section are still relevant.

**McLachlan’s Model**

This model is identical to McLachlan’s electrical conductivity model except electrical resistivity \( \rho \) is replaced with thermal resistivity. For disambiguation, thermal resistivity is denoted by \( P \).

\[
\frac{(1 - \phi)(P_m^{1/\ell} - P_h^{1/\ell})}{P_m^{1/\ell} + \left(\frac{1 - \phi_c}{\phi_c}\right)P_h^{1/\ell}} + \frac{\phi(P_m^{1/\ell} - P_f^{1/\ell})}{P_m^{1/\ell} + \left(\frac{1 - \phi_c}{\phi_c}\right)P_f^{1/\ell}} = 0
\]

(Equ 15.)

Where:

- \( \phi \) - Filler volume fraction
- \( P_m \) - Thermal resistivity of the composite
- \( P_h \) - Thermal resistivity of the filler
- \( t \) - Critical exponent
- \( \phi_c \) - Critical volume fraction
- \( P_f \) - Thermal resistivity of the polymer
Lewis-Nielsen Model

The Lewis-Nielsen model for electrical conductivity is directly applicable to thermal conductivity where electrical conductivity ($\sigma$) is replaced with thermal conductivity ($K$), thus giving:

$$K_m = K_i \left(1 + \frac{AB\phi}{1 - B\Psi\phi}\right)$$  \hspace{1cm} (Equ 16.)

$$B = \frac{K_h / K_i - 1}{K_h / K_i + A} \quad \Psi \approx 1 + \left(\frac{1 - F}{F^2}\right)\phi$$

Where:

- $K_m$ - Thermal conductivity of the composite
- $K_i$ - Thermal conductivity of the polymer
- $A$ - Function of aspect ratio and orientation
- $B$ - is equal to 1 for polymer systems
- $\phi$ - Filler volume fraction
- $K_h$ - Thermal conductivity of the filler
- $F$ - Packing fraction

Mamunya Model

The mamunya model below differs slightly from the electrical model and has been used to explain the steeper rise of thermal conductivity with increasing volume fraction $^{[68]}$.

$$\log \lambda = \log \lambda_p + (\log \lambda_f - \log \lambda_p) \left(\frac{\phi}{F}\right)^N$$  \hspace{1cm} (Equ 17.)

Where:

- $\lambda$ - Thermal conductivity
- $\lambda_p$ - Thermal conductivity of the polymer
- $\lambda_f$ - Thermal conductivity of the filler
- $\phi$ - Filler volume fraction
- $F$ - Packing Factor
- $N$ - Exponent
The model proposes that the ratio of filler to matrix thermal conductivity is not more than $10^3$ orders of magnitude whereas it can be $10^{10}-10^{20}$ orders of magnitude for electrical conductivity \cite{68}. The lack of thermal percolation threshold is due to the thermal conduction properties of the matrix where the polymer will have its own thermal conductivity regardless of filler content.

**Chosen Model**

For thermal conductivity the Mamunya model was chosen based on similar reasoning to the electrical models where McLachlan’s critical exponent (t) would be difficult to incorporate if unknown. As the Lewis-Nielsen model has been shown to incur a major limitation with the prediction of electrical conductivity with regards to surface energy, it was unstated as to whether similar inaccuracies would transfer to thermal conductivity. As stated before, the main reason for excluding this model was the use of filler conductivity in the calculations.

Mamunya stated that previous modelling work \cite{69-72}, showed an absence of percolation behaviour. Also work conducted to account for the additional thermal conductivity \cite{73, 74} did not take into account a realistic filler geometry connected to the packing factor. Therefore it was thought that the Mamunya model, as a result of previous investigations, would give better results and account for more of the filler parameters and processing through the use of the exponent N just like the exponent t for electrical conductivity.

**6.2.3 Mechanical strength**

Mechanical property models need to take into account size and shape of filler particles whether they are spherical, elliptical or fibre like. The matrix plays a big role in the overall calculation where the mechanical properties of the pure matrix material should be known as well as the ratio of the filler to matrix should be known. As mentioned previously in chapter 6, for this study the modelling of spherical particles is assumed and imperfect spherical particles are assumed to be perfectly spherical. Therefore the
models presented here are models for spherical particles and do not account for other particle shapes.

The models detailed here are elastic and flexural modulus models that are well known for predicting mechanical properties of composites. Many accurate tensile and flexural strength models that require the use of FEM are beyond the scope of this thesis and so elastic and flexural modulus will be used to gauge mechanical behaviour.

**Kerner’s Equation**

The Kerner equation is given by:

\[
\frac{E_c}{E_m} = 1 + \frac{15(1 - \nu_m) V_f}{8 - 10\nu_m V_m} 
\]

(Equ 18.)

Where:

- \(E_c\) - Elastic modulus of the composite
- \(E_m\) - Elastic modulus of the matrix
- \(\nu_m\) - Poisson’s ratio of the matrix
- \(V_f\) - Filler volume fraction
- \(V_m\) - Matrix volume fraction

This model is useful for composites containing randomly dispersed spherical or nearly spherical filler particles in a polymer matrix. It assumes that there is some adhesion between filler and matrix and that the filler is more rigid than the matrix \(^{75, 76}\).
Hirsch’s Model

Hirsch’s empirical model uses a combination of equal strain and equal stress conditions in the filler and matrix phases [77].

\[ E_c = x(E_fV_f + E_mV_m) + (1 - x)[(E_fE_m)/(E_fV_m + E_mV_f)] \]  

(Equ 19.)

Where:

- \( E_c \) - Elastic modulus of the composite
- \( x \) - Empirical factor
- \( E_f \) - Elastic modulus of the filler
- \( V_f \) - Volume fraction of the filler
- \( E_m \) - Elastic modulus of the matrix
- \( V_m \) - Volume fraction of the matrix

The empirical factor, \( x \), is obtained from experimental data and varies between 0 for isostress and 1 for isostrain.

Guth Model

The Guth model is shown below for spherical particles:

\[ E_c = E_m \left(1 + K_E V_f + 14.1V_f^2\right) \]  

(Equ 20.)

Where:

- \( E_c \) - Elastic modulus of the composite
- \( E_m \) - Elastic modulus of the matrix
- \( K_E \) - Einstein coefficient
- \( V_f \) - Filler volume fraction.
Modeling

The Einstein Coefficient is an important factor in the equation and can be calculated by the Poisson’s ratio of the matrix and the relative Einstein coefficient ratio. Where $K_E = 2.5$ for a material with a Poisson’s ratio of 0.5 \cite{63, 78, 79}.

**Chosen Model**

As mentioned previously, the rule of mixtures can provide accurate predictions when the differences between elastic moduli of the two phases are small but generally is used only as an estimate for elastic modulus rather than a numerical method for modelling \cite{60}. The Kerner equation assumes adhesion between the filler and matrix and so may not do well for fillers with compatibility problems in polymer matrices \cite{75}.

Hirsch’s model is an accurate predictor of modulus as proven by Shyang et al \cite{75} and Kalaprasad et al \cite{80} by comparison with numerous other models. However it is an empirical model and is reliant on experimental data such as the elastic modulus of the filler that would be difficult to obtain for powdered materials.

Guth’s model significantly over predicted the results along with the rule of mixtures as described in the work of Shyang et al \cite{75}. Shyang et al used spherical hydroxyapatite (HA) particles as reinforcement in a polymethyl methacrylate (PMMA) matrix. They found that Hirsch’s model came closest to the experimental results and the Kerner’s equation was slightly less accurate than Hirsch’s model.

The study of spherical HA particles in PMMA was thought to be closely related to the aims of this current study of conductive fillers in polyethylene for mechanical properties. With this in mind, Kerner’s equation was chosen to model the elastic and flexural moduli of the composites used in this study. Although Hirsch’s model would be more accurate, Kerner’s equation would be less reliant on experimental data for parameters used in the model.
6.3 Summary

To help understand the properties and behaviours of the composite results presented in chapter 5, electrical, thermal and mechanical models have been chosen from numerous models that have been developed. Three models from section 6.2 have been chosen from the literature; the Mamunya model for electrical conductivity...

\[ \sigma = \sigma_c + (\sigma_m - \sigma_c) \cdot \left( \frac{\phi - \phi_c}{F - \phi_c} \right)^t \]

where \( F = \frac{V_f}{V_f + V_p} \) (Equ 21.)

the Mamunya model for thermal conductivity...

\[ \log \lambda = \log \lambda_p + (\log \lambda_f - \log \lambda_p) \left( \frac{\phi}{F} \right)^N \]

and Kerner’s equation for elastic and flexural modulus.

\[ \frac{E_c}{E_m} = 1 + \{ [15(1 - \nu_m)V_f ]/(8 - 10\nu_m V_m) \} \]

(Equ 23.)

All three models have been chosen as accurate predictors of their respective properties. They assume one filler component, a monodispersed filler and particles that are spherical. Therefore the models do not contain parameters for multiple fillers, multiple fillers sizes or aspect ratios.
6.4 Modeling of Experimental Data.

This section presents further background behind the chosen models and the results of the modeling in comparison to the experimental data from chapter 5.

6.4.1 Electrical Conductivity Models

Derivation of the Mamunya electrical conductivity model

From percolation theory the equation below describes the dependence of electrical conductivity on the filler volume content in the region above the percolation threshold.

\[
\sigma = \sigma_o (\phi - \phi_c)^t
\]

(Equ 24.)

Where:
\(\sigma\) - Conductivity
\(\sigma_o\) - Constant
\(\phi\) - Filler volume fraction
\(\phi_c\) - Filler volume fraction at percolation threshold
\(t\) - Exponent for the conductivity increase

Above the filler volume fraction at the percolation threshold \((\phi_c)\), the constant \((\sigma_o)\) and exponent \((t)\) is used to describe the conductivity \((\sigma)\) dependence on the filler volume fraction \((\phi)\). However when applied, equation 24 does not produce agreement with experimental data as it does not take into account geometric parameters of the filler \(^{[68]}\).

Mamunya \(^{[67]}\) introduced the maximum possible conductivity parameter \(\sigma_m\) and the packing factor parameter \(F\) to equation 24 in the form of normalised filler concentration \((\Phi)\) and normalised mixture conductivity \((\Sigma)\) as shown below.

\[
\Phi = \left(\frac{\phi - \phi_c}{F - \phi_c}\right) \quad \Sigma = \left(\frac{\sigma - \sigma_c}{\sigma_m - \sigma_c}\right)
\]

(Equ 25.)
Packing factor $F$ is given by $F = \frac{V_f}{V_f + V_p}$ and is the maximum filler volume fraction.

