Graphene Composites for Electromagnetic Interference Shielding

Submitted in total fulfillment of the requirements of the degree of Masters by Research (Engineering)

Liam Anderson

Faculty of Science, Engineering and Technology
Swinburne University of Technology
Melbourne, Australia

2021
Declaration

This is to certify that:

1. The following thesis contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the examinable outcome.

2. To the best of the candidate's knowledge, this thesis contains no material previously published or written by another person except where due reference is made in the text of the examinable outcome.

3. The work is based on the joint research and publications; the relative contributions of the respective authors are disclosed.

Liam Anderson, 2021
Publications

Some of the work presented in this thesis has been published in the following:


Software Development

1. A 1D Finite Difference Time Domain algorithm was developed using MATLAB. Based on the inputs of thickness, frequency, electrical conductivity, permittivity and magnetic permeability the shielding effectiveness, reflection and absorption can be visualized and calculated. GitHub repository is available here: liam-anderson-l12/FDTD-MATLAB: A one dimensional Finite Difference Time Domain (FDTD) simulation written in MATLAB (github.com). The incident wave is defined as gaussian wave.

2. Using the Python library Tkinter, a GUI was created which plots the shielding effectiveness, reflection and absorption of a plane wave incident on a flat surface. The user inputs here are thickness, electrical conductivity, magnetic permeability and permittivity. The GitHub repository for this work can be found here: liam-anderson-l12/Shielding-Effectiveness:- GUI based on analytical model of plane wave reflection from a planar surface (github.com).

3. Various codes which output the thermal conductivity, electrical conductivity and permittivity of graphene/polymer nanocomposites were constructed based on the micromechanical models outlined in this work. The GitHub repository for this work
can be here: liam-anderson-l12/Shielding-Effectiveness-- GUI based on analytical model of plane wave reflection from a planar surface (github.com).

4. In order to convert from the S-parameter values obtained from the waveguide measurement into bulk material electromagnetic properties a MATLAB file was constructed. The GitHub repository for this work can be here: liam-anderson-l12/NRW-conversion: NRW conversion (github.com)

Acknowledgements
I extend my gratitude to the many people and organizations involved in the completion of this thesis. This includes members both inside and out of Swinburne, providing me with both academic and personal support. To begin the acknowledgments, I need to congratulate my principal supervisor, Dr Nishar Hameed, for his continuous support, encouragement and assessment of my work throughout the whole candidature. In addition, Dr Azadeh Mirabedini for her willingness to teach and assist me through the many processes involved in material fabrication and characterization. Without the support of my two supervisors, this thesis would not have been possible.

Further support from whom was critical in the completion of this thesis came from the people across the organizations including - Swinburne smart materials lab, RF engineering lab, DMTC Limited (Australia), the Centre for Micro Photonics and the Factory of the Future. Thankfulness goes to the following people. Dr Mazhar Peerzada for his guidance and willingness to help in the area of carbon fibre fabrication. Jimmy Thomas for his assistance in composite fabrication. Premika Govindaraj for assistance with nanocomposite fabrication. Prof. Peter Cadusch for his help with the construction of both micro and macro scale models. Dr Arezou Soltani Panah for assistance with programming. Dr Steve Iskra and Metin Pekgor for help in dielectric probe material characterization. Phasor Innovation and RMIT university for assistance in waveguide EMI testing. Lastly, Swinburne university for providing the facilities for me and many others to conduct collaborative research.
Abstract

The mitigation of electromagnetic pollution is becoming an increasing issue due to the proliferation and miniaturization of electronic components. In order to reach adequate electromagnetic compatibility (EMC) between devices, electromagnetic interference (EMI) shields must be considered. Therefore, materials that possess shielding properties are to be considered, and their shielding effectiveness (SE) is to be characterized.

Graphene-enhanced polymer composites are recently introduced as a replacement for metal-based EMI shielding materials owing to their low cost, resistance to corrosion, tuneable properties, straightforward and versatile processability and lightweights in comparison to conventional metal-based materials. However, problems exist in the proper processing and characterization of these novel materials. Thus, producing materials with consistent properties in large quantities remains challenging.

The SE can be determined from the bulk electromagnetic material properties - permittivity, permeability and conductivity using analytical or numerical solutions. Due to the heterogeneity of graphene-based composites, characterization of these values remains difficult. This work attempts to critically review and summarise the state-of-art concerning the physical dispersion methods and homogenization modelling techniques surrounding these materials.

A continuum-based model is developed from analysis of the micro-scale electromagnetic properties, which is then paired with existing composite modelling techniques – effective medium theory (EMT). Allowing for the prediction of the macro-scale electromagnetic properties from the pre-determined properties of the polymer matrix and carbon-based filler.

Various graphite nanoplatelet (GnP) reinforced epoxy composites were fabricated and characterized and their EMI characteristics were then contrasted against theoretical predictions made by this model.

Further applications of both the model and the developed material were also investigated. The model was incorporated with ab initio developed Finite Difference Time Domain (FDTD) numerical algorithm in order to demonstrate compatibility with existing EMI shielding software. Additionally, the fabricated GnP/Epoxy material was incorporated into an in situ fabricated carbon fibre reinforced plastic (CFRP) in order to demonstrate compatibility with existing large-scale composites.
## Contents

Declaration ............................................................................................................. II  
Publications .......................................................................................................... III  
Software Development ........................................................................................... III  
Acknowledgements ............................................................................................... IV  
Abstract ............................................................................................................... V  
List of Figures ........................................................................................................ X  
List of Tables ........................................................................................................ XII  
Nomenclature ......................................................................................................... XIII  
Acronyms and Initialisms ...................................................................................... XV  

### Introduction

1.1 Research Background ..................................................................................... 1  
1.2 Thesis Outline ................................................................................................. 6  
  1.2.1 Significance ................................................................................................. 6  
  1.2.2 Objectives .................................................................................................. 7  
  1.2.3 Sequence of Chapters ................................................................................ 7  

### Literature Review

2.1 Composites ....................................................................................................... 9  
2.2 The Birth of Nanotechnology .......................................................................... 10  
2.3 Carbon-based Nanofillers ............................................................................. 11  
2.4 Graphene ......................................................................................................... 12  
2.5 Graphene Materials Synthesis .................................................................... 12  
  2.5.1 Bottom-Up Approaches of Graphene Synthesis ....................................... 13  
  2.5.2 Top-down Approaches of Graphene Synthesis .......................................... 16  
2.6 Graphene Polymer Dispersion Methods ..................................................... 22  
  2.6.1 Chemical Dispersion Methods ................................................................. 22  
  2.6.2 Mechanical Dispersion Methods .............................................................. 25
2.6.3 Aligned Graphene-Polymer Dispersions.................................................................31
2.7 Graphene Filler Types and Matrix Materials.................................................................32
  2.7.1 Graphene in acrylonitrile-butadiene-styrene.........................................................32
  2.7.2 Graphene in High density polyethylene .................................................................33
  2.7.3 Graphene in polypropylene .........................................................................................34
  2.7.4 Graphene in Epoxy ....................................................................................................35
  2.7.5 Graphene in Polyvinylidene fluoride ........................................................................36
  2.7.6 Graphene in Polyurethane .........................................................................................37
  2.7.8 Graphene in Polylactic acid .......................................................................................38
  2.7.9 Graphene in Polyvinyl alcohol ..................................................................................39
  2.7.10 Graphene in polymethyl methacrylate .....................................................................40
  2.7.11 Graphene in Polydimethylsiloxane ..........................................................................41
  2.7.12 Graphene in Polycarbonate .....................................................................................42
  2.7.13 Graphene in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate ..................42
2.8 Graphene’s Environmental Impact ...................................................................................43
2.9 Graphene-based disruptive technologies .........................................................................44
  2.9.1 Graphene Inks and Coatings .....................................................................................44
  2.9.2 Graphene-enabled Composites ..................................................................................44
  2.9.3 Graphene-based Energy Storage Devices .................................................................45
  2.9.4 Graphene Electronics ...............................................................................................45
  2.9.5 Graphene-enabled Water Purification .......................................................................45
  2.9.6 Graphene Materials for Thermal Management .........................................................46
2.10 Graphene Nanocomposite Applications .......................................................................46
  2.10.1 Graphene/Polymers in Defence and Transport Industries ....................................47
  2.10.2 Graphene/Epoxy in Carbon Fibre Composites .........................................................48
  2.10.3 Radar Absorbing Materials ......................................................................................51
  2.10.4 Graphene Foams .......................................................................................................51
2.10.5 Alternative Graphene Shielding Materials .................................................. 52
2.11 Meta-analysis of EMI shielding graphene/polymers ........................................... 53
2.12 Modelling of Graphene nanocomposites for EMI Shielding .............................. 57
  2.12.1 Electromagnetic Responses of Materials ...................................................... 57
  2.12.2 Electromagnetic Interference Shielding ....................................................... 59
  2.12.3 Numerical Methods for EMI Simulation ...................................................... 64
  2.12.4 Multiscale Modelling ................................................................................... 65
  2.12.5 Micromechanics of Graphene Nanocomposites ........................................... 66
      2.12.5.2 Electron Tunneling ................................................................................ 68
      2.12.5.3 Agglomeration ....................................................................................... 68
      2.12.5.4 Imperfect Interface & Nanocapacitance .................................................. 69
      2.12.5.5 Frequency-Dependent Conductivity and Permittivity ............................... 70
      2.12.5.6 Thermal Conductivity Modelling ............................................................ 71
  2.12.6 Effective Medium Theory for EMI ............................................................... 72
2.13 Experimental Characterization of GnP/Epoxy Composites for EMI Shielding ...... 76
  2.13.1 Characterization of Graphene Flakes and Dispersions ................................... 76
  2.13.2 Testing Methods for the Measurement of EMI Parameters ............................. 81

Research Design ........................................................................................................ 87

3.1 Sample Fabrication ............................................................................................... 88
  3.1.1 GnP/Epoxy Sample Preparation ..................................................................... 88
  3.1.2 GnP/epoxy/carbon fibre composites Sample Preparation .............................. 89
  3.1.3 GnP/PVA films ............................................................................................... 90

3.2 Modelling and Software Design ........................................................................... 90
  3.2.1 Micromechanical Model Construction .......................................................... 91
  3.2.2 Analytical Model of Shielding Effectiveness Construction ............................. 96
  3.2.3 Numerical Model of Shielding Effectiveness Construction ............................ 97
  3.2.4 Further Numerical Modelling of Shielding Effectiveness ............................... 99
3.2.5 NRW Conversion Method Construction ................................................................. 100

3.3 Experimental Characterization Processes ................................................................. 101

3.3.1 Scanning Electron Microscopy ................................................................................ 101
3.3.2 Dielectric Probe ...................................................................................................... 102
3.3.3 Waveguide Analysis ............................................................................................... 102

Results/Findings ............................................................................................................. 104

4.1 Dielectric Probe Results ............................................................................................ 104

4.1.1 GnP/Epoxy Dielectric Probe Results ...................................................................... 104
4.1.2 GnP/epoxy/carbon fibre composite Dielectric Probe Results ............................... 112

4.2 Waveguide Results .................................................................................................. 113

4.2.1 GnP/Epoxy Waveguide Results ........................................................................... 114
4.2.2 GnP/PVA Nanocomposite Film Waveguide Results ........................................... 116
4.2.3 GnP/epoxy/carbon fibre composites Waveguide Results .................................... 116
4.2.4 Explanation of inaccuracies in the Results ........................................................... 117
4.2.5 Theoretical Prediction of GnP/epoxy properties within the X-band ..................... 118

Conclusion and Recommendation .................................................................................. 120

5.1 Conclusion ................................................................................................................ 120
5.2 Recommendations for Future work ........................................................................ 121
List of Figures

Figure 1 - Recreation of the first Radio Transmitter built by Guglielmo Marconi. Adapted with permission from ref. [3].........................................................................................................................2

Figure 2 - a visual representation of some possible EMI inducing features in a common environment. Adapted with permission from Ref. [5] .................................................................................4

Figure 3 – Graphical depiction of the difference in conductivity between homogenous, well dispersed and poorly dispersed materials. Image produced by author ..................................................................5

Figure 4 (a) polymer matrix composites (PMCs), (b) ceramic matrix composites (CMCs), and (c) metal matrix composites (MMCs) gathered from ref. [19] ..........................................................10

Figure 5 - (a) A schematic of a typical thermal CVD setup. (b) Schematic of a typical plasma CVD setup. Gathered from Ref. [26] ........................................................................................................14

Figure 6 - Schematic representation of graphene synthesis processes by the (a) "bottom-up" and (b) "top-down" approaches. Reproduced with permission from Ref. [28]. ..........................15

Figure 7 - an outline of some of the processes involved in top-down graphene synthesis. Image produced by author ........................................................................................................16

Figure 8 - Schematic diagram of planetary ball mill. Gathered from ref. [1]..........................26

Figure 9 - Schematic diagram of mixer mill reactor periodic motion. Gathered from ref. [1] 27

Figure 10 - Image of a three-roll mill. Gathered from ref. [93]...........................................28

Figure 11 - Image of a bath sonicator (left) and probe sonicator (right). Adapted with permission from ref. [96]. ..........................................................................................................................29

Figure 12 - Image of a laboratory-scale high shear mixer. Gathered from ref. [98]...........30

Figure 13 - Image of graphene foam (left), microscopic Image of graphene foam (right) and SE value before and after bending (bottom). Gathered from ref. [182].................................52

Figure 14 - An explanation of some common types of electric polarizations in a material. Adapted from [192]. ......................................................................................................................58

Figure 15 - Schematic of a shielding material (green) under incidence from an electromagnetic plane wave positioned in air.................................................................59

Figure 16 – Schematic showing the different contributions to EMI shielding ..................60

Figure 17 – Plots demonstrating the dependence SE, R, A and M have on conductivity (a), frequency (b), permittivity (c), thickness (d) and permeability (e). .................................................63

Figure 18 - Schematic depiction of a highly agglomerated graphene nanocomposite. Image produced by author ................................................................................................................69
Figure 19 - Schematic of Maxwell-Wagner-Sillars effects due to the formation of numerous nanocapacitors in the graphite-polymer composites; Reproduced with permission from Ref. [14]................................................................................................. 71

Figure 20 - (a) bright field images taken by the modulated polarization parameter imaging system using 100x objective of a chemically prepared graphene overlapped to 1 to 6 layers on a glass slide, reproduced with permission from Ref. [244]. (b) Single-layer crystallites of graphite on top of an oxidized Si wafer visualized by AFM (scale bars: 1 μm.), reproduced with permission from Ref. [245]. (c) Micrographs of an AFM image of graphene sheets deposited onto a mica substrate from an aqueous dispersion, reproduced with permission from Ref. [109] (d) STM topographic images of a single layer of graphene where a honeycomb structure is observed, reproduced with permission from Ref. [253] (e) SEM images of a graphite flake sample, reproduced with permission from Ref. [254] (f) a representative TEM image of graphene sheets deposited onto a mica substrate from an aqueous dispersion, reproduced with permission from Ref. [109]........................................................................................................................... 80

Figure 21 - Waveguide attached to a Vector Network Analyzer. Gathered from ref. [270]. ..83

Figure 22 - VNA attached to a dielectric probe. Gathered from ref. [271]......................... 83

Figure 23- schematic of a typical open-space EMI measurement. Gathered from ref. [272]. ..84

Figure 24 - (a) Two-point probe schematic. (b) Four-point probe schematic. Gathered from ref. [273]................................................................................................................................. 86

Figure 25 – An outline of the procedure taken in characterization of GnP/Epoxy...............88

Figure 26 - Images of the carbon fibre epoxy resin infusion process. ...............................89

Figure 27 – Screenshot of Shielding Effectiveness GUI..................................................... 96

Figure 28 - Screen shot of FDTD in MATLAB at three different time steps. Red depicts the magnetic field strength and blue depicts the electric field. The shielding object is place at 0.06 with thickness 0.01 and the wave source is a gaussian. ................................................................. 97

Figure 29 - Example R,A,T plots from the FDTD model constructed in MATLAB..........99

Figure 30 - xFDTD software simulation screenshot showing wave propagation after striking aircraft. ..............................................................100

Figure 31 – SEM image of GnP/epoxy. ........................................................................101

Figure 32 – HP 85070A dielectric probe kit attached to HP 8752C Network analyzer.......102

Figure 33 -ROHDE and SCHWARZ ZNB-40 Vector Network Analyzer ......................103

Figure 34 - GnP/Epoxy Conductivity as a Function of Frequency ...............................106

Figure 35 - EMI Shielding of 5-micron GnP/Epoxy at 5wt.%. ........................................107

Figure 36 – AC electrical conductivity of GnP/Epoxy at 6 GHz. .................................109
Figure 37 - Relative Permittivity of GnP/Epoxy at 6 GHz .............................................. 111
Figure 38 – Experimental data showing the SE values of GnP/Epoxy at different weight
loadings of 5-micron GnP at 6 GHz .............................................................................. 112
Figure 39 - Permittivity and AC electrical conductivity of GnP reinforced carbon fibre..... 113
Figure 40 – GnP-5 (3 wt.%)/Epoxy AC Conductivity and Permittivity in the X-band. .... 114
Figure 41 - ABS X-band Relative Permittivity .................................................................. 115

List of Tables
Table 1 – Important values relating to EMI shielding for different graphene/polymers. ....... 55
Table 2 – Summary of electrical conductivities for GnP-loaded polymer composites at various
loadings .................................................................................................................................. 67
Table 3 - Permittivity and AC Electrical Conductivity of GNP/Epoxies at 0.3 GHz .......... 104
Table 4 - Permittivity and AC Electrical Conductivity of GNP/Epoxies at 6 GHz ........... 105
Table 5 - Input Parameters for GnP/Epoxy electrical conductivity model. ..................... 108
Table 6 -Input parameters for GnP/Epoxy permittivity model. ...................................... 110
Table 7 – Permittivity and AC electrical conductivity of GnP reinforced carbon fibre at 0.3
GHz....................................................................................................................................... 112
Table 8 – Permittivity an AC electrical conductivity of GnP reinforced carbon fibre at 6GHz.
.............................................................................................................................................. 113
Table 9 - Relative Permittivity and AC Conductivity of 5-micron GnP/Epoxy averaged over
the X-band............................................................................................................................... 115
Table 10 - Relative Permittivity and AC Conductivity of 25-micron GnP/Epoxy averaged over
the X-band. ............................................................................................................................ 115
Table 11 - Relative Permittivity and AC Conductivity of GnP/PVA averaged over the X-band.
.................................................................................................................................................. 116
Table 12 - Relative Permittivity and AC Conductivity of GnP reinforced Carbon Fibre averaged
over the X-band. ....................................................................................................................... 116
Table 13 - Values of 5-Micron GnP/Epoxy at a loading of 5 wt.% for different frequencies
within the X-band. As predicted by the micromechanical model. ................................. 118
Table 14 - Input Parameters for X-band GnP/Epoxy electrical conductivity model. .......... 118
Nomenclature