The new conductivity equation takes the form of:

$$\Sigma = \phi^t \quad \text{or} \quad \frac{(\sigma - \sigma_c)}{(\sigma_m - \sigma_c)} = \left[ \frac{\phi - \phi_c}{F - \phi_c} \right]^t \quad \text{(Equ 26.)}$$

Rearranged to make $\sigma$ the subject:

$$\sigma = \sigma_c + (\sigma_m - \sigma_c) \cdot \left( \frac{\phi - \phi_c}{F - \phi_c} \right)^t$$ \quad \text{(Equ 27.)}

Therefore the inputs into the Mamunya electrical conductivity model were the volume fraction at the percolation threshold ($\phi_c$), conductivity at the percolation threshold ($\sigma_c$), maximum conductivity ($\sigma_m$) and packing factor ($F$). The packing factor as calculated above is the maximum filler volume fraction at a given type of packing, considering particle shape/geometry, where ideally for statistically packed spherical particles $F = 0.64 \ [81]$. The dry powder compaction that has been used by Mamunya et al [82] and Clingerman et al [64] to acquire $F$ was considered unrepresentative of the maximum volume fraction obtainable through processing (i.e. with matrix present). The void space among the dry powder particles had been equated to the volume fraction of polymer ($V_p$) as used in equation 27 but is unlikely to occur during processing with various processing techniques and conditions.

Therefore, as the maximum volume fraction was gained during processing, in other words the point at which no more filler could be added, the packing factor for the following models was equal to the maximum volume fraction attained in the data set. Consequently the maximum conductivity was then the conductivity at the maximum volume fraction of the data set, i.e. the maximum conductivity obtained in the same data set. The critical exponent $t$ was the variable in which the model was fit to the experimental data and is described further in the next sections.
Carbon Black

Due to the overlap and close proximity of in plane and through plane conductivity data displayed in figure 23 in chapter 5 for the injection moulded carbon composites, a new plot of the average of the in plane and through plane data was used for the model. The new plot is shown below in figure 47.

![Electrical Model For Injection Moulded PE-Carbon Composite](image)

Figure 47 - Averaged in plane and through plane conductivity plot for the electrical conductivity of the injection moulded carbon composites. The model fitting is shown with a solid line.

As there were only three experimental data points for the modeling where the minimum and maximum conductivities and volume fractions are used in the model equation, the only point used to fit the model to the experimental data was the remaining data point at 56 wt%. To create the plot, weight percentage was converted to volume percentage and the calculated conductivities were plotted against weight percentage. The same was done for all plots in section 6.4 except for the thermal conductivity plots. By rearranging the Mamunya model (shown in equ 28.) to gain a value for the critical exponent (t) at 56 wt%, t was found to be 2.31.
\[
\tau = \ln \left( \frac{\sigma - \sigma_c}{\sigma_m - \sigma_c} \right) \div \ln \left( \frac{\phi - \phi_c}{\phi_m - \phi_c} \right) \tag{Equ 28.}
\]

According to percolation theory the value of \( \tau \) is in the range of 1.6-1.9 \(^{[56]}\). In the work of Mamunya et al it was stated that the percolation theory with \( \tau \) values of 2.4 to 3.2 still hold true for systems with dispersed random filler distributions. The accepted universal value for \( \tau \) (\( \tau_{un} \)) is 1.7 \(^{[83]}\), any increase in \( \tau \) is denoted by \( \tau = \tau_{un} + \tau_{add} \) where \( \tau \) additional (\( \tau_{add} \)) would infer the conductivity contribution of different mechanisms. Mechanisms such as tunnelling conductivity and complex conductive cluster structures with the presence of nodes and blobs \(^{[68]}\).

Sub models, that are beyond the scope of this thesis to describe fully, have been used to calculate \( \tau \) based on filler contact patterns such as Balberg’s model for tunnelling conductivity \(^{[84]}\) and the Links-nodes-blobs (LNB) model \(^{[85]}\). Balberg gave a \( \tau \) value of 2.8 for Cabot-black compared to a Ketjen-black \( \tau \) value of 2.0 where the tunnelling conductance \( g \) was determined by the complexity of the structure of the carbon aggregates. Defined as high and low structures, the higher \( \tau \) value would denote higher complexity in the aggregate structure and lower \( \tau \) value for lower structure complexity as shown below in figure 48.

![Figure 48 - Balberg’s Structures \(^{[84]}\) - (a) No structure, (b) low structure, (c) high structure.](image)

The LNB model that is applicable to \( \tau \) values greater than 2 describes conductivity through link, node and blob structures. Links are lengths of single bonds which if cut
will interrupt the current flow, nodes are sites that are connected to the boundaries by at least three independent paths and blobs are multiple connected paths on a backbone where each path carries a fraction of the backbone current. These structures are shown below in figure 49.

Figure 49 - Links Nodes and Blob structures\textsuperscript{[85]} - (a) Nodes, (b) Links, (c) Blobs. $\xi$ is a unit length.

As with Balberg’s model, the higher the $t$ value the more complex the structure. Unknown proportions of the contributions from tunnelling and LNB, is the most likely outcome of the conductivity mechanism for the carbon model.

**Errors**

The possible maximum and minimum $t$ values for the electrical conductivity were investigated by adjusting the model to fit data within the scatter bar ranges that would produce a shallow curve (minimum $t$) and a steep curve (maximum $t$). The maximum conductivities for 40 and 56 wt% were used with the minimum conductivity at 65 wt% to produce a minimum $t$ value. The maximum conductivities for 40 and 65 wt% and minimum conductivity for 56 wt% was used to produce a maximum $t$ value. The $t$ value range was found to be:

Minimum $t$: 0.93

Maximum $t$: 8.24
Graphite

The electrical conductivity data for the injection moulded graphite model was kept as presented in chapter 5; however the data for the compression moulded graphite model was altered in the same way for the carbon data (i.e. the in plane and through plane was averaged) presented in figure 47. The plot for the injection moulded graphite model can be seen in figure 50 and the plot for the compression moulded graphite model can be seen in figure 51.

Figure 50 - In plane electrical conductivity plot for graphite model. The model is represented by the solid line and fit to the experimental data points.

In the same way as was done for the carbon data, the graphite model fitting was done with equation 28 to gain a value of $t$. The values of $t$ gained for the injection and compression moulded models were 2.98 and 5.69 respectively.
Figure 51 - Averaged data plot combining in plane and through plane electrical conductivities for compression moulded graphite composites.

The t value for the injection moulded model is still within Mamunya’s statement of the percolation theory holding true for such a high critical exponent and the conduction mechanisms can still be explained by the tunnelling and LNB models as was described for the carbon composites. However the t value for the compression moulded data was very high but comparable to the work of Celzard et al [86] where high values of 7 (in plane) and 10 (through plane) for the critical exponents of their anisotropic graphite composite have been observed. Celzard et al concluded that the particles were more or less covered by a thin layer of polymer hindering direct particle contact and therefore conduction would occur via tunnelling. They reasoned that the conductivity in the highly loaded samples were several orders of magnitude less than the basal plane conductivity of the graphite powder so the high interparticle resistances must have been due to the thin polymer layers.

The same could be said for the compression moulded graphite data where the sharp increase in conductivity at 57 wt% could have resulted from thinner polymer layers due to the combination of increased processing pressure and increased in filler content.
Errors

As with the carbon data, the maximum and minimum t values were investigated. The minimum t values were gained by using the minimum conductivities at 39 and 67 wt% and the maximum conductivities at 50 wt%. The maximum and minimum t values for the injection and compression composite models are as follows:

<table>
<thead>
<tr>
<th>Injection moulding</th>
<th>Compression moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum t: 2.30</td>
<td>Minimum t: 2.86</td>
</tr>
<tr>
<td>Maximum t: 4.21</td>
<td>Maximum t: 7.91</td>
</tr>
</tbody>
</table>

6.4.2 Thermal Conductivity Models

**Derivation of Mamunya thermal conductivity model** [68]

A function proposed by Lichtenecker below,

\[
\lambda = \lambda_p^{(1-\phi)} \cdot \lambda_f^\phi
\]  

(Equ 29.)

Where:

\(\lambda\) - Thermal conductivity
\(\lambda_p\) - Thermal conductivity of the polymer
\(\lambda_f\) - Thermal conductivity of the filler
\(\phi\) - Volume fraction

that satisfies both the thermal conductivity and resistance:

\[
\lambda = f(\lambda_p, \lambda_f, \phi) \quad 1/\lambda = f(1/\lambda_p, 1/\lambda_f, \phi)
\]  

(Equ 30.)

was used as a base equation for the Mamunya model [68, 87]. Taking the logarithm and rearranging equation 29, the equation becomes:
\[
\log \lambda = \log \lambda_p + (\log \lambda_f - \log \lambda_p) \phi
\]

(Equ 31.)

In order to explain the steeper rise in thermal conductivity (\(\lambda\)) with increasing filler volume fraction (\(\phi\)) the packing factor \(F\) was added to take into account the realistic filler geometry. The equation becomes,

\[
\log \lambda = \log \lambda_p + (\log \lambda_f - \log \lambda_p)(\phi/F)^N
\]

(Equ 32.)

Where:

- \(\lambda\) - Thermal conductivity
- \(\lambda_p\) - Thermal conductivity of the polymer
- \(\lambda_f\) - Thermal conductivity of the filler
- \(\phi\) - Volume fraction
- \(F\) - Packing factor
- \(N\) - Exponent

The absence of a percolation threshold is due to the comparable thermal conductivities of the filler and matrix where their ratio is of \(10^3\) in magnitude compared to a \(10^{10}-10^{20}\) order of magnitude for electrical conductivity \([68]\). A percolation threshold only appears at conductivity ratios above \(10^5\) and have applied only to systems with conductive sites within a non-conductive medium.

If \(F=1\) and \(N=1\) where a continuous second phase is present in the matrix then equation 32 reduces back to the Lichtenecker equation. For dispersed fillers the packing factor still changes from 0 to 1 however in this study \(F\) is always less than 1.

In keeping with the data analysis conducted by Mamunya et al \([66, 68]\), the thermal conductivity (\(\lambda\)) models were plotted together with the experimental data on a \(\log \lambda\) vs filler volume fraction graph. This was done so that thermal conductivity behaviour according to the exponent \(N\) in the thermal conductivity model, could be analysed where deviations from \(N=1\) (for linear relationships) results in a change in local filler concentration in the shell structure shown in figure 52.
Figure 52 - Representation of a shell structure [68] where $L$ is the polymer phase diameter and $n_d$ is the number of particles ($n$) multiplied by the particle diameter ($d$).