\( f \)  
Frequency

\( \rho \)  
Resistivity or Density

\( E \)  
Electric field intensity vector

\( H \)  
Magnetic field intensity vector

\( D \)  
Electric flux density vector

\( B \)  
Magnetic flux density vector

\( J \)  
Electric current density vector

\( \varepsilon \)  
Permittivity

\( \sigma \)  
Electric conductivity

\( \mu \)  
Magnetic permeability

\( \text{SE} \)  
Shielding effectiveness

\( R \)  
Reflection

\( A \)  
Absorption

\( M \)  
Multiple Reflection Factor

\( \eta \)  
Impedance

\( \gamma \)  
Propagation constant or Scaling parameter

\( \alpha \)  
Attenuation or Aspect ratio

\( \beta \)  
Phase constant
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>Filler concentration</td>
</tr>
<tr>
<td>t</td>
<td>Thickness or Time</td>
</tr>
<tr>
<td>ω</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>δ</td>
<td>Skin depth</td>
</tr>
<tr>
<td>S</td>
<td>Eschelby Tensor</td>
</tr>
<tr>
<td>k</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>a,b</td>
<td>Agglomeration parameters</td>
</tr>
<tr>
<td>Gthick</td>
<td>Graphene Thickness</td>
</tr>
<tr>
<td>Ithick</td>
<td>Interlayer Thickness</td>
</tr>
<tr>
<td>F</td>
<td>Cauchy’s cumulative probabilistic function</td>
</tr>
<tr>
<td>τ</td>
<td>Tau function</td>
</tr>
<tr>
<td>p(ω)</td>
<td>Dyre’s hopping function</td>
</tr>
<tr>
<td>l</td>
<td>Parallel / In-plane</td>
</tr>
<tr>
<td>⊥</td>
<td>Perpendicular / Out-of-plane</td>
</tr>
<tr>
<td>N</td>
<td>Number of graphene layers</td>
</tr>
<tr>
<td>Acronyms and Initialisms</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>CNT</strong></td>
<td>carbon nanotube</td>
</tr>
<tr>
<td><strong>GnP</strong></td>
<td>graphite nanoplatelet</td>
</tr>
<tr>
<td><strong>RF</strong></td>
<td>radio frequency</td>
</tr>
<tr>
<td><strong>SE</strong></td>
<td>shielding effectiveness</td>
</tr>
<tr>
<td><strong>EM</strong></td>
<td>electromagnetic</td>
</tr>
<tr>
<td><strong>EMW</strong></td>
<td>electromagnetic waves</td>
</tr>
<tr>
<td><strong>EMI</strong></td>
<td>electromagnetic interference</td>
</tr>
<tr>
<td><strong>VNA</strong></td>
<td>vector network analyzer</td>
</tr>
<tr>
<td><strong>NA</strong></td>
<td>network analyzer</td>
</tr>
<tr>
<td><strong>SNA</strong></td>
<td>scalar network analyzer</td>
</tr>
<tr>
<td><strong>CVD</strong></td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td><strong>GO</strong></td>
<td>graphene oxide</td>
</tr>
<tr>
<td><strong>rGO</strong></td>
<td>reduced graphene oxide</td>
</tr>
<tr>
<td><strong>GIC</strong></td>
<td>graphene intercalation compounds</td>
</tr>
<tr>
<td><strong>TRG</strong></td>
<td>thermally reduced graphene oxide</td>
</tr>
<tr>
<td><strong>CRG</strong></td>
<td>chemically reduce graphene oxide</td>
</tr>
<tr>
<td><strong>PDMS</strong></td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td><strong>PEDOT:PSS</strong></td>
<td>poly(3,4-ethylenedioxythiophene):polystyrenesulfonate</td>
</tr>
<tr>
<td><strong>ABS</strong></td>
<td>acrylonitrile butadiene styrene</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td><strong>HDPE</strong></td>
<td>high Density Polyethylene</td>
</tr>
<tr>
<td><strong>PP</strong></td>
<td>polypropylene</td>
</tr>
<tr>
<td><strong>PU</strong></td>
<td>polyurethane</td>
</tr>
<tr>
<td><strong>PVDF</strong></td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td><strong>PLLA</strong></td>
<td>poly (L-lactide)</td>
</tr>
<tr>
<td><strong>PVA</strong></td>
<td>polyvinyl acetate</td>
</tr>
<tr>
<td><strong>PMMA</strong></td>
<td>poly (methyl methacrylate)</td>
</tr>
<tr>
<td><strong>CFRP</strong></td>
<td>carbon fibre reinforced polymers</td>
</tr>
<tr>
<td><strong>AFM</strong></td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td><strong>SEM</strong></td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td><strong>EMA</strong></td>
<td>effective medium approximation</td>
</tr>
<tr>
<td><strong>OM</strong></td>
<td>optical microscopy</td>
</tr>
<tr>
<td><strong>TEM</strong></td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td><strong>NRW</strong></td>
<td>Nicholson-Ross-Weir</td>
</tr>
<tr>
<td><strong>SCL</strong></td>
<td>short-circuit line</td>
</tr>
<tr>
<td><strong>FDTD</strong></td>
<td>finite difference time domain</td>
</tr>
<tr>
<td><strong>FEM</strong></td>
<td>finite element method</td>
</tr>
<tr>
<td><strong>FVM</strong></td>
<td>finite volume method</td>
</tr>
<tr>
<td><strong>FIT</strong></td>
<td>finite integration method</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

This section covers the research background which includes the developments in the field leading up to what it is today. This is followed by a thesis outline which covers the significance of the research, the research objectives and a summary of the chapters to come.

1.1 Research Background

In the 1920s, the radio became a common household appliance, bringing people’s attention to how radio frequency (RF) radiation interferes with electronic devices. Electromagnetic (EM) waves are formed when changing electric and magnetic fields caused by the movement of charge perpetuate each other. James Clerk Maxwell’s work led to the finding that these EM waves are light, covering the full spectrum from low-frequency radio waves to gamma rays. Modern broadcast technology typically relies on radio frequency and microwave frequencies up to about 20GHz. With a vacuum velocity of \( \approx 3 \times 10^8 \) m/s, electromagnetic energy is continually travelling around us.

The first-ever known recorded experiments on electromagnetism were in 600 BCE by the ancient Greek scientist Thales. His experiments involved rubbing fur on substances to generate static electricity. He noted that charged substances attracted dust and hair. Roughly 200 years later, over the other side of the globe, Chinese navigators used loadstone compasses. In the 17th and 18th Century many experiments were conducted on different materials and their electromagnetic interactions with each other. This includes the work by William Gilbert, Benjamin Franklin, Charles-Augustin de Coulomb, Luigi Galvani and Alessandro Volta. By the late 19th century, a strong empirical foundation of electromagnetism was formed, electronic technology including circuits, batteries and lightbulbs were becoming available. Along with this an understanding in the link between electricity, magnetism, and light was beginning to form. In 1873 James Clerk Maxwell published “Treatise on Electricity and Magnetism” [1]. In which Maxwell summarized the work of those who came before him into a series of equations, creating a robust theoretical understanding of the field which ultimately lead to what is still today the basis of modern electromagnetism. By understanding the interaction between electric and magnetic fields, Maxwell postulated the existence of a wave created by this interaction. It just so happened that mathematically solving for the wave’s speed showed that it matched the speed of light as recorded by other experiments happening at the time. Thus, EM waves are light, and light is EM waves. This was later experimentally verified By Heinrich Hertz; thus,
the unit of frequency Hz was named in his honor. Ten years later, EM waves were first used to communicate wirelessly with the invention of the radio by Guglielmo Marconi. This system features a battery, spark gap, telegraph key, induction coil and monopole antenna, all depicted in Figure 1.

Figure 1 - Recreation of the first Radio Transmitter built by Guglielmo Marconi. Adapted with permission from ref. [2]

Nowadays, there is ever-increasing proliferation and miniaturization of electronic devices with shorter propagation paths and higher transmission frequencies. For instance, new technology such as the Internet of Things (IoT) and 5G rely heavily on networks of ubiquitous high frequency beamforming antennas. As a result, there is increasing concern about the environmental impact this technology has [3]. EM radiation in the Gigahertz (GHz) range can
cause disruption to anything from microchips, cars, airplanes and ourselves. EMC is therefore imperative to the design of electronic equipment, ensuring the users’ safety and the long jeopardy of the devices. EMC is often considered by modelling transmitter and receiver arrays; this serves as a cost-effective way to ensure EMC in a simulated environment. Alternatively, experimental characterization methods can be implemented in order to test the shielding effectiveness (SE) of the materials present. Although, measuring the propagation of electromagnetic energy in the environment these materials are intended to be used in can be quite difficult, particularly for large parts. It is apparent that there is a necessity for both the modelling of electromagnetic energy and materials which can absorb or reflected unwanted electromagnetic (EM) radiation.

Figure 2 depicts a radio receiver in the center of the image, surrounded by some possible sources of interference. Notably, interference can come from both conducting and radiative sources. Lightning, radio and tv broadcast, mobile radio, ignition, and electric motors are sources of radiative interference. While conductive noise from the AC power circuit that supplies the radio receiver, is a possible form of conductive noise. In this case, the power line could be categorized either as a conductive or radiative source.
Figure 2 - a visual representation of some possible EMI inducing features in a common environment. Adapted with permission from Ref. [4]

EMI is a serious threat to airplanes as malfunction caused by EMI could very easily be fatal. Airplanes navigation systems such as autopilot, course deviation indicator, compass, horizontal situation indicator, instrument landing system, EFIS have all reported having experiences interference from portable CD players, computers, portable radios and phones [5]. Obviously, this is undesirable as pilots strongly rely on these systems to steer, land and take off the airplane.

EMI shielding is achieved by minimizing the signal passing through a system either through surface reflections or absorption of the radiated power [6]. EMI shielding materials contain mobile charge carriers and/or polarization losses which limit the transmission of these Hertzian waves.

Great effort has been dedicated to the development of EMI shielding materials [6]. Shielding materials have applications ranging from commercial appliances all the way to quality information technology, defense safety systems and the aerospace industry. Metal-based components in the form of a sheet, screen or foam are regarded as established shielding materials due to their high conductivity. Of the metals used for shielding, galvanized steel and aluminum are the most cost-effective and widely used [7]. However, their weight penalty, lack
of flexibility, corrosion susceptibility and processing difficulties restrict their applications [8, 9] and ultimately lead to undesirably high lifetime costs. The emergence of lightweight yet high-performance electroconductive polymer composite offers the possibility of facile fabrication along with lower lifetime costs [10-12]. Such advanced shielding composites are fabricated via the inclusion of conductive fibres, sheets or particles into a polymer matrix. Carbon nanotubes (CNT) and graphene have both recently presented themselves as viable candidates for superior EMI shielding polymer nanocomposite fillers [13, 14]. Although CNTs may enable higher electrical properties than graphene [15], their low yield production, relatively high production costs, toxicity and complex processes hinder their development at a large-scale toward practical applications [16]. The use of graphite nanoplatelets (GnPs) in powder form has recently gained interest as one of the most effective, low-cost, and scalable approaches to produce graphene/polymer composites with enhanced shielding properties. In this regard, one of the main challenges lies in the proper processing of graphene to achieve a uniform dispersion of GnPs within the polymer matrix. This generally means maintaining the aspect ratio of the graphite particles while reducing the agglomeration or restacking of graphene sheets, ensuring percolation at lower filler loadings. Large sheet size graphene allows for higher conductivity as less graphene-to-graphene junctions occur. Unfortunately, large sheet size graphene is more likely to degrade and/or agglomerate during the dispersion stage. Agglomerated nanocomposites have non-uniform properties that vary largely throughout the material, which is depicted in Figure 3 with reference to conductivity. A poor dispersion (red) will give rise to localized areas of high and low conductivity, ultimately leading to an undesirable non-uniformity and higher loadings needed to reach percolation.

![Diagram](image_url)

*Figure 3 – Graphical depiction of the difference in conductivity between homogenous, well-dispersed and poorly dispersed materials. Image produced by author*
The shielding effectiveness (SE) of any material is determined by the sum contributions from reflection and absorption. SE can be determined experimentally, often using a vector network analyzer (VNA) attached to an antenna network with the material placed between the transmitter and receiver. SE can also be determined theoretically by solving Maxwell’s equations analytically or numerically from the bulk properties - conductivity, permittivity and permeability. Likewise, these bulk properties can be measured experimentally or theoretically approximated via knowing the properties of the constituent parts of the composite. Herein, a continuum based micromechanical model is established which allows for the prediction of the bulk material properties based the microscale behavior of graphene polymer nanocomposites. Further analytical and numerical approaches are taken in order to compute the SE of these materials. The constructed models, which predict material properties, work in conjunction with the in situ fabricated materials in order to facilitate a wholistic characterization process, which has both experimental and theoretical components.

Micro and macro scale EMI shielding graphene/polymer composite modeling approaches are constructed in order to complement empirical schemes of fabrication and characterization. Theoretical approaches are particularly valuable as they not only (1) eliminate the need for costly and lengthy experimentation but also (2) provide insight into the micromechanics that influence the macroscopic electromagnetic reflection, absorption and transmission. Various graphene polymer composites are fabricated, and their bulk electromagnetic properties and EMI shielding parameters are characterized.

1.2 Thesis Outline
1.2.1 Significance
Delicacies in both the synthesis of graphene and nanocomposite fabrication processes, lead to a substantial variance in results. This can be attributed to many things. More generally, these factors will fall under graphene choice, the dispersion method and the interfacial properties of the chemical system. In order to push graphene composites closer to commercial application, it is crucial that the processing factors that significantly influence the end properties are well understood. Using analytical methods, the following work outlines the various factors involved in developing functional graphene composites. Starting with the micro-scale electromagnetic behaviour, certain critical factors are pinpointed. Which includes graphene aspect ratio, electron tunnelling, electron hopping, nano capacitance, etc. Graphene nanocomposites are
fabricated in conjunction with this analytical understanding and experimental characterization techniques are used to compare with results with theoretical predictions. The work not only addresses the issues involved in both modelling and fabrication of graphene nanocomposites, but the discrepancies that often occur between analytical predictions and the physical world.

Additionally, in order to push the advantages of graphene materials closer to market it is crucial to demonstrate how this technology can be integrated seamlessly into the existing world. This is done so by 1. Integrating the results from the micromechanical model into a known EMI numerical algorithm and 2. Integrating constructed graphene nanocomposites into/onto composite structures.

1.2.2 Objectives
In order to be able to produce functional graphene nanocomposites for commercial purposes, the material must be understood thoroughly. Therefore, with EMI shielding capabilities as the area of focus, a descriptive picture of the microscopic to the macroscopic is given. Computational modelling is ubiquitous throughout the EM field; therefore, practicality demands that the constructed micro-scale models must be compatible with existing numerical EM solvers. The objectives of the research conducted during this candidature can be categorized as follows:

1. Construction of an optimised model which explores the percolation behaviour of graphene/polymer composites. The model must also be compatible with existing EMI numerical solvers.

2. Development and characterization of GnP enabled EMI shielding nanocomposites containing different concentrations of GnP loadings to validate their properties against the constructed model


Fabrication, characterization and modelling of the graphene polymer composite lead to a comprehensive picture of this material’s capabilities and limitations to be used as an EMI shield, which is the primary goal of this research project.

This work addresses the need for better EMI shields and commercial utilization of graphene.

1.2.3 Sequence of Chapters
The Thesis consists of five chapters.
Chapter 1 gives the background of the research topic “Graphene Composites for EMI Shielding” and describes the direction of research. Addressing the need for a better understanding of the electromagnetic propagation mechanisms in these new materials. The objectives of this research are also outlined here.

Chapter 2 provides a review on the fabrication, characterization and modeling techniques surrounding graphene/polymer EMI shields. Various published work in this area is reviewed and contrasted.

Chapter 3 Includes the research design. It outlines how all the samples were fabricated and characterized. It also explains how all the software was constructed, and an outline of the mathematical modelling used to develop the software.

Chapter 4 includes the results and findings of this research. Plots are presented which show the measured and predicted electromagnetic behavior of the constructed materials. Some words are given on the significance of these trends.

Chapter 5 concludes the work by summarizing the key points and providing a scope for future research.
Chapter 2

Introduction

The following section features a comprehensive overview of the published literature and state-of-the-art methods surrounding the fabrication, characterization, modelling and applications of graphene/polymer nanocomposites. Firstly, a description is given on what is a nanocomposite and why graphene nanocomposites are heavily anticipated materials. Various graphene synthesis and fabrication methods are then extensively detailed. Which includes some discussion of the many forms of graphene and ways they can be combined with different polymers to make different nanocomposites. The potential and current applications of these materials are then discussed. The electromagnetic response of materials is then investigated in order to give a comprehensive picture of what mechanisms are responsible for the blocking of EM waves. A discussion of common analytical and numerical approaches to EM wave propagation modelling is then provided. Following this, a more in-depth look into the micro-scale electromagnetic properties of graphene nanocomposites is given. Lastly, a review of some common experimental characterization methods for EMI shielding is given. This serves to investigate the many physical, chemical and computational facets of graphene enabled EMI shielding materials.

2.1 Composites

Composites are materials consisting a combination of two or more natural/ artificial elements with different physical or chemical properties, where the component materials combine and contribute their most useful traits to enhance the properties of the final product for a particular application. Composite materials have been utilized by humans for at least as long as recorded history. Ancient Mesopotamian and Egyptians both utilized the combination of materials to create such things as plywood, straw reinforced mud brick and pottery and face masks. Such materials allowed for better technology which ultimately led to a stronger society. One such example is the Mongolian composite bow made in 1200 AD by the Mongols [17]. This bow was made from a combination of bone, glue and wood and infamously ensured Genghis Khan’s reign. With the emergence of plastics in modern times, composite materials have seen a resurgence. Which is largely due to the inherent brittle nature of plastics. Therefore, reinforcements are needed for large scale structural applications. In 1935 Owens corning combined glass fibres with polymer to create some of the first modern plastic composites, now known as fibreglass. The demands of World War two included the need for materials that
possessed high strength to weight ratio. Which was the key motivation to bring fibreglass into mass production.

Classification of composite materials occurs at two different levels; the first criterion of classification is based on the matrix constituent. The leading composite families include organic matrix composites (PMCs), metal matrix composites (MMCs), and ceramic matrix composites (CMCs). The term OMC typically refers to two classes of composites, including polymer matrix composites (PMCs) and carbon matrix composites, so-called carbon-carbon composites. The second criterion is based on the reinforcement phases; here, fibre-reinforced composites (FRCs), laminar composites, or particulate composites are distinguished. FRC can be further separated into those containing discontinuous or continuous fibres, respectively, as reinforcements. Figure 4 [18] features images of a PMC, CMC and MMC. In Figure 4 (left) a magnified image the fibre reinforcement structure can be seen.

![Figure 4 (left) polymer matrix composites (PMCs), (middle) ceramic matrix composites (CMCs), and (right) metal matrix composites (MMCs) gathered from ref. [18]](image)

2.2 The Birth of Nanotechnology

Nanotechnology has emerged in the last decades of the twentieth century with the development of new enabling technologies for imaging, manipulating, and simulating matter at the atomic scale. These new technologies enabled nano-scale fabrication and characterization and led to many discoveries in the field of nanomaterials. The mechanisms behind what gives matter at the nano-scale different physical and chemical properties to its larger counterparts have become apparent. All materials possess different behaviour at this size; however, the most drastic changes are observed in conductors and semiconductors. Some of the novel characteristics of nanomaterials include electron confinement and surface plasmon resonance [19]. Due to their size, nanomaterials can be challenging to handle throughout production and application. One such idea to handle nanomaterials is to embed them into larger matrix materials. This leads to what is described as nanocomposite. While nanocomposites themselves have existed for many
years, with examples including Damascus swords and stain glass windows, the potential to utilize nanocomposite technology has still not yet been met.