For deviations from $N=1$, the model fitting to the thermal conductivity data was done using a least squares fit to gain optimum values for $N$. The least squares fit was done using the formula below:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}}$$  \hspace{1cm} \text{(Equ 33.)}$$

$$SS_{res} = \sum (x_i - f_i)^2 \quad SS_{tot} = \sum (x_i - \bar{x})^2$$

Where:

$SS_{res}$ - Sum of squares of the residuals
$SS_{tot}$ - Total sum of squares
$x$ - Experimental data
$\bar{x}$ - Mean of the experimental data
$f$ - Modeled data
Figure 53 above shows the modelling results of the injection and compression moulded composites. The compression moulded model showed good fit to the experimental data points with $N=0.93$ for the linear relationship ($R^2$ value of 0.959). When $N$ deviates (positively) from 1 as can be seen in the injection moulded model plot where $N=1.96$ with ($R^2$ value of 0.980), the structure has displayed a more dense packing of the filler resulting in an increased local filler concentration $^{[68]}$ thus higher conductivity. It can be inferred that a negative deviation from $N=1$ suggests that less packing of the filler has resulted in a lower local filler concentration. Although the magnitude of the thermal conductivity for injection moulding remains lower than the compression mouldings due to lower processing pressure.
Errors

The maximum and minimum N values were investigated in a similar way as the exponents for the electrical conductivity. The minimum N values were obtained by using the minimum thermal conductivities at 0 and 0.5 volume fraction and fitting the model using a least squares fit to the maximum thermal conductivities of the remaining volume fractions. The opposite was done to obtain the maximum N values. The maximum and minimum N values obtained were:

Injection moulding          Compression moulding
Minimum t: 2.55             Minimum t: 2.25
Maximum t: 1.62             Maximum t: 0.58

Graphite

Figure 54 - Results of the thermal conductivity models (solid lines) for injection and compression moulded graphite composites fitted to the experimental data.
The modeling results of the injection and compression moulded graphite shown in figure 54 display a linear relationship for the injection moulded data where again \( N=1 \) with an \( R^2 \) value of 0.976 and a nonlinear relationship for the compression moulded data where \( N=0.66 \) with an \( R^2 \) value of 0.990. As has been stated previously for the carbon composite model for injection moulding, a negative deviation from \( N=1 \) suggests that less packing of the filler has resulted in a lower local filler concentration. However with lower local concentrations reducing thermal performance within the same data set, the increased processing pressure for compression moulding has generated higher thermal conductivities overall when compared to injection moulding.

**Errors**

The \( N \) value ranges for the injection and compression moulded models were found in the same way as it was done for the carbon models. The minimum and maximum \( N \) values were:

<table>
<thead>
<tr>
<th></th>
<th>Injection moulding</th>
<th>Compression moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum t:</td>
<td>1.17</td>
<td>0.74</td>
</tr>
<tr>
<td>Maximum t:</td>
<td>0.89</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Magnetite**

The model fitting to the magnetite composite data shown in figure 55 for injection and compression moulding gave negative deviations from \( N=1 \) where for injection moulding \( N=0.52 \) (with \( R^2 = 0.934 \)) and for compression moulding \( N=0.64 \) (with \( R^2 = 0.938 \)). Both plots generating a hyperbolic curve where rate of increase in thermal conductivity decreases with increasing magnetite content and represented reduced local filler concentrations.
Figure 55 - Injection and compression moulded thermal conductivity models, shown in solid lines, for the polyethylene magnetite composites.

**Errors**

As before the minimum and maximum N values were investigated in the same way. The minimum and maximum N values obtained were:

<table>
<thead>
<tr>
<th>Injection moulding</th>
<th>Compression moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum t: 0.72</td>
<td>Minimum t: 0.80</td>
</tr>
<tr>
<td>Maximum t: 0.42</td>
<td>Maximum t: 0.53</td>
</tr>
</tbody>
</table>
6.4.3 Mechanical Models

Kerner’s equation \[76\] can be used for any modulus \[88\] where the parameter \(E_m\) (modulus of the matrix) represents the required modulus of the user. The Kerner’s equation for elastic and flexural modulus were plotted using inputs for the elastic and flexural modulus of the pure polyethylene denoted by \(E_m\) in the equation below.

\[
E_c = E_m \cdot 1 + \frac{[15(1 - \nu_m)V_f]}{(8 - 10\nu_mV_m)}
\]  
(Equ 34.)

Where:

- \(E_c\) - Elastic/flexural modulus of the composite
- \(E_m\) - Elastic/flexural modulus of the matrix
- \(\nu_m\) - Poisson’s ratio of the matrix
- \(V_f\) - Filler volume fraction
- \(V_m\) - Matrix volume fraction

However, the equation does not take into account different fillers within the same type of matrix where variations in magnitude of the modulus would occur with different types of filler. Variations in the results with different fillers would originate from filler properties such as size, shape and surface energy (compatibility with the matrix). Plots using the Kerner’s equation gave shallow increases in modulus with increasing filler content and did not fit the data due to the large step increase in moduli with the addition of fillers.

The modelling results presented in the next section use an adapted form of the Kerner’s equation where the initial volume fraction of the filler (\(V_f\)) is no longer zero and the data points for the polymer elastic and flexural moduli are ignored. The initial volume fraction of each plot is equal to the first set of experimental data gained, i.e. the lowest filler content in the data set and the elastic and flexural modulus (\(E_m\)) of the matrix is the modulus value at the lowest filler content. If the lowest filler volume fraction in the data set is \(V_f'\) and the new (matrix) elastic/flexural modulus is \(E_{m'}\) then the following equation is procured.
\[ E_c = E_m' [1 + \{15(1 - \nu_m)V_f - V_f'\}/(8 - 10\nu_m(1 - V_f - V_f'))]\]  

(Equ 35.)

Where:  
\( E_c \) - Elastic/flexural modulus of the composite  
\( E_m' \) - Elastic/flexural modulus of the matrix  
\( \nu_m \) - Poisson’s ratio of the matrix  
\( V_f \) - Filler volume fraction  
\( 1-V_f \) - Matrix volume fraction (\( V_m \))  
\( V_f' \) - Lowest filler volume fraction

The adapted equation sets the origin of the plot at the lowest filler volume fraction and any increases in filler volume fraction are relative to the new origin. Therefore if \( V_f' = 0.1 \) and the next data point is at \( V_f = 0.25 \) then the increase in volume fraction computed by the equation is 0.15. However data is still plotted with modulus (\( E_c \)) vs. the original volume fraction (\( V_f \)) that has been converted to weight percentage. Data for pure polyethylene is also plotted for comparison but is not part of the model fitting.

**Carbon Black**

![Elastic Modulus Model for Injection and Compression Moulded Carbon Composites](image)

Figure 56 - Elastic modulus models for the injection and compression moulded carbon composites
In figure 56, the model for the injection moulded carbon composite data showed good agreement until 56 wt% and 65 wt% where the model over predicted the elastic modulus. Due to this the $R^2$ value was low at 0.696. The model for the compression moulded data over predicted and did not give an $R^2$ value, therefore the model did not entirely fit the data but was still within the scatter bars showing reasonable prediction.

According to Speake et al. [89], the experimental data points should lie lower than the model if there was poor stress transfer from matrix to filler as Kerners equation assumes continuous stress transfer across the filler-matrix boundary. This can explain the results shown in figure 56, where the poor stress transfer could have been due to the interstitial carbon particles within the polymer network as can be seen in figure 39. It can be seen that there is less carbon to polyethylene contact at higher weight percentages than the model accounts for where the most brittle composite data points, 57 wt% and 65 wt% for injection mouldings and 26 wt% and 32 wt% for compression mouldings, lay lower than the model.

![Flexural Modulus Model for Injection and Compression Moulded Carbon Composites](image)

Figure 57 - Flexural modulus models for injection and compression moulded carbon composites.
The flexural modulus models displayed in figure 57 for the injection and compression moulded carbon composites showed poor agreement with the experimental data with $R^2$ values no higher than 0.53. In both, injection more than compression, the models under predicted with shallower gradients than the experimental data. For the compression moulded samples it is unclear as to whether the data would have deviated further from the model due to the limited number of data points. However the injection moulded samples displayed a large deviation from the model with no data points after 26 wt% lying close to the model.

**Graphite**

![Elastic Modulus Model for Injection and Compression Moulded Graphite Composites](image)

Figure 58 - Elastic modulus models for injection and compression moulded graphite composites.

Figure 58 above shows the elastic modulus modeling results for the injection and compression moulded graphite composites. The injection moulded model fitted the experimental data very well giving an $R^2$ value of 0.976 however the compression moulded model over predicted in the same way as the carbon compression moulded model and did not fit the data very well (no $R^2$ value gained).
Generally the data points lay slightly lower than the model, as with the carbon composites, this was an indication of lesser stress transfer across the filler-matrix boundary than the model predicted. However, the model lay within the scatter bars of the experimental datasets except at 39 wt% for compression moulded samples. The microstructure (shown in figure 42d) at such a weight percentage could have been the point at which the reduction in polymer, ie reduction in filler-matrix interfaces starts to have a negative effect on the modulus and deviate from the model.

Figure 59 - Flexural modulus models for injection and compression moulded graphite composites.

Similar to the elastic modulus model, the flexural modulus model shown in figure 59 showed good agreement with the experimental data for in injection moulding with an \( R^2 \) value of 0.965. However the compression moulded model under predicted and gave a low correlation (\( R^2 = 0.480 \)) with the data. As with the flexural results for the carbon composites where deviations were observed, the model may not account for differences in test speed and processing. Slow test speeds could transfer greater loads to the specimen before fracture resulting in greater modulus than the model and variations within and between injection and compression mouldings may generate similar increases in modulus compared to the model.
Magnetite

Figure 60 - Elastic modulus models for injection and compression moulded magnetite composites.

The elastic modulus modeling results in figure 60 shows good correlation for both injection and compression moulded magnetite composites with $R^2$ values of 0.960 and 0.745 respectively. The experimental data points for the injection moulded samples followed the model with very little deviation, the compression moulded samples had two points at 40 wt% and 60 wt% that deviated from the model with scatter bars outside of the trend.

Due to the low volume fraction resulting from the high density of the filler, it can be said that in the range of 9 wt% to 71 wt% the filler does not have a great influence on the composite elastic modulus especially when compared to carbon and graphite. The comparable magnitude of the moduli and the pure polyethylene samples together with the shallow increase in modulus would support such a statement. As can be seen from the magnetite micrographs (figures 43 and 44) there was very little adhesion between the filler and matrix that would have added to the reduced influence of the filler on the composite elastic modulus.
The little influence that the magnetite does have on the composites with increasing filler content may come from the un-bonded particles preventing the collapse of the matrix rather than acting as holes providing some increase in modulus \cite{75}.
Chapter 7.0

Discussion

The microstructures of the composites together with the processing techniques play an important role in the properties of the samples. The resulting electrical, thermal and mechanical properties observed could all be related to the microstructure and the processing techniques.

The magnetite and graphite microstructures for both injection and compression moulded grades showed little difference between them with regards to filler dispersion with increasing filler content where there were visible increases in filler content with increasing loading. Although it is less clearly seen for the graphite as it is for the magnetite microstructures, the random distribution of filler particles was fairly evenly spread. Therefore the two roll mill mixing technique was fairly homogenous resulting in the even spread where no clustering of particles were seen throughout the micrographs.

All fillers were mixed to maximum loading until no more could be physically mixed without resulting in crumbling forms of the composites. This meant that all tests conducted on the composites were done to the maximum filler loading and higher filler loadings could not be obtained without the intervention of other materials such as compatibilisers.

Overall the carbon composites performed better in electrical conductivity than their graphite and magnetite counterparts with 26.58 S/cm for in plane conductivity for injection moulded samples. Although, the compression moulded data for carbon was limited, the mismatch in percolation threshold for the in plane and through plane conductivities indicated a variable structure with low conductivities at low weight
percent as a result of the compression moulding. The graphite conductivities were two orders of magnitude less than the carbon grades and the magnetite composites exhibited the worst conductivities in the microsiemen range.

The lack of readings for the injection moulded graphite through plane conductivity would suggest some orientation of the filler during injection moulding in favour of the in plane conductive direction. However the sudden electrical conduction at the highest graphite loading outperformed the in plane conductivity and would suggest no preferential orientation, also the FEGSEM micrographs showed no obvious alignment in such a direction. It is highly likely that the data was the result of a poor filler with anisotropic conductivity.

The magnetite composites for both injection and compression moulding showed poor conductivity across the whole range. This showed that the magnetite performed the worst out of the three fillers having conductivities in the milli and micro siemen range where not all samples within the same dataset conducted. This data was considered not good enough for a graphical plot and was not accurately comparable with the other fillers due to the lack of full sets of data. As the density of the magnetite was very high (5.02 g/cm³) thus the volume percent of the magnetite in the matrix was low when converted from weight percent. Therefore there was far less magnetite filler present in the matrix than the carbon and graphite composites even at a maximum content of 71 wt%.

The spread of five results for all data points ensured accuracy in the experimentation however the lack of conductivity for most of the composite grades, i.e. below the percolation threshold produced plots of three sets of data. The three sets of data were not considered enough for plotting accurate trend lines and so were plotted with line graphs.

Inaccuracies associated with the electrical conductivity measurements were contact probe force and time taken for stable measurements. These errors were considered negligible as the jaw width of the clamping apparatus was kept constant by the 20mm spacers resulting in a constant probe pressure provided by the spring probes. Sufficient time was given before taking readings to allow for the measurements to stabilise.
Although the change in resistance measurement approaching the stable point was an exponential decrease, any change in readings around the pseudo-stable point were to the 3rd decimal place i.e. one thousandth of the resistance range was considered negligible.

It is possible that the observed percolation thresholds could have been lower due to the approximately 10wt% step increases that would have reduced the resolution (number of electrically conductive data points). As the initial graphite loadings displayed near zero conductivities the inaccuracy in percolation threshold was not big, however the initial carbon loadings exhibited a maximum of 7.17 S/cm where the real percolation threshold would have laid between 32 wt% and 40 wt%.

Throughout, there was no agreement between the ideal filler content at maximum electrical conductivity and the ideal filler content at maximum mechanical strength due to increased brittleness at high filler loadings. Nor was there much agreement between the ideal filler content at maximum flexural and tensile strengths where peak tensile strengths occurred at lower filler content compared to peak flexural strengths. This could be attributed to the difference in failure mechanism between the tensile and flexural tests. There was agreement on the ideal filler content for electrical and thermal conductivities where the filler content at maximum electrical conductivity was equal to the filler content of the maximum thermal conductivity due to greater conduction paths being set up with increasing filler content.

Overall the compression moulded samples produced higher thermal conductivities than the injection moulded samples and would have been due to the increase in processing pressure bringing particles closer into contact with each other. The best thermally conductive filler was the compression moulded graphite grade followed closely by the carbon grades and then the magnetite grades. The better performance of the graphite over the carbon in the thermal conductivity tests when compared to the electrical conductivity tests could be attributable to phonon contribution. It is possible that the increased number of particle to particle interfaces in the carbon composites due to many nano particles had disrupted the lattice vibrations throughout the conductive path. Therefore the larger graphite particles spanning many thousands of nanometers would have offered better thermal conduction paths with regards to lattice vibration.
Unlike the graphite and magnetite composites, the delayed increase in thermal conductivity with the addition of filler of the injection moulded carbon composites demonstrated that the thermal conductivity was dominated by the polymer phase. Only at 26wt% did the filler begin to contribute to the thermal conduction paths within the material.

As stated previously in chapter 5, the thermal conductivity measurements were sensitive to the thermocouple readings where accuracy to one hundredth of a degree centigrade was employed to reduce the error. Surface roughness as well as the thermal paste used to minimise the surface roughness could have added to the errors but were minimised by polished surfaces and minimal paste thicknesses as well as high thermal conductivity paste (8.7W/mK). The errors themselves would not have been eliminated but reduced considerably and although unquantifiable the same errors would have been present in all measurements and so relative measurements would not have been affected.

The point of maximum mechanical strength with regards to weight percentage varied from filler to filler with graphite performing the best and magnetite performing the worst. This can be explained by adhesion and wetting between the filler and polymer phase where better adhesion and wetting would have hindered crack propagation due to the dissipation of fracture energy on delamination. This can be seen in the FEGSEM micrographs where there was no visible sign of incompatibility in the graphite composite structures as was seen with the magnetite composite structures. The magnetite composite structures would have allowed fast crack propagation via the air gaps, mentioned in chapter 5, where the magnetite had not been wetted by the polyethylene.

From the FEGSEM micrographs it is difficult to see the degree of wetting or adhesion between the carbon particles and polymer phase due to the nanoscale microstructure where the carbon particles act as an interstitial phase between the polymer network. The carbon particles/agglomerates appear to be wetted less than the graphite particles and therefore the mechanical properties peak at low loadings (26-40 wt%). However the nature of the microstructure would have provided better rigidity due to the (interstitial) smaller particle diameters creating a more integrated network of filler and polymer where crack propagation would most likely occur through the filler phase and
Discussion

not the polymer phase. This is why the maximum mechanical strengths of the carbon composites at low loadings are comparable to the maximum mechanical strengths of the graphite composites at high loadings.

Overall the graphite composites exhibited the highest tensile and flexural strengths for both injection and compression moulding techniques compared to the carbon and magnetite. The lowest performer being the compression moulded carbon for tensile and flexural tests due to unmouldable material above 32 wt% where the material fractured on de-moulding. The increasing elastic and flexural moduli across the whole range of the samples shows that the filler becomes beneficial by adding to the rigidity of the composite structures but only to a certain point. The point at which the composites begin to fail at reduced stress implies that the further reduction in the polymer phase results in the reduction in the composites ability to resist deformation and fracture. The increase in filler phase beyond this point shows that the microstructure provided more opportunity for crack initiation and fracture propagation.

There was a general trend of injection moulded grades exhibiting greater mechanical strength than the compression moulded grades that can be explained by agglomeration. During mixing on the two roll mill, it is likely that any filler agglomerates would not have been broken up by the low shear forces inherent to the technique. During injection moulding, the mixing via the screw and therefore shot filling occurring before injection would have been able to break up the agglomerates where compression moulding would not as there is no mixing involved. The agglomerates would have allowed faster crack propagation via the shorter route around the agglomerate at the agglomerate-polymer interface where little crack energy would have been dissipated. Smaller particles (i.e. non agglomerates) would increase the route taken by the crack and hinder propagation by introducing more filler-polymer interfaces therefore increasing crack energy dissipation through increased delamination.

The trend does not extend to magnetite composites where the mechanical properties, in tensile only as there was no data for flexural properties, between the injection and compression mouldings were almost identical. When viewed under the FEGSEM, it can be seen that no agglomeration is visible and so the material would have behaved in
a similar manner with the two processing techniques regardless of injection moulder premixing.

The lack of mechanical test data due to sample slippage for tensile testing could not be rectified but did not impact on the datasets obtained as trends in the data could already be observed. The errors arising from averaged sample thickness values used in the tensile and flexural equations were considered small as thicknesses along the same sample varied by five hundredths of a millimetre.

On the whole compression moulding was better than injection moulding with regards to electrical and thermal properties but not with respect to mechanical properties. This was mainly due to the processing pressures employed, 10 bar for injection moulding and 22 bar for compression moulding. The increase in pressure may have created greater material compression during processing forming a more densely packed microstructure creating more electrical and thermal conduction paths.

The injection mouldings were expected to reveal an orientated microstructure with anisotropic properties where the filler particles were not spherical, however this was not seen in the FEGSEM micrographs and the materials’ properties did not reflect this. Therefore it was assumed that injection and compression moulding presented no differences between each other, other than their processing parameters and moulding/de-moulding technique. Therefore composites with isotropic properties as well as spherical particles were assumed for the modeling.

The models chosen for this study have been applied to similar research where spherical particles have been assumed as a filler in an elastic matrix \cite{62, 64, 68}. The Mamunya model for electrical and thermal conductivities were semi-empirical models where the exponents $t$ and $N$ for electrical and thermal conductivities respectively were used to find the best fit.

Due to the nature of the electrical conductivity model together with three experimental data points per plot, the maximum and minimum conductivities were fixed and the model was tuned to fit the remaining data point providing an exact fit with the experimental data. The $t$ values gained, 2.31 and 2.98 for injection moulded carbon and
graphite respectively, that were greater than the universal value of 1.7 explained that there was a presence of tunnelling conductivity and links, nodes and blobs. These alternative conduction mechanisms due to increased filler structure complexity have contributed to the sharp increases in electrical conductivity observed. However the degree of filler structure complexity and tunnelling conductivity cannot be determined by the Balberg and LNB theories [84, 85]. Similarly the compression moulded graphite composites exhibited a t value approaching 7 which was observed by Celzard et al [86] for their anisotropic graphite filler however the level of anisotropy cannot be determined.