The simplest of nanocomposites, being a two-phase nanocomposite, possess two components, a filler material and matrix material. The goal is to mix the materials in such a way that the desired properties of both materials are maintained in the resulting nanocomposite. In addition, it is sometimes observed that the resulting materials can possess synergistic effects whereby the resulting material’s properties outweigh the sum of each of its components.

2.3 Carbon-based Nanofillers
Carbon is extremely versatile, it can be both insulative and conductive, depending on its molecular binding and functionalization. It can be added to polymer matrices to form a nanocomposite which maintains the properties of the carbon source. Carbon atoms can form up to four covalent bonds with each other in various ways. Three common allotropes of carbon are diamond, graphite and amorphous carbon. The different molecular structures present in each allotrope give rise to varying properties. Diamond has a strong periodic crystalline structure, while graphite is made of stacked flat sheets of carbon atoms, and therefore, has anisotropic behaviour, while amorphous carbon possesses no crystalline structure. These various carbon structures can also be made into nanoparticles, with known nanoforms including but not limited to nanodiamonds, carbon nanotubes, fullerenes, and graphene. Researchers have made various efforts to utilize carbon to create both nanocomposites and composites. Among nanocarbon materials, graphene and CNT are the most widely researched in the field of nanocomposites due to their superior chemical, thermal, physical, and electrical properties. As electrical conductivity is a criterion of EMI shielding, these two materials are the most often found in carbon nanocomposite EMI shields. As mentioned, CNTs may enable higher electrical conductivity than graphene [15], though their low yield production, relatively high production costs, toxicity and complex processes hinder their development at a large-scale toward practical applications [16]. Graphene possesses a large surface area to volume ratio (mono-layer graphene has the largest of any material), relatively low-cost and simple processability. Along with its superior electrical, mechanical, and thermal properties, graphene is proving to be a nanofiller of the future. As it stands, platelet agglomeration and poor interfacial adhesion serve as the biggest inhibitors to a good dispersion [20]. More work needs to be done in this area in order to bring the benefits of graphene to market.
2.4 Graphene
A carbon atom has six electrons across the 1s², 2s², 2pₓ and 2pᵧ orbitals. Bringing carbon atoms together results in the promotion of one electron from the 2s orbital to a 2pₓ orbital. The formation of graphite results in three sp² orbitals created by the hybridization of the 2s², 2pₓ and 2pᵧ orbitals. The sp² hybridized orbitals form the strong in-plane bonds, while the 2pₓ orbital creates the weaker out of plane bond between graphite sheets. Pulling apart the weak bonds graphite sheets results in graphene. In graphene, the 2pₓ electrons are no longer used for bonding and are what give graphene its unique electrical and optical properties.

Graphene has been labelled and marketed as a wonder material ever since it was first unambiguously synthesized in 2004. The combination of multifunctional properties offered by graphene made it one of the key enablers for many applications, generating new products that cannot (or maybe difficult to) be obtained with current technologies or materials. Extensive research in the era has pushed technological development and scientific research as it continues to do so today, becoming increasingly prevalent in all areas of technology. Some of these include coatings, composites, energy storage, electronics, water purification and thermal management. Saying that the creation of new disruptive technologies based on graphene materials is conditional to overcoming several challenges throughout the value chain, modelling, safety protocols, etc.

2.5 Graphene Materials Synthesis
It is widely known that graphene quality and its intrinsic properties are strongly affected by the synthesis method chosen. Graphene materials are produced either by the bottom-up assembly of carbon atoms, or top-down methods, which involve the treatment of graphite ore to produce graphene. Chemical vapour disposition (CVD) is the most common of the bottom-up approaches that has been extensively studied in literature for the synthesis of graphene. One of the biggest benefits of bottom-up approaches is that fine control over a small number of atoms is often achieved, though sophisticated equipment is often needed to so. Top-down approaches may be considered less environmentally friendly as they rely on graphite or as precursor, although currently they remain the cheaper and more scalable than bottom-up approaches. Common top down approaches can be categorized under chemical synthesis, chemical exfoliation and mechanical exfoliation [21], though it a combination of approaches is often found.
2.5.1 Bottom-Up Approaches of Graphene Synthesis

Several bottom-up approaches have been reported in the literature for graphene synthesis, which includes pyrolysis, epitaxial growth, and CVD [21] (discussed below). Pyrolysis is the use of elevated temperatures to decompose materials, which is sometimes found to be assisted by using an acid. Epitaxial growth is a form of crystal growth whereby the crystalline structure is made with a well-defined orientation relative to the substrate’s crystalline structure [21]. Chemical vapour deposition is a specific type of epitaxial growth commonly used for the synthesis of high-quality, high-performance, solid graphene materials, typically under vacuum [21]. These methods are briefly discussed in the following sections.

2.5.1.1 CVD Graphene

CVD is the most common bottom-up approach for graphene synthesis. In this method, a carbon-containing precursor is turned into a gas. The gas is then injected into a chamber whereby the carbon atoms fall and undergo nucleation on a substrate, while all other atoms pass through the chamber outlet. These leaves large-area monolayer or multilayered graphene sheets. The electrical conductivity here is limited by grain boundaries in the polycrystalline graphene formation [22]. CVD methods can produce graphene with almost defect-free large surface areas, though they involve high production costs and sophisticated operational setups. In addition, handling high-quality graphene from its substrate into a polymer matrix will be a delicate process, often involving the degradation of the graphene structure and properties. Despite this, CVD graphene composites have shown some of the highest reported conductivity values of all graphene composites at 810 S/m [23] and 420 S/m [24].
Figure 5 - (a) A schematic of a typical thermal CVD setup. (b) Schematic of a typical plasma CVD setup. Gathered from Ref. [25]

Figure 5a shows a typical CVD setup that features gas inlets and outlets along with mass flow controllers for monitoring gas levels. In addition to that, it also features a system for heating the substrate holder and gas along with temperature sensors to gauge the heating. Figure 5b depicts a CVD system that uses plasma to decompose the gas source, instead of heat. Plasma sources may include radio frequency discharges, pulsed discharges or microwave discharges [25]. A major advantage of this system is that it requires less heat than a thermal CVD machine.
Many factors are involved in achieving the desired material from this method, including proper handling during the transfer from substrate, adequate pressure and temperature in the chamber, choice of substrate material, and choice of gas.

Ermk, J. et al. [26] compared the microscopic inhomogeneities and electrical properties of graphene produced by plasma and thermal CVD. It was reported that although thermal CVD produced graphene appeared more inhomogeneous, meaning it possessed a larger number of microscopic grain boundaries, plasma CVD had undesirable non-conductive openings. Ultimately, the plasma CVD graphene had electrical conductivities two order of magnitudes lower and was thicker. Development in both thermal and plasma CVD approaches are still underway.

Figure 6 - Schematic representation of graphene synthesis processes by the (a) "bottom-up" and (b) "top-down" approaches. Reproduced with permission from Ref. [27].
2.5.2 Top-down Approaches of Graphene Synthesis

Top-down methods focus on breaking a graphite precursor into atomic layers from a stack (see Figure 6 - Schematic representation of graphene synthesis processes by the (a) "bottom-up" and (b) "top-down" approaches. Reproduced with permission from Ref. [27]. [28]. Top-down approaches offer high-quality monolayer graphene but have difficulties in forming products with consistent properties, have low-yield and rely heavily on tedious procedures [29]. Some commonly found graphene products with scalable production methods are achievable through top-down approaches, some approaches are shown in Figure 7. These materials include graphene oxide (GO), reduced graphene oxide (rGO) and GnPs. GO is highly functionalized, hydrophilic and readily exfoliated in water, yielding stable GO dispersions, which are often produced either by Hummer’s, Brodie’s, Staudenmaier’s, or similar methods [30]. GO possesses a much lower conductivity which is unsuitable for many potential applications, in which conductivity is a requirement [31]. Therefore, the functionalization must be reversed via thermal [32, 33] or chemical reduction [34-36] approaches, producing rGO. A maximum conductivity of $6 \times 10^4$ S/m has been reported for rGO through chemical reduction [37].

![Diagram of graphene synthesis process](image)

**Figure 7 - an outline of some of the processes involved in top-down graphene synthesis. Image produced by author.**

In contrast, alternative methods can be used to produce GnPs. These are often produced by a combination of chemical, mechanical and thermal treatment of bulk graphite [28]. This can be generally considered as a more cost-effective and less wasteful strategy as the production process requires less steps and involves less harmful chemicals. In particular, GnPs have recently shown substantial potential as a low-cost and effective filler for the production of multi-scale smart composites [38].
2.5.2.1 Chemical Synthesis

Established chemical synthesis methods can only produce GO, which can then be later reduced to produce electrically conductive graphene. The synthesis of GO was first demonstrated by Brodie [39] in 1859, which involved graphite, potassium chlorate and nitric acid. Staudenmaier later improved upon this method [40]. Today Hummers method is the most used method for the synthesis of graphene oxide, which involves KMnO₄ and NaNO₃ oxidation of graphite concentrated in H₂SO₄ [41]. Even though these methods resulted in the synthesis of high-quality defect-free graphene, they all involve the use of toxic chemicals. More recently, efforts have been made to look for greener graphite oxide production methods [30].

2.5.2.1.1 GO Reduction

There are various ways to reduce GO into rGO, some of which are described below. A more comprehensive overview of the broad range of GO reduction strategies can be found here [42]. The thermal reduction strategies investigated include thermal annealing, microwave and photoreduction. The chemical reduction strategies include chemical reagent reduction, photocatalyst reduction, electrochemical reduction and solvothermal reduction.

2.5.2.1.1.1 Thermal annealing

Thermal annealing is a commonly found approach used to reduce GO into rGO. The process can be relatively simple, involving the rapid heating of GO which supplies enough energy to the oxygen-containing functional groups attached to the graphene sheets. This allows both the separation of graphene sheets and the evaporation of oxygen-containing functional groups. It is predicted that a pressure of 2.5 MPa is enough to separate GO layers [43]. Thermal annealing can be used to produce large quantities of graphene from GO, though it is often found that the graphene sheets are small in size and wrinkled [44] due to carbon atoms from the graphene plane being removed during the decomposition of oxygen-containing functional groups [42]. It is predicted that roughly 70% of the graphite oxide mass remains after this process [44].

2.5.2.1.1.2 Microwave reduction

Microwave reduction is another widely studied method for reducing GO to produce graphene. Here Microwaves irradiation is used as the heating source as opposed to conventional heating methods. Which may allow for the heating across the GO to be more uniform and rapid [42]. In 2010, Zhu et al. [45] demonstrated a facile method for simultaneous exfoliation and reduction of GO using a conventional microwave oven. The reduction process took as little as one minute. The authors then went on to use this graphene to produce ultracapacitors, demonstrating its adequacy for application.
2.5.2.1.1.3 Photo Reduction

Similar to that of microwave reduction, it is found that optical frequency light can also be used to reduce GO. A high-power flash from a commercial flash supplies enough heat to induce the reduction process. A method which is utilized by Cote et al. [46] in order to synthesize electronic components directly onto polymer substrates. Here, a flash from a Xenon lamp triggers the deoxygenation process instantaneously while also fusing the conductive material to the polymer substrate. A significant advantage of this process is that a conductive pattern can easily be printed onto the polymer substrate using a light shield. The reported electrical conductivity of the produced pattern is roughly 10 S/cm. Which is at adequate levels for EMI shielding.

2.5.2.1.1.4 Chemical reagent reduction

Using chemical reagents is another alternative to reducing GO into graphene. As the process relies on the chemical reaction, it can take place at room temperature and therefore, sophisticated equipment is generally not needed. Which can be a possible route for saving cost. The most common chemical used for this process is hydrazine [42]. Both hydrazine and some of its derivatives, including dimethylhydrazine and hydrazone hydrate have been used to partially reduce GO. In addition, metal hydrates such as sodium borohydride, sodium hydride and lithium aluminium hydride have been investigated and proven to be strong reducing reagents. Unfortunately, they are all strongly reactive with water, which is the main dispersion medium used for GO. It is reported that reduction using hydrazine as the reagent was able to produce reduced graphene oxide films with a carbon to oxygen ratio of 12.5 and electrical conductivity of 99.6 S/cm [42]. Interestingly, a paper published by Fernandez-Merino et al. [47] was able to achieve similar results to those reported above by using Vitamin C as a replacement for hydrazine. The use of Vitamin C had various benefits, including non-toxicity, higher chemical stability in water and less rGO sheet agglomeration.

2.5.2.1.1.5 Photocatalyst reduction

The photoreduction process described above involved the direct heating and reduction of GO via incidence under a flash of light. Alternatively, approaches whereby photocatalysts are used to facilitate photochemical reactions which cause GO reduction, have also been investigated by scientists. One such commonly used photocatalyst includes titanium dioxide (TiO₂) [42]. Under incidence from UV light, charge separation occurs on the titanium surface. If submerged in ethanol, the holes are gathered in order to produce ethoxy radicals. Which leaves a high density of electrons on the TiO₂, which react with the functional groups within GO, ultimately
leading to reduced graphene oxide. This process is explored by William et al. [48], whereby a colloid of reduced graphene and TiO$_2$ in ethanol is achieved.

2.5.2.1.1.6 Electrochemical reduction
Oxygen-containing function groups present in GO were found to be practically removed via electrochemical processes. Which has been investigated by various researches [49], [50], [51], [52]. The reduction process is made possible by an electrochemical cell and an aqueous buffer solution. After a thin film of GO is deposited on a substrate, which serves as one electrode component in the electrochemical cell. It was found that the maximum reduction of GO occurred at -0.87 V in a 0.1M KNO$_3$ solution [52].

2.5.2.1.1.7 Solvothermal reduction
The last of the GO reduction methods described here is solvothermal reduction. This method has been explored by various researches [53], [54], [55] and is often noted as being both simple, along with the potential of being environmentally friendly. The reduction process here involves placing GO in a sealed container with a solvent and heating the solution past the solvents boiling point. Zhou et al. [55] investigated this process using water as the solvent. The findings paved the way for a possible green chemistry route of reducing GO. It was reported that not only where functional groups removed, but some aromatic structures in the graphene lattice were also recovered.

2.5.2.2 Chemical Exfoliation
Chemical Exfoliation relies on graphene intercalation compounds (GICs), which will intercalate into the graphite layers and assist in the exfoliation process. GICs can include alkali metals, organic solvents, ionic liquids and strong acids. The GIC used strongly depends on the process involved. Chemical exfoliation methods will always rely on the assistance of thermal, mechanical, or electrical energy to break apart the graphene layers, which will be subsequently dispersed in a liquid. Below a description and comparison of each of the different GIC’s is given. A key benefit of this method is that it eliminates the functionalization and reduction steps along with any graphene sheet defects that may occur during these processes.

2.5.2.2.1 Alkali Metals
Alkali metals are commonly found as effective GICs. This may include, though, is not limited to KCl, LiCl, RbCl, NaCl, and CsCl. Generally, alkali metals have small ionic radii, which means they can fit in between graphite layers more easily. In 2012, Park et al. [56] demonstrated a scalable process for the production of a graphene conductive film using alkali
metal as the intercalation compound in the exfoliation process. It was reported that high-quality flakes were synthesized from graphite using KCl–NaCl–ZnCl$_2$. The graphene structure was confirmed by X-ray diffraction and was able to produce a transparent conductive film with a transparency of roughly 75% and electrical conductivity of roughly 930 Ω/□. More recently, Dalal et al. [57] adopted an electrochemical exfoliation process whereby graphite foil was exfoliated into graphene flakes with the assistance of KCL and a driving voltage to further facilitate the intercalation. The result was graphene, with an average of 10-13 layers.

2.5.2.2.2 Organic Solvents
Organic solvents have found to be effective at exfoliating graphite into graphene [58], [59], [60]. Some commonly found solvents used include N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF). Choi et al. [58] investigated 1-propanol as a solvent for the direct synthesis of graphene from graphite. It was reported that a homogenous graphene dispersion was achieved after sonication of the solution followed by centrifugation in order to remove the solvent. On the other hand, Xu et al. used CO$_2$ expanded NMP as the graphite intercalation solution and found that when paired with mechanical agitation and sonication, they were also able to successfully synthesize few-layer graphene.

2.5.2.2.3 Ionic Liquids
Research has also been conducted to apply ionic liquids as GIC’s [61-64]. In 2015, Matsumoto et al. [63] demonstrated the synthesize of graphene from graphite with a 93% exfoliation efficiency using microwave irradiation paired with molecularly engineered oligomeric ionic liquids. Here, a high concentration of single-layer graphene was synthesized in less than 30 mins. Earlier work using ionic liquids was unable to achieve monolayer graphene, thus showing that the novel idea of using molecularly engineered ionic liquids provides a better yield of high-quality graphene.

2.5.2.2.4 Strong Acids
Effective exfoliation of graphite into graphene has also been achieved via the use of strong acids [65-67]. Yang et al. [65] utilized 1-pyrenesulfonic acid sodium salt in order to achieve a stable dispersion of few-layer graphene in water with an exfoliation efficiency greater than 70%. The authors suggested that this solution would be best suited for inks in tattoo-based electrochemical sensors. Roughly five years later, Zhao et al. [67] used a similar method to achieve a stable dispersion of few-layer graphene in water with an exfoliation efficiency of 92%. Here the acid used to assist in exfoliation was tannic acid. Both methods used sonication to influence the dispersion process.
2.5.2.3 Mechanical Exfoliation/Cleavage

The famous “scotch tape” method was the first method used to isolate and observe single and few-layer graphene [68]. Mechanical exfoliation methods have since been improved upon [69], though issues of scalability still remain. Here, top-down graphene synthesis methods have been broken down into chemical synthesis, which involves the oxidization and sometimes reduction of GO; chemical exfoliation, which involves the use of chemicals to exfoliate graphite directly into graphene; and lastly, mechanical exfoliation, which uses shear forces to break apart graphite layers. As mentioned, various processes are often used together to achieve the synthesis of graphene. For example, using shear forces from sonication in conjunction with exfoliating chemicals. Though, there are examples of further exploration into pure mechanical methods of graphene synthesis that more closely resemble the “scotch tape” method. One such example can be found in the study performed by Jayasena and Subbiah [69]. This method involved a sharpened single-crystal diamond energized by ultrasonic vibrations to mechanically cleave pyrolytic graphite into graphene layers. AFM, TEM and Raman spectroscopy were all used to confirm and characterize the obtained graphene, which had a thickness in the order of tens of nanometres.