Although the magnitude of the various conduction mechanisms cannot be determined, the t values are useful in gauging relative conductivity behaviour between fillers. However they do not provide information on levels of conductivity (maximum and percolation threshold) that would have to be gained experimentally. The differences between the possible minimum and maximum t values in the extreme cases were very high for the carbon electrical conductivity and somewhat high for the graphite conductivity. This was a result of the large scatter ranges present in the datasets however it demonstrates the possible errors transferred to the models from the experimental data.

The tuning of the thermal conductivity model was done by a least squares regression fit for seven to eight data points per plot where the data did not present a linear trend. A linear trend would indicate good agreement with the thermal conductivity model assumptions and deviations for linearity indicated changes in local filler concentration in relation to the shell structure model which could be related to this study. The injection moulded carbon which had an N value of 1.96 (positive deviation) indicated an increase in local filler concentration generating higher conductivity. The compression moulded carbon, graphite and magnetite and the injection moulded magnetite all displayed a negative deviation (N<1) indicating low local filler concentrations. As with the electrical conductivity model, conductivity behaviour can be explained from the theory but the model is heavily reliant on empirical data.

The possible maximum and minimum N values for each of the composite types were fairly close to the average N values gained representing narrow scatter in the
experimental datasets that would have been transferred to the models. All maximum and minimum N values would not have impacted on the definition of the possible microstructures inferred from the average N exponents.

The t and N exponents found by tuning for electrical and thermal conductivity models were on the whole greater than those by Mamunya and Clingerman where the ambient processing pressures of Mamunya \(^{[67, 68]}\) as well as the unspecified holding pressure of Clingerman \(^{[64]}\) could have produced low exponents. Therefore the increase in processing pressure could be one contributor to greater t and N values due to increases in filler structure complexity with increasing pressure.

The original Kerner’s equation for modulus predictions did not fit the experimental data and did not account for various fillers within the matrix as it did not take into account the mechanical properties of the filler unlike other models. Although mechanical properties of the fillers used in this study could not be obtained, a modified Kerner’s equation was used to gain predictions based on initial experimental results at the lowest filler loading and also accounted for different processing techniques.

Although the modified Kerner’s equation predicted elastic and flexural modulus better than the original equation, positive and negative deviations from the model were observed. According to Speake et al \(^{[89]}\), stress transfer across filler matrix interfaces could explain the observations where over predictions of the model would indicate poor stress transfer and under predictions would indicate increased stress transfer than the model would assume.

As a production technique, injection moulding was a better process due to its fast cycle times and simple processing parameters as shown by the differences in tables 4 and 5 on pages 40 and 43. Largely the injection moulded samples exhibited better material stability than the compression moulded samples shown by low scatter bar ranges. Where samples fractured on mould release from compression moulding, i.e. above 32wt% for carbon composites, it is unknown as to whether injection moulding would have presented a similar problem if it too had employed a holding pressure of 22 bar.
Due to the unobtainable data above 32 wt% for compression moulded carbon, the injection moulded carbon data offered the best performance as can be seen in table 7 on page 146. Table 7 compares the DOE targets, literature values and commercially available products from table 3 with the best results gained from the carbon, graphite and magnetite composites. All three composites in table 7 are the maximum filled grades showing maximum electrical and thermal conductivities. The flexural and tensile properties are given at the maximum filled grades but were not the maximum values for those composite grades; the maximum mechanical strengths are shown in parentheses.

The carbon and magnetite data displayed in the table are the best results from both injection and compression moulded data; however the mechanical data for the compression moulded graphite at 57 wt% was not the best overall mechanical performance when compared to the injection moulded data. The injection moulded graphite at 57 wt% gave a flexural and tensile strength of 37.66 MPa and 27 MPa respectively, however the electrical and thermal properties of this grade were less than those presented in table 7.

The magnetite flexural strength is not given as no data was collected for the magnetite grades due to unfractured samples, the tensile strength of the magnetite was also not given as the 71 wt% samples were not gripped by the tensometer and therefore were not tested.
<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Conductivity (S/cm)</th>
<th>Flexural Strength (MPa)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Corrosion Current / Rate</th>
<th>Tensile Strength (MPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>586 μA/cm² (Air) [31]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt; 100 μm per year [22]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS316L - YZU001 Coating [32]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1 μm per year</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SS316L - CNT/PTFE Coating [27]</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SS316L - TiNxOy Coating [30]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7 μA/cm²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium - YZU001 Coating [22]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.247 μm per year</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>POE-PhA / Graphite / C-Fibre [36]</td>
<td>16.6</td>
<td>17.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.68</td>
</tr>
<tr>
<td>CNT-PET / PVDF 6Vol%</td>
<td>0.059[1] / 0.011[2] [38]</td>
<td>-</td>
<td>-</td>
<td>34 [37]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CNT-PET 12Vol%</td>
<td>0.25 [37]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chopped Fibre / Carbon powder [33]</td>
<td>200-300</td>
<td>175 MPa (+26 MPa)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>BMC 940 [Appendix G]</td>
<td>70</td>
<td>38</td>
<td>13.4</td>
<td>-</td>
<td>-</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>(35.07 @ 40wt%)</td>
<td></td>
<td></td>
<td></td>
<td>(23.97 @ 26wt%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(21.41 @ 23wt%)</td>
<td></td>
<td></td>
<td></td>
<td>(23.97 @ 26wt%)</td>
<td></td>
</tr>
<tr>
<td>71wt% PE - Magnetite (c)</td>
<td>0.0014[1] / 1.26x10⁶[4]</td>
<td>-</td>
<td>1.05[1]</td>
<td>-</td>
<td>(20.38 @ 9wt%)</td>
<td>3.84[9]</td>
</tr>
</tbody>
</table>


(i)/(c) - Injection / Compression grade. * Calculated from ashing tests.

Table 7 - Comparison of bipolar plate properties from table 3 with the best results gained from the polyethylene carbon, graphite and magnetite composites. All values are a maximum for the particular grade specified unless further information is specified in brackets.
The unfractured samples of the magnetite composites do not mean that the material is unsuitable for use in a fuel cell environment. The material was flexible and would have adapted to any variations in clamping force and to a small extent changes in membrane thickness due to hydration. The electrical results for the magnetite in the milli and micro siemen range however preclude it from use as a bipolar plate material especially when the target conductivity is greater than 100 S/cm.

None of the fillers met the electrical and thermal conductivity requirements for the DOE targets for 2015, at best only approximately 25 % of the electrical conductivity and 10% of the thermal conductivity target was reached with the carbon and graphite fillers respectively. Although not a DOE requirement, the composites displayed the lowest tensile strengths compared to other data available in the table and a recommendation was made of >16 MPa based on the carbon and graphite composites in this study. The approximate extension at break for such a tensile strength was 2mm and was viewed as a potential weakness should the bipolar plates undergo this mode of failure. However the carbon and graphite grades did meet the flexural requirement and was less than the author’s recommended density target.

A lot of the materials from the literature did not meet any of the crucial DOE targets i.e. electrical, thermal and flexural targets, nor did most of the commercially available materials meet the electrical targets if through plane conductivities are considered. The only materials from the literature and the only materials that convincingly surpassed the DOE targets were the chopped fibre / carbon powder bipolar plate material from Besmann et al [35] and the Conduplate LT-X, MT-X, HT-X from Nedstack. The chopped fibre / carbon powder displayed an electrical conductivity near to that achievable with pure graphite ie 3 times greater than the DOE target and 7 times the flexural strength requirement; however there was no data for the thermal conductivity. The Nedstack materials at best displayed double the electrical, thermal and mechanical requirements, however as with the chopped fibre / carbon powder the electrical conductivity was not specified as in plane or through plane. In plane conductivities are generally higher than the through plane conductivities (as shown in table 7).

Overall many of the materials would not meet the future materials property requirements set out by the DOE, although the Conduplate LT-X, MT-X, HT-X and
Schunk FU4369/HT materials look promising as they have already surpassed the properties of stainless steel. Stainless steel however is still a material for the future as it maintains good mechanical strength at very low bipolar plate thicknesses which increases fuel cell power density. The chopped fibre / carbon powder material, although offers great performance, was labour intensive to produce and would not meet future mass production requirements and so is not a very promising material for the future with regards to cost.

The choice of materials for bipolar plate applications would depend mainly on cost, volume, mass production and longevity requirements and so both polymeric and metallic materials would satisfy future demands in differing ways based on specific end user applications.
Chapter 8.0

Conclusions

It is known that polymers filled with conductive fillers could provide some level of conductivity whilst retaining the benefits of corrosion resistance (filler dependant) and fast manufacture. By the careful selection of filler and matrix, the materials can also be of low cost and low mass.

The low cost carbon, graphite and magnetite fillers in this study were mixed in a polyethylene matrix and tested for electrical and thermal conductivities as well as tensile and flexural mechanical properties. Fast manufacturing techniques such as injection and compression moulding were employed to create further potential for low cost through mass production.

During manufacture:

- The actual filler content differed from the intended filler content at the various composite loadings.
- The usual alignment of non-spherical fillers (i.e. the graphite) in the injection moulding direction was not observed.

Due to the difference between the actual filler contents of various grades and their intended compositions, the two roll mill mixing process was not entirely reliable but FEGSEM micrographs showed that fairly homogenous mixtures were obtained. The two roll mill process however is not a mass production process and would not offer suitable throughput if coupled with injection moulding. The somewhat non-spherical shape of the graphite powder was assumed to display some degree of alignment in
Conclusions

injection moulding direction however the FEGSEM micrographs showed no obvious alignment and results showed no preferential orientation. The data was assumed to be the result of a poor filler with anisotropic properties.

Post test:

- The carbon composites performed better in electrical conductivity for injection moulded samples than other composites.
- Injection moulded composites exhibited greater mechanical strength than the compression moulded composites with better material stability on the whole.
- The graphite filler exhibited the best mechanical properties and thermal conductivity for both injection and compression mouldings.
- Compression moulded samples produced higher thermal conductivities overall.

The carbon composites performed better in electrical conductivity for injection moulded samples due to the closer packing of the relatively smaller particles providing greater physical inter particle contact. The injection moulding grades displayed greater mechanical properties due to reduced agglomeration during pre-mixing lengthening fracture paths and therefore increasing fracture energy dissipation. Out of the three fillers, graphite exhibited greater mechanical properties due to better adhesion and wetting in the polyethylene matrix, the FEGSEM micrographs showed no sign of incompatibility of the graphite. This would have hindered crack propagation through increased dissipation of fracture energy on delamination. Compression moulded samples produced higher thermal conductivities due to the increase in processing pressure bringing particles closer together. The best thermally conductive filler was the compression moulded graphite where the better performance was attributable to phonon contribution.
Modeling:

- Spherical particles were assumed for the carbon, graphite and magnetite fillers.

- Mamunya models for electrical and thermal conductivities and Kerner’s equation for mechanical properties were chosen to model the composites.

- Parameters were tuned to fit the Mamunya models to the experimental data and the Kerner’s equation was modified to account for filler type and processing.

- Models showed reasonable agreement with the experimental data where deviations from the models denoted specific composite behaviours.

Due to the random alignment of non-spherical particles shown by the FEGSEM micrographs and proven by electrical conductivity results, the modelling assumed spherical particles for all filler types. The models chosen and model fitting were used to describe filler-matrix behaviour in the composite materials. The Kerner’s equation was modified to account for filler type and processing where the original equation only predicted composite behaviour from the pure polymer properties.

Overall the injection moulding process was superior due to its fast cycle times and simpler processing parameters, the composite manufactured exhibited better material stability when compared to compression moulding. The injection moulded carbon composite at 65 wt% was chosen as the best composite from this investigation where the density was low and flexural strength requirements meet the 2015 DOE target but fall short of the electrical and thermal conductivity requirements.

Though the corrosion tendency of metals and low conductivity of polymer composites still exist, it was concluded that both metallic and polymeric based bipolar plates have roles to play in future fuel cell markets. The choice of material would depend mainly on cost, volume/mass production and application specific requirements.
Chapter 9.0

Future Work

The recommendations for future work include improvements to the manufacture of the composites, possible avenues to improve the materials used in this study and additional testing / modeling to gauge further composite behaviour.

Manufacture and materials

The two roll mill used may not have had enough shear force to break up agglomerates of the carbon and graphite powders which had a negative effect on mechanical strength where crack propagation was increased via a reduction in crack energy dissipation. In order to improve on this, the following is recommended:

- Compounding as an alternative mixing process.
  - The increased shear forces in the screw of a compounder much like the screw in an injection moulder would be suitable for the break up of agglomerated power.
  - The process requires some trial and error to attain intended weight percentage mixtures after which mass production can be pursued.

- Compatibilisers.
  - Additives to the composite (pre-mixed with the filler) to lower the difference in surface energy between filler and matrix would allow improved wetting and adhesion between filler and matrix to reduce crack propagation.
Future Work

Testing and modeling

As injection moulding was superior to compression moulding, compression moulding can be discounted and injection moulding optimised to enhance composite properties. Also further study into the affects of pressure on the composite microstructures and its implication on modelling should be addressed. The following is recommended:

- Injection moulding at different holding pressures.
  - Different holding pressures during injection moulding should be employed to further investigate the balance of electrical/thermal conductivity and mechanical strength.

- Adaptations to the models to account for increases in processing pressure.
  - An increase in pressure during processing would affect the volume fraction of the matrix where the compressibility of the molten polymer comes into play. An initial investigation into the compressibility of polyethylene at different temperatures and its associated volume change can be seen in appendix M.

- Further studies of the LNB and Balberg models.
  - A closer look at tunnelling and links, nodes and blobs with respect to their occurrence and proportions thereof in order to gain better understanding of conduction paths and mechanisms.
  - Grinding and polishing of the microstructure to reveal the conduction paths is required to aid in the further study. This would lead to a study of anisotropic properties, i.e. variations between through plane and in plane properties.
# Appendix A

Monarch 800 carbon black physical and chemical properties. Extract from:


<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance:</strong></td>
<td>Black Powder or Pellets</td>
</tr>
<tr>
<td><strong>Odor:</strong></td>
<td>None</td>
</tr>
<tr>
<td><strong>pH:</strong></td>
<td>4 - 11 [50 g/l water, 68°F (20°C)] (non-oxidized carbon black)</td>
</tr>
<tr>
<td></td>
<td>2 - 4 (oxidized carbon black)</td>
</tr>
<tr>
<td><strong>Boiling Point/Range:</strong></td>
<td>Not applicable</td>
</tr>
<tr>
<td><strong>Melting Point/Range:</strong></td>
<td>Not applicable</td>
</tr>
<tr>
<td><strong>Water Solubility:</strong></td>
<td>Insoluble</td>
</tr>
<tr>
<td><strong>Density:</strong></td>
<td>1.7 - 1.9 g/cm³ @ 20°C</td>
</tr>
<tr>
<td><strong>Bulk Density:</strong></td>
<td>200-680 kg/m³ (Pellets)</td>
</tr>
<tr>
<td></td>
<td>20-360 kg/m³ (Fluffy)</td>
</tr>
<tr>
<td><strong>Specific Gravity:</strong></td>
<td>Not determined</td>
</tr>
<tr>
<td><strong>% Volatile (by Weight):</strong></td>
<td>&lt; 2.5% (950°C) (non-oxidized carbon black)</td>
</tr>
<tr>
<td></td>
<td>2 - 8% (oxidized carbon black)</td>
</tr>
<tr>
<td><strong>Evaporation Rate:</strong></td>
<td>Not applicable</td>
</tr>
<tr>
<td><strong>Partition Coefficient (n-octanol/water):</strong></td>
<td>Not determined</td>
</tr>
</tbody>
</table>

Cabot Corporation, Ellesmere Port, Cheshire, UK.
Appendix B

HMA018 high density polyethylene datasheet.


ExxonMobil™ HDPE HMA 018
High Density Polyethylene Resin

Product Description
HMA 018 is an easy flow HDPE grade, characterized by high gloss and dimensional stability.

General
Availability
- Africa & Middle East
- Asia Pacific
- Europe
Additive
- Thermal Stabilizer: Yes
- UV Stabilizer: No
Applications
- Food Packaging Containers
- Housewares: Multiwall
- Thin-Walled
Revision Date
- March 2010

Resin Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Value (English)</th>
<th>Typical Value (SI)</th>
<th>Test Based On</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.954 g/cm³</td>
<td>0.954 g/cm³</td>
<td>ExxonMobil Method</td>
</tr>
<tr>
<td>Melt Index (190°C/2.16 kg)</td>
<td>30 g/10 min</td>
<td>30 g/10 min</td>
<td>ASTM D1236</td>
</tr>
<tr>
<td>Thermal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Deflection Temperature (1.45 MPa)</td>
<td>147 °F</td>
<td>64.0 °C</td>
<td>ISO 1134</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>294 °F</td>
<td>129 °C</td>
<td>ASTM D3418</td>
</tr>
<tr>
<td>Molded Properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Stress at Yield</td>
<td>3190 ps</td>
<td>22.0 MPa</td>
<td>ISO 527-2/1A/20</td>
</tr>
<tr>
<td>Tensile Strain at Yield</td>
<td>10 %</td>
<td>10 %</td>
<td>ISO 527-2/1A/50</td>
</tr>
<tr>
<td>Tensile Strain at Break</td>
<td>&gt; 100 %</td>
<td>&gt; 100 %</td>
<td>ISO 527-2/1A/60</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>13,100 ps</td>
<td>900 MPa</td>
<td>ISO 1879</td>
</tr>
<tr>
<td>Environmental Stress-Crack Resistance</td>
<td>&lt; 1.00 hr</td>
<td>&lt; 1.00 hr</td>
<td>ASTM D1693</td>
</tr>
<tr>
<td>Impact</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notched Izod Impact Strength</td>
<td>1.90 ft-lb/in³</td>
<td>4.00 kJ/m³</td>
<td>ISO 180/A1A</td>
</tr>
</tbody>
</table>

Additional Information
The molded properties were measured on 4 mm (157.5 mil) thick injection molded specimen based on ISO 291-1.
1. 3.45 MPa, 70 psig
2. ESCR was measured on 2 mm (76.7 mil) thick compression molded plate (50%, 10% Ig25%, 50%0, 122°F)

Legal Statement
Contact your ExxonMobil Chemical Customer Service Representative for potential food contact application compliance (e.g. FDA, EU, HPP).

This product is not intended for use in medical applications and should not be used in any such applications.

Notes
1. Product may not be available in all or some countries in the identified Availability regions. Please contact your Sales Representative for complete Country Availability.

Typical properties: these are not to be construed as specifications.

© 2010 Exxon Mobil Corporation. To the extent the user is entitled to disclose and distribute this document, the user may forward, distribute, and/or photocopy this copyrighted document only if unaltered and complete, including all of its headers, footers, disclaimers, and other information. You may not copy this document to a Web site. ExxonMobil does not guarantee the typical (or other) values. Analysis may be performed on representative samples and not the actual product shipped. The information in this document relates only to the named product or materials when not in combination with any other product or materials. We based the information on data believed to be reliable on the date compiled, but we do not represent, warrant, or otherwise guarantee, expressly or impliedly, the merchantability, fitness for a particular purpose, suitability, accuracy, reliability, or completeness of this information or the products, materials, or processes described. The user is solely responsible for all determinations regarding any use of material or product and any process in its territories of interest. We expressly disclaim liability for any loss, damage, or injury directly or indirectly suffered or incurred as a result of or related to anyone using or relying on any of the information in this document. There is no endorsement of any product or process, and we expressly disclaim any contrary implication. The terms, "we", "our", "ExxonMobil Chemical", or "ExxonMobil" are used for convenience, and may include any one or more of ExxonMobil Chemical Company, Exxon Mobil Corporation, or any affiliates they directly or indirectly steward. ExxonMobil, the ExxonMobil Chemical Emblem, the Interlocking X Device, Enable, Exceed, Exact, Esaco, Escorene, Escorr, Inter, NTX, Polybilt, Paxon and Optema are trademarks or service marks of Exxon Mobil Corporation.
Appendix C

Schunk bipolar plate material grade FU4369 datasheet.