2.5.2.4 GnP Synthesis

The use of GnP has recently become one of the most effective, low-cost, and scalable methods for the production of graphene-based materials. The main method for the GnP synthesis is mechanical cleavage, which is then often followed by chemical exfoliation [70]. Another commonly found approach for GnP synthesis is plasma exfoliation [70], which has not been discussed here yet. Which is a one-step, dry processing method that allows for the cheap production of GnP. It takes place in an RF or microwave plasma reactor with vacuum conditions applied to remove any contaminants. Functionalization & synthesize of GnP can take place in this one step.

It can be concluded that there are many methods to achieve many different types of graphene. Top-down methods, which rely on the treatment of bulk graphite often involve a multitude of thermal, mechanical and chemical processes. At the same time, bottom-up methods can yield quality graphene in fewer steps without the need for a graphite precursor. However, issues of scalability and cost remain. There is a large variety of processes that can be used to achieve many different forms of graphene. Thus, it is best if the choice of synthesis is directly related to the application. For instance, large flat monolayer graphene may not be best for polymer
dispersions as they will often agglomerate, roll, twist, and crumple in the dispersion stage. Such reasoning influenced the choice of GnP as the graphene type of focus here.

2.6 Graphene Polymer Dispersion Methods
Graphene platelets in the dry, powdery form is the most cost-effective approach to produce graphene-enabled materials. Though, the usefulness of a dry conductive powder is limited, and therefore, it is sensible to disperse the powder into a polymer where it can then be applied in processes and products similar to that of virgin plastics.

An optimal graphene dispersion must be homogenous, as shown in Figure 3 – Graphical depiction of the difference in conductivity between homogenous, well dispersed and poorly dispersed materials. Image produced by author. In graphene composites, Van der Waals forces between graphene particles cause graphene to agglomerate during the dispersion stage. This is undesirable as the required properties intrinsic to graphene will no longer be maintained. In addition, higher loading will be needed to reach percolation. An Ideal dispersion will have a network of connected graphene particles with minimal overlap and twisting, rolling, or bending of sheets. In addition, less connection between sheets is ideal, which can be achieved via larger sheet graphene, though it is often observed that larger sheet size graphene will result in agglomeration, particularly at higher loadings [71]. This leads to an optimal point at which the processing conditions are matched to the materials used, leading to a homogenous dispersion. For example, sonication times which are matched to the aspect ratio of graphene so that it is well dispersed though there is minimal breakage or crumpling of particles. Proper processing of graphene is crucial in achieving a uniform and stable dispersion [31]. Graphene polymer dispersion techniques can be categorized into (1) chemical dispersion methods and (2) physical dispersion methods.

2.6.1 Chemical Dispersion Methods
Chemical dispersion methods can be categorized as methods that use solvents or surfactants in order to create strong interactive links between filler and matrix components. However, they generally possess a low-yield production, relatively high production costs, and complex processes. This hinders their development for large-scale, practical applications [72]. Such Chemical methods can be broken up into covalent bonding methods, including small organic molecules or modified polymers and non-covalent bonding methods, which may include using π-π interactions, ionic bonding, hydrogen bonding and chemical plating [72].
2.6.1.1 Covalent Bonding

Early attempts on the improvement of graphene’s dispersion state relied heavily on the use of small organic molecules such as N,N0-Dicyclohexylcarbodiimide, thionyl chloride, 1-ethyl-3-(3-(Dimethyl amino)-1-propylamine)-carbodiimide and isocyanate [73-76]. Stankovich et al.[76] utilized the organic molecule isocyanate in order to functionalize sheets of GO. The functionalization allowed for a more stable dispersion of GO in polar aprotic solvents, which is often difficult to achieve due to GO’s hydrophilic behaviour. Fourier transform infrared spectroscopy and elemental analysis demonstrated the functionalization of GO’s carboxyl and hydroxyl groups, resulting in amides and carbamate esters, respectively. This work is claimed to be the first example of dispersion of GO in organic solvents, which was achieved via the organic functionalization of GO.

In more recent times, research has moved towards using polymers for the functionalization of graphene materials [72]. Which has the added benefits of further versatility as electrical properties, monomer type, molecular weight and topological structure of polymers can be modified. This is exemplified in the study done by Veca et al. [75], where they demonstrated the functionalization of few-layer graphene using poly(vinyl alcohol) via ester linkages. After functionalization, the obtained graphene material was able to be adequately dispersed in both aqueous and organic solvents. Demonstration and microscopic analysis on functionalized graphene in hot water and DMSO were given. It was further hypothesized that the method would work for a large variety of solvents. Noh et al. [77] developed a graphene dispersion method which they described as solvent-free and was able to achieve a graphene loading of up 20% without significant agglomeration. The method involved mixing dry graphene powder with cyclic butylene terephthalate (CBT) oligomer powder in a mechanical mixer, the dry mixture was then pressed between two hotplates, after which the polymerized materials was obtained. The authors explored different graphene sources, including GnP, GO, and chemically converted graphene (CCG). It was found that CCG possessed the best dispersion properties due to the presence of phenyl groups, while GO came second best due to oxygen-containing functional groups. Though GnP displayed the worst dispersion properties, an adequate dispersion with an electrical conductivity reaching 16 S/m was achieved. These electrical conductivity values were further confirmed with the use of an effective medium model.
2.6.1.2 Non-Covalent bonding

Non-covalent binding mechanism may consist of ionic bonding, chemical plating, hydrogen bonding and π-π interactions. Each bonding type has been explored by various researchers as a method of improving graphene’s dispersion properties.

In the case of utilizing π-π interactions for bonding, graphene’s out-of-plane π electrons are able to bond with organic molecules that have the same conjugated structure [72]. Increasing graphene’s dispersion in water for the removal of contaminants such as copper has been investigated. Humic acid (HA) π-π bonding with graphene was investigated as a functionalization method to increase copper absorption and water dispersion [78]. Through extended X-ray absorption fine structure spectroscopy (EXAFS), it was concluded by Yang et al. that humic acid functionalization increased the copper absorption properties for few-layer reduced GO. However, it had little effect on the copper absorption properties of few-layer GO. The chemical Pyrene is another example of an organic molecule with a conjugated structure able to bond with graphene in a π-π like manner. Which was investigated by Parzis et al. [79], who concluded that Pyrene is superior to other surfactants or polymers in obtaining graphene dispersion in aqueous solvents. In another case, Iqbal et al. [80] were able to increase dispersibility of graphene in polyethylene (PE) utilizing π-π interactions. Which was achieved by mixing the graphene material with PE and oxidized PE, ultimately creating an electrically conductive graphene/PE nanocomposite.

The utilization of ionic bonds has also been investigated as a method to negate agglomeration of graphene particles in dispersions [81-84]. It was first identified by Li et al. [83] that GO’s ability to maintain a stable dispersion in water wasn’t purely due to its hydrophilicity but that the surface carboxyl present in GO has a negative charge which creates a repulsion between GO particles that prevents agglomeration. Ever since then, various researchers have attempted to utilized ionic bonds to obtain a stable graphene dispersion. One such example includes Hassan et al. [84], whereby nanostructures of graphene/polyaniline were synthesized for supercapacitor electrodes. The novel process involved binding cationic PANI nanospheres and anionic GO sheets, followed by the chemical reduction GO into rGO. In other work, Liang et al. [82] utilized an amphiphilic surfactant (quaternary ammonium salt) with positives charges, adding into an aqueous solution of dispersed graphene, then lastly mixing it with the organic solvent trichloromethane. This work was a key step in the realization of non-covalent bonding methods for graphene dispersion.
As chemical plating refers to the metallic plating of graphene for graphene dispersion within a metal matrix, hydrogen bonding is the last of the graphene chemical dispersion methods used to disperse graphene with a polymer matrix. The focus is on polymer matrices, and therefore, only hydrogen bonding methods will be discussed further here. Hydrogen bonding onto graphene allows the joining of organic molecules with graphene oxide via the hydroxyl and carboxyl groups that are present on the graphene oxide surface. Which forms a strong non-covalent bond. Hydrogen bonding mechanisms have been observed and utilized by various researchers in order to disperse graphene throughout various matrix materials [85-88]. Sayyar et al. [87] created a dispersion of graphene throughout chitosan-lactic acid whereby a uniform dispersion was maintained via hydrogen bond between the graphene filler an matrix. This was used to form a conductive hydrogel suitable for bio-applications such as tissue engineering. Kang et al. [86] developed a graphene oxide/carboxylated acrylonitrile-butadiene rubber (GO/XNBR), which possessed strong gas barrier properties and high mechanical strength. This graphene rubber nanocomposite was fabricated by a simple green method that involved the stirring a GO/water dispersion with XNBR, coagulating with CaCl$_2$, then two-roll milled with the addition of 2,4-Dichlorophenol. It was confirmed with Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) that strong hydrogen links were formed between the XNBR matrix and the hydroxyl and carboxyl groups present in GO. In other work, Qi et al. [85] dispersed GO in PVA to produce a water-induced shape memory composite, whereby a strong hydrogen peak was confirmed by FTIR. Liu et al. [88] were able to achieve a uniform dispersion of GO in thermoplastic polyurethane (TPU). The dispersion was maintained by strong hydrogen bonds between the TPU matrix and GO. Thermal reduction of GO was then undertaken to achieve a rGO/TPU with optimized dielectric properties.