<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>1.90 g/cm³</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>40 MPa</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>50 MPa</td>
</tr>
<tr>
<td>Young's modulus</td>
<td></td>
</tr>
<tr>
<td>dynamic</td>
<td>24 GPa</td>
</tr>
<tr>
<td>flexural</td>
<td>10 GPa</td>
</tr>
<tr>
<td>Hardness Rockwell HR10/40</td>
<td>100</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>55 W/mK</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>$10^{-6}$/K</td>
</tr>
<tr>
<td>20 - 140 °C (70 - 265 °F)</td>
<td></td>
</tr>
<tr>
<td>xy in plane</td>
<td>15</td>
</tr>
<tr>
<td>z through plane</td>
<td>38</td>
</tr>
<tr>
<td>Specific electrical resistance</td>
<td></td>
</tr>
<tr>
<td>80 in plane</td>
<td>90</td>
</tr>
<tr>
<td>z through plane</td>
<td>150</td>
</tr>
<tr>
<td>Heat deflection temperature</td>
<td></td>
</tr>
<tr>
<td>190 °C / 370 °F</td>
<td></td>
</tr>
</tbody>
</table>

The data shown above are not guaranteed, but typical values based on our experience. It should be understood that a spread of results can occur due to variations in materials and production processes. Please find the standards for the determination of our material properties at www.schunk-group.com/skt/dm.
Appendix D

Eisenhuth datasheet for BMA5 bipolar plate material.

http://www.eisenhuth.de/pdf/SIGRACET_Datenblaetter.pdf

©SIGRACET - BPP
Bipolar Plate - PPG 86 (Polypropylene)

Physical Properties (Typical Values)
Physikalische Eigenschaften (Typische Werte)

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>lbs/ft³</td>
<td>115</td>
</tr>
<tr>
<td>Rohdichte</td>
<td>g/cm³</td>
<td>1.85</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>psi</td>
<td>5,000</td>
</tr>
<tr>
<td>Biegefestigkeit</td>
<td>N/mm²</td>
<td>40</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>psi</td>
<td>1.6 · 10⁴</td>
</tr>
<tr>
<td>E-Modul (aus Biegeversuch)</td>
<td>N/mm²</td>
<td>11,600</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>psi</td>
<td>7,300</td>
</tr>
<tr>
<td>Druckfestigkeit</td>
<td>N/mm²</td>
<td>50</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>btu/ft·h·°F</td>
<td>0.1</td>
</tr>
<tr>
<td>Wärmeleitfähigkeit</td>
<td>W/m·K</td>
<td>14</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>°F · 10⁻⁶</td>
<td>15</td>
</tr>
<tr>
<td>Wärmeequivalenzkoeffizient</td>
<td>°K · 10⁻⁶</td>
<td>27</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>μΩm</td>
<td>180</td>
</tr>
<tr>
<td>Spezifischer elektrischer Widerstand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>μΩm</td>
<td>550</td>
</tr>
<tr>
<td>Spezifischer elektrischer Widerstand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical Resistance</td>
<td>mΩ cm²</td>
<td>12</td>
</tr>
<tr>
<td>Elektrischer Widerstand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeability Coefficient (Air)</td>
<td>in²/s</td>
<td>1.085 · 10⁻⁶</td>
</tr>
<tr>
<td>Permeabilitätskoeffizient (Luft)</td>
<td>cm/s</td>
<td>7 · 10⁻⁶</td>
</tr>
<tr>
<td>Recommended Max. Operating Temperature</td>
<td>°F</td>
<td>≤ 175</td>
</tr>
<tr>
<td>Empfohlene max. Betriebstemperatur</td>
<td>°C</td>
<td>≤ 80</td>
</tr>
</tbody>
</table>

Addendum: is suitable for both compression molding and injection molding.

registered trademark of SGL Carbon Group companies
This information is based on our present state of knowledge and is intended to provide general notes on our products and their uses. It should therefore not be construed as guaranteeing specific properties of the products described or their suitability for a particular application. Any existing industrial property rights must be observed.
The quality of our products is guaranteed under our “General Conditions of Sale”.

DS FC 002 - BPP PPG 86 - Rev01

09 2004/1.5 3NÄ Printed in Germany
Appendix E

Eisenhuth datasheet for BMA5 bipolar plate material.

http://www.eisenhuth.de/pdf/SIGRACET_Datenblaetter.pdf

<table>
<thead>
<tr>
<th>Physical Properties (Typical Values)</th>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk Density</td>
<td>lbs/ft³</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>Rohdichte</td>
<td>g/cm³</td>
<td>2,1</td>
</tr>
<tr>
<td></td>
<td>Flexural Strength</td>
<td>psi</td>
<td>5,800</td>
</tr>
<tr>
<td></td>
<td>Biegfestigkeit</td>
<td>N/mm²</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Flexural Modulus</td>
<td>psi</td>
<td>1.8·10⁴</td>
</tr>
<tr>
<td></td>
<td>E-Modul (aus Biegeversuch)</td>
<td>N/mm²</td>
<td>12,000</td>
</tr>
<tr>
<td></td>
<td>Compressive Strength</td>
<td>psi</td>
<td>8,700</td>
</tr>
<tr>
<td></td>
<td>Druckfestigkeit</td>
<td>N/mm²</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Thermal Conductivity</td>
<td>btu/ft·h·°F</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Wärmeleitfähigkeit</td>
<td>W/m·K</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Coefficient of Thermal Expansion</td>
<td>1/°F·10⁻⁶</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>Wärmeausdehnungskoeffizient</td>
<td>1/K·10⁻⁶</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Electrical Resistivity II</td>
<td>µΩ·m</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Spezifischer elektrischer Widerstand</td>
<td>µΩ·m</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Electrical Resistivity II</td>
<td>µΩ·m</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Electrical Resistance I•</td>
<td>mΩcm²</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Elektrischer Widerstand</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permeability Coefficient [Air]</td>
<td>in³/s</td>
<td>1.55·10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>Permeabilitätskoeffizient [Luft]</td>
<td>cm³/s</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>Recommended Max. Operating Temperature</td>
<td>°F</td>
<td>≤ 250</td>
</tr>
<tr>
<td></td>
<td>Empfohlene max. Betriebstemperatur</td>
<td>°C</td>
<td>≤ 120</td>
</tr>
</tbody>
</table>

**Addendum:** is suitable for compression molding but not for injection molding.

*registered trademark of SGL Carbon Group companies

This information is based on our present state of knowledge and is intended to provide general notes on our products and their uses. It should therefore not be construed as guaranteeing specific properties of the products described or their suitability for a particular application.

Any existing industrial property rights must be observed.

The quality of our products is guaranteed under our “General Conditions of Sale”.

DS FC 001 - BPP BMA 5 - Rev01

09 2004/1.5 NÄ Printed in Germany
Appendices

Appendix F

Eisenhuth datasheet for BBP4 bipolar plate material.

http://www.eisenhuth.de/pdf/SIGRACET_Datenblaetter.pdf

**SIGRACET - BPP**

Bipolar Plate - BBP 4 (Phenolic Resin)

<table>
<thead>
<tr>
<th>Physical Properties (Typical Values)</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>lbs/ft³</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>g/cm³</td>
<td>1.97</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>psi</td>
<td>5,800</td>
</tr>
<tr>
<td>Biegefestigkeit</td>
<td>N/mm²</td>
<td>40</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>psi</td>
<td>2.0 · 10⁴</td>
</tr>
<tr>
<td>EModul (aus Biegeversuch)</td>
<td>N/mm²</td>
<td>14,000</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>psi</td>
<td>11,000</td>
</tr>
<tr>
<td>Druckfestigkeit</td>
<td>N/mm²</td>
<td>75</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>bth/ft · h · °F</td>
<td>12</td>
</tr>
<tr>
<td>Wärmeleitfähigkeit</td>
<td>W/m · K</td>
<td>20</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>1/F · 10⁻⁴</td>
<td>1.8</td>
</tr>
<tr>
<td>Wärmeausdehnungskoeffizient</td>
<td>1/K · 10⁻⁴</td>
<td>3.2</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>µΩm</td>
<td>50</td>
</tr>
<tr>
<td>Spezifischer elektrischer Widerstand</td>
<td>µΩm</td>
<td>240</td>
</tr>
<tr>
<td>Electrical Resistance</td>
<td>mΩ cm²</td>
<td>5</td>
</tr>
<tr>
<td>Elektrischer Widerstand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeability Coefficient (Air)</td>
<td>in³/s</td>
<td>0.775 · 10⁻⁴</td>
</tr>
<tr>
<td>Permeabilitätskoeffizient (luft)</td>
<td>cm³/s</td>
<td>5 · 10⁻⁴</td>
</tr>
<tr>
<td>Recommended Max. Operating Temperature</td>
<td>°F</td>
<td>≤ 355</td>
</tr>
<tr>
<td>Empfohlene max. Betriebstemperatur</td>
<td>°C</td>
<td>≤ 180</td>
</tr>
</tbody>
</table>

Addendum: is suitable for both compression molding and injection molding.

Rev.01 09 2004/1.5 3NÄ Printed in Germany
Appendix G

BMC940 datasheet from Bulk Moulding Compounds Inc.


### Preliminary Technical Data

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>BMC 940-14868</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through Plane (Z direction) S/cm</td>
<td>32</td>
<td>Vendor</td>
</tr>
<tr>
<td>In Plane (XY direction) S/cm</td>
<td>70</td>
<td>Vendor</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.89</td>
<td>ASTM D792</td>
</tr>
<tr>
<td>Mold Shrinkage, %</td>
<td>0.08</td>
<td>ASTM D952</td>
</tr>
<tr>
<td>Water Absorption, % - 24 hr/23°C, %</td>
<td>&lt;0.06</td>
<td>ASTM D570</td>
</tr>
<tr>
<td>Flexural Modulus, GPa</td>
<td>28</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>Flexural Strength, MPa</td>
<td>9.5</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>% Retention after 2250 hr @ 50% MeOH reflux</td>
<td>90</td>
<td>ASTM D900</td>
</tr>
<tr>
<td>% Retention after 2250 hr @ 100% MeOH reflux</td>
<td>80</td>
<td>ASTM D900</td>
</tr>
<tr>
<td>Izod Impact, notched, N M/cm</td>
<td>0.15</td>
<td>ASTM D256</td>
</tr>
<tr>
<td>Instrumented Impact, 23°C</td>
<td></td>
<td>ASTM D3765</td>
</tr>
<tr>
<td>Max Load, lbs.</td>
<td>TBD</td>
<td></td>
</tr>
<tr>
<td>Total energy, ft-lb</td>
<td>TBD</td>
<td></td>
</tr>
<tr>
<td>Energy to Max Load, ft-lb</td>
<td>TBD</td>
<td></td>
</tr>
<tr>
<td>Compressive Creep</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 hr @ 80°C, %</td>
<td>TBD</td>
<td></td>
</tr>
<tr>
<td>1000 hr @ 80°C, %</td>
<td>TBD</td>
<td></td>
</tr>
</tbody>
</table>
Appendices

Appendix G (continued)

**Typical Data**

**BMC 940 Vinyl Ester Bipolar Plate Material**

**Compression Molding Grade**

<table>
<thead>
<tr>
<th>Thermal</th>
<th>Value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA-Modulus, GPa @ 25°C</td>
<td>13.8</td>
<td>ASTM D4065</td>
</tr>
<tr>
<td>100°C</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>150°C</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>175°C</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Glass Transition Temp (Tg), °C</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>Flammability (@ 0.140&quot; thickness)</td>
<td>94V0</td>
<td>UL 94</td>
</tr>
<tr>
<td>Thermal Expansion, μm/m °C</td>
<td>TBD</td>
<td>E831</td>
</tr>
</tbody>
</table>

**Thermal Conductivity @ 25°C**

| Specific Heat, J/g-K | 0.846 | E1461-92 |
| Diffusivity, cm²/s | 0.0889 |
| Conductivity, W/m-K | 13.4 |

**Processing Information**

| Cure time | 30-60 seconds |
| Mold temperature | 300°-320°F |
| Recommended tonnage | > 40 MPa on projected part area |
| Press close speed | <2 seconds after material begins flowing |
| Post bake, 330°F | 13 minutes (after reaching 350°F) |

**Important Notice:**

The information and statements herein are believed to be reliable, but are not to be construed as a warranty or representation for which we assume legal responsibility. Users should undertake sufficient verification and testing to determine the suitability for their own particular purpose of any information or products referred to herein. **NO WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE IS MADE.** Nothing herein is to be taken as permission, inducement or recommendation to practice any patented invention without a license.

BMC Molding Compounds, Inc.
1600 Pottawattamie
West Chicago, IL. 60185
Telephone: (630) 377-1065
Fax: (630) 377-7395
E-mail: bmc@bmcmailing.com

“**The Fastest Growing Material Technology in the World Today!**”

Page 2 of 2
Appendix H

Conduplate LT datasheet from Nedstack BV, Netherlands.

http://www.fuelcellmarkets.com/content/images/articles/Conduplate_LT(1).pdf

**Bipolar plates for PEM fuel cells**

**Conduplate LT**

<table>
<thead>
<tr>
<th>Material properties*</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation temperature (max)</td>
<td>100</td>
<td>°C</td>
</tr>
<tr>
<td>Electrical conductivity (in plane)</td>
<td>50</td>
<td>μΩm</td>
</tr>
<tr>
<td>Electrical conductivity (through plane)</td>
<td>81</td>
<td>μΩm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>28</td>
<td>W/(m.K)</td>
</tr>
<tr>
<td>Density</td>
<td>1800</td>
<td>kg.m⁻¹</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>(28\times10^{-6})</td>
<td>K⁻¹</td>
</tr>
<tr>
<td>Hydrogen permeability</td>
<td>(50\times10^{-6})</td>
<td>cm²/s</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>30</td>
<td>Mpa</td>
</tr>
<tr>
<td>Size (max)</td>
<td>600 * 600</td>
<td>mm</td>
</tr>
<tr>
<td>Plate thickness (min)</td>
<td>0,5</td>
<td>mm</td>
</tr>
</tbody>
</table>

*Properties given are based on our best present knowledge, and based on measurements on flat molded plates. Properties of shaped molded cell plates can differ slightly from those given for flat molded plates.*

---

**Nedstack Fuel Cell Components BV**

Vesting address: Westervoortdijk 73, 6827 AV Arnhem

P.O. Box 5167, 6802 ED Arnhem, The Netherlands

tel. +31 26 3664 278, fax +31 26 3665 129,

e-mail: info@nedstack.com, website: www.nedstack.com

March 2005
Appendix H (continued)
Conduplate MT-X datasheet from Nedstack BV, Netherlands.

http://www.fuelcellmarkets.com/content/images/articles/Conduplate_MT-X(1).pdf

**Bipolar plates for PEM fuel cells**

**Conduplate MT -X**

<table>
<thead>
<tr>
<th>Material properties*</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation temperature (max)</td>
<td>125</td>
<td>°C</td>
</tr>
<tr>
<td>Electrical conductivity (in plane)</td>
<td>60</td>
<td>μΩm</td>
</tr>
<tr>
<td>Electrical conductivity (through plane)</td>
<td>91</td>
<td>μΩm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>24</td>
<td>W/(m.K)</td>
</tr>
<tr>
<td>Density</td>
<td>2000</td>
<td>kg.m⁻¹</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>25×10⁻⁶</td>
<td>K⁻¹</td>
</tr>
<tr>
<td>Hydrogen permeability</td>
<td>50×10⁻⁶</td>
<td>cm²/s</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>35</td>
<td>Mpa</td>
</tr>
<tr>
<td>Size (max)</td>
<td>600 x 600</td>
<td>mm</td>
</tr>
<tr>
<td>Plate thickness (min)</td>
<td>0.5</td>
<td>mm</td>
</tr>
</tbody>
</table>

*Properties given are based on our best present knowledge, and based on measurements on flat molded plates. Properties of shaped molded cell plates can differ slightly from those given for flat molded plates.

Nedstack Fuel Cell Components BV
Visiting address: Westervoordeijk 73, 6827 AV Arnhem
P.O. Box 5167, 6802 ED Arnhem, The Netherlands
Tel. +31 26 3664 278, Fax +31 26 3665 129,
e-mail: info@nedstack.com, website: www.nedstack.com

March 2005
Appendix H (continued)

Conduplate HT-X datasheet from Nedstack BV, Netherlands.

http://www.fuelcellmarkets.com/content/images/articles/Conduplate_HT-X(1).pdf

---

**Bipolar plates for PEM fuel cells**

**Conduplate HT -X**

<table>
<thead>
<tr>
<th>Material properties*</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation temperature (max)</td>
<td>225</td>
<td>°C</td>
</tr>
<tr>
<td>Electrical conductivity (in plane)</td>
<td>46</td>
<td>μΩm</td>
</tr>
<tr>
<td>Electrical conductivity (through plane)</td>
<td>73</td>
<td>μΩm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>40</td>
<td>W/(m.K)</td>
</tr>
<tr>
<td>Density</td>
<td>1800</td>
<td>kg.m⁻¹</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>12*10⁻⁶</td>
<td>K⁻¹</td>
</tr>
<tr>
<td>Hydrogen permeability</td>
<td>50*10⁻⁶</td>
<td>cm²/s</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>45</td>
<td>Mpa</td>
</tr>
<tr>
<td>Size (max)</td>
<td>600*600</td>
<td>mm</td>
</tr>
<tr>
<td>Plate thickness (min)</td>
<td>0.5</td>
<td>mm</td>
</tr>
</tbody>
</table>

* Properties given are based on our best present knowledge, and based on measurements on flat molded plates. Properties of shaped molded cell plates can differ slightly from those given for flat molded plates.
Appendix I

Example of load vs extension data for the tensile tests of the injection moulded carbon composites.

Example of load vs extension data for the tensile tests of the compression moulded carbon composites.
Appendix J

Example of load vs extension data for the tensile tests of the injection moulded graphite composites.

Example of load vs extension data for the compression moulded graphite composites.
Appendix K

Example of load vs extension data for the tensile tests of the injection moulded magnetite composites.

Example of load vs extension data for the tensile tests of the compression moulded magnetite composites.
Appendix L

Comparison of Mamunya’s Model for electrical conductivity incorporating surface energy measurements [67] with experimental data of this study. The polar and dispersive surface energy measurements for the filler and polymer were measured using a Dataphysics OCA 20 Goniometer. The following values were used in equation 12 on page 106.

\[
\begin{align*}
\text{Constant A} : & \quad 0.28 & \text{Surface energy of filler } \gamma_f : & \quad 64.2 \\
\text{Constant B} : & \quad 0.036 & \text{Surface energy of polymer } \gamma_p : & \quad 32.1 \\
& & \text{Interfacial tension } \gamma_{pf} : & \quad 5.507
\end{align*}
\]

![Electrical Model For Injection Moulded PE-Carbon Composite Using Mamunya's Model Incorporating Surface Energy [66, 67]](image)

Figure 61 - Comparison of Mamunya’s model for electrical conductivity with experimental data obtained in this study for injection moulded carbon composites.

In figure 61, the model does not match the experimental data as the model is predicting the sharp increase after the percolation threshold and then the slow increase approaching the maximum electrical conductivity as illustrated in figure 46 on page 101. The experimental data only represents the initial portion of a full conductivity profile before the sharp increase in conductivity.
Appendix L (continued)

The electrical conductivity in figure 61 was not logged, as shown in figure 62, so that a clearer comparison could be made. An extract from Mamunya et al. [67] is shown in figure 62 below showing Mamunya’s modeling results with experimental data.

![Figure 62 - Extract from Mamunya et al. [67] showing the electrical conductivity trends of modelled data and experimental data.](image)
Appendix M

The compressibility at 160 °C, 190 °C and 220 °C of branched polyethylenes with average density of 0.78 g/cm³ was investigated by Chung [90]. The results of compressibility (β) vs temperature are shown in figure 61 below.

![Polyethylene Compressibility with Increasing Temperature](image)

The results in figure 63 show a linear relationship between compressibility and temperature and an extrapolation represented by the dashed line was made up to 240 °C to cover the full processing temperature range used in this study.

The compressibility equation below was re-arranged to find the volume percent change in polyethylene with increasing temperature at a pressure change of 10 bar.

\[ \beta = \frac{\delta V}{V \cdot \delta P} \]

\[ \delta V = \beta \cdot V \cdot \delta P \]  

(Equ 36.)

Where:  
β - Compressibility  
V - Initial volume  
δV - Change in volume  
δP - Change in pressure
Appendix M (continued)

Figure 64 presents the results of percentage volume change for various volumes with increasing temperature for a 10 bar change in pressure as an example. It shows that the compressibility of polyethylene increases with increasing temperature although to a lesser extent shown by the reduced difference between each step in gradient with increasing temperature.

![Figure 64 - The volume percent change of polyethylene at 10 bar of pressure for increasing temperature.](image)

On the next page, figure 65 gives an example of how compressibility increases with increasing pressure at a constant temperature (160 °C). The step increases in gradient with increasing pressure are constant.
Figure 65 - The volume percent change of polyethylene at 160 °C with increasing pressure.

Note: No time dependant compressive properties were observed [90].
References


References


References