2.6.2 Mechanical Dispersion Methods

Outlined below are three commonly found physical methods of dispersing graphene within polymers. Generally, the process consists of dispersing graphene within the appropriate liquid polymer precursor through sonication, milling or high-shear mixing. The curing process is then undertaken with the graphene nanofiller dispersed. With all mechanical dispersion methods, there is a trade between using mechanical agitation to limit agglomeration while ensuring that the mechanical forces do not damage the graphene structure. In addition, it commonly found that a combination of dispersion methods can yield good results. Some mechanical dispersion methods are discussed below.
2.6.2.1 Milling

Milling equipment includes but is not limited to planetary ball milling and three-roll milling, otherwise known as calendaring. The milling process uses mechanical forces to ensure the graphene cannot agglomerate. Ball milling has realised graphene dispersions in many matrix systems. For instance, Guo et al. [89] demonstrated that the ball milling process can disperse GnP into epoxy in order to enhance its thermal conductivity. In comparison, Yu et al. [90] used a ball milling process to produce a ZnO/graphene composite with heightened lithium storage capability. Alternatively, three-roll milling, or calendaring is a process whereby high shear forces are applied to the dispersion via three rolls. This process has shown to be a favourable method in both the dispersion and exfoliation of graphene composites. For example, Li et al. [91] demonstrated a simple methodology that was able to produce GNP/epoxy composites from epoxy and natural flake graphite. Along with superior mechanical and thermal properties, an electrical conductivity of $10^{-2}$ S/m was achieved at graphene loading of 3 wt.%.

![Figure 8 - Schematic diagram of planetary ball mill. Gathered from ref. [92]](image)

Figure 8 is a schematic depiction of a typical planetary ball mill, which consists of two vertical cylindrical reactors attached to a support disk and equally spaced from the centre. It may be found with some planetary ball mills, that there are four vertical cylindrical reactors. The name planetary ball mill comes from the orbital motion imposed onto the balls and cylindrical reactors, which is like planetary motion. Here, two centrifugal forces are present, caused by the support disk rotation and the cylindrical reactor rotation. This phenomenon causes the balls in the reactor to possess a complex motion, which involves two main states of the ball travelling along the reactor wall and secondly, colliding with other balls. Placing two powders in the reactor with the balls will result in a uniform combination of the two.
Mixer mills differ from planetary ball mills in that the motion of the reactor is designed to be more complicated. Figure 9 shows the motion that a typical reactor goes through in one period. This is made possible by securing the reactor to a clamp and inducing high-frequency swinging motion along with a lateral movement. The movement causes both the balls and the sample inside the reactor to undergo complex motion, which involves driven and dampened motion in all three directions. Along with a large occurrence of strong collisions, which ultimately allows for a high degree of powder mixing. Commonly found mixer mills include Retch mixer mill 200 and 400, Super Misuni ball mill and SPEX Mixer/Mill 8000. The SPEX mixer/mill is the most commonly found throughout laboratories [92].
A shown in Figure 10 - Image of a three-roll mill. Gathered from ref. [93], a three-roll mill is a machine that possess three rolls for the dispersion of two or more materials. A significant development for these machines occurred in the 19th century, which involved both the single roll mill and five-roll mill. Today, three roll milling is the most found throughout laboratories. The setup includes the feed roll, centre roll, apron roll, material feed and material outlet. Unlike the ball milling processes outlined above, three roll milling is usually used to disperse pastes, not dry powders. The material feed is between the centre roll and the feed roll, which rotate at different speeds. Due to this difference in rotation speeds, the very high shear force is applied to the material. The material then moved into the space between the centre roll and apron roll, experiencing an even higher shear force. A sharp edge is then used to remove the material from the apron roll.

2.6.1.2 Sonication
Another dispersion method commonly adopted to produce graphene nanocomposites is sonication. Though nanocomposites have been produced with enhanced mechanical, thermal and electrical properties via sonication, this process has not yet been proven to be scalable. Despite this, sonication is a ubiquitous tool in laboratory-scale material science and therefore commonly adopted to produce graphene nanocomposites. Ghaleb et al. [94] investigated the effect of sonication time and filler loading using both graphene nano-powder and carbon nanotubes dispersed in epoxy. A maximum electrical conductivity of roughly $10^{-2}$ was found after only 20 minutes and 1 vol% of GnP filler. It was also reported that although higher
sonication times lead to more homogenous dispersions with fewer agglomerations, GnP damage was apparent at these higher sonication times. Ultimately leading to degradation of the final composite properties. Yue et al. [95] adopted a process whereby graphene and carbon nanotubes where both dispersed in epoxy via a simultaneous magnetic stirring and sonication process. Findings showed that synergistic effects occur at a CNT and GNP ratio of 8:2 whereby the percolation threshold was decreased.

Figure 11 shows two different devices used for sonicating and dispersing materials. On the left is a sonication bath and on the right is a probe sonicator. Both can be used to apply ultrasonic energy to disperse two or more materials. In a bath sonicator, ultrasonic energy is passed through the water and applied to the container which holds the sample. In addition to the temperature and sonication time, the dispersion state will be affected by how much water is placed in the dish, whether there is contact between the container and dish and the location of the container. Therefore, in order to keep the processing condition constant, a clamp is used, as shown in Figure 11. On the other hand, the probe sonicator is placed directly into the sample which means that more tremendous energy is applied. In both cases, it is essential to keep the temperature at levels which do not induce unwanted chemical reactions.

2.6.1.3 Higher Shear Mixing
Higher Shear mixer, or sometimes just “mechanical mixer” is another commonly found piece of equipment used to disperse graphene within polymers. It is often found that graphene dispersions produced via this method will often have higher loadings. Which is due to the higher shear force inducing graphene sheets breakage. The smaller sheet sizes mean higher
loadings are needed to achieve percolation. In saying this, higher shear forces allow for less agglomeration, and therefore, a higher filler concentration. For example, researches produced rubbery epoxy composites using a 15-micron sheet size GnP with an out-of-plane conductivity of roughly 1.1 S/m, at a filler loading of 25 wt.%, using a mechanical mixing process [97]. Interestingly, an in-plane conductivity of around 0.8 S/m was reported. This outcome implies that the GnPs had a slight tendency to orientate themselves perpendicular to the force of gravity during the curing process.

![Figure 12 - Image of a laboratory-scale high shear mixer. Gathered from ref. [98]](image)

A picture of a typical laboratory-scale high shear mixer is depicted in Figure 12. It is commonly found that these instruments are used for the dispersion of a dry powders such as GnPs into a liquid. Similar to the sonication tip, the nozzle or “workhead” is placed inside the sample, and it is ensured that there is no contact between the nozzle and the walls of the sample container. These mixers come with nozzles with different functions, though they all operate on the
premise of applying high shear mechanical forces for dispersion. The mixer featured in Figure 12 is a Silverson L5M-A, which works in a process that involves suction into the workhead, followed by high shear milling via a rotary blade within the workhead, and the expulsion of the milled matter back into the main body of the sample. This process of suction, milling and extrusion can be repeated for prolonged periods of time at different rotary speeds.

2.6.3 Aligned Graphene-Polymer Dispersions

Creating an aligned structure of graphene filler throughout the polymer matrix has recently gained much interest due to the novel and superior properties of these nanocomposites. Such properties may include highly anisotropic behaviour, liquid crystallinity and low percolation thresholds [99]. Yousefi et al. [99] successfully dispersed in rGO in an epoxy polymer matrix in an aligned manner, which yielded a nanocomposite with a SE of 38 dB and a high dielectric constant of greater than 1400 at 3wt% of rGO. The high dielectric constant is attributed to charge accumulation at the filler-matrix interface due to the Maxwell-Wagner-Sillars effect. Which was further increased by the fact that the filler-matrix interface has a large surface area due to the aligned structure. There are various ways to align the graphene particles within the matrix, which may include but is not limited to alignment caused by strategic evaporation of solvents, flow-directed assembly or alignment via electromagnetic fields. Yan et al. [100] demonstrated the fabrication of an aligned graphene nanosheet (GnS)/epoxy composite via a magnetic field. This resulted in a nanocomposite with a high anisotropic thermal conductivity. GnSs were first magnetically functionalized with Fe$_3$O$_4$, allowing them to strongly react with the magnetic field that was applied during the dispersion stage. After the addition of the curing agent, the mixture was stirred for eight hours under a magnetic field of 300mT. The aligned structure was confirmed by Raman spectroscopy and Scanning electron microscopy results. In other work, Wu et al. [101] described graphene flakes alignment throughout an epoxy matrix using the application of an external electrical field during the curing process. It is reported that these nanocomposites exhibited a 60% increase in thermal conductivity and close to 900% increase in mode I fracture toughness from that of the pure epoxy. In addition to a 7-8 order of magnitude increase in electrical conductivity. The fabrication process involved sonication the GnP and liquid resin, followed by calendaring. After which the curing agent was added, and the samples were left in a silicon mould to cure. During the curing process, an alternating electric field was applied to the sample supplied by a signal generator and wideband amplifier. Optical microscopy, TEM and SEM were all employed to observe the aligned morphology.
The electrical conductivity was reported to be roughly two orders of magnitude higher in the direction parallel to the alignment than in the direction perpendicular to the alignment.

### 2.7 Graphene Filler Types and Matrix Materials

This section investigates the various research efforts made to disperse graphene in a range of polymer matrices. CVD grown graphene, rGO and GnPs are the three most studied forms of graphene used in conductive graphene polymer dispersions. The choice of the polymer matrix ultimately depends on the end use. Both thermoset or thermoplastic polymers (or a combination of both) can be used for dispersing graphene dispersions. Thermoplastics are cooled to a temperature at which they solidify, while thermosetting polymers are cured by crosslinking the molecular chains in order to create a solid structure. Also, each host matrix offers different degrees of compatibility with the added filler, viscosity, and physiochemical properties. Acrylonitrile-butadiene-styrene (ABS), high density polyethylene (HDPE), polypropylene (PP), epoxy, polyvinylidene fluoride (PVDF), polyurethane (PU), poly-L-lactide (PLLA), Poly(vinyl alcohol) PVA, Poly(methyl methacrylate) (PMMA), Polydimethylsiloxane (PDMS), polycarbonate (PC), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) etc., are a few of many polymer choices that were used as the host matrix for graphene dispersion. Each can be used as a dispersion matrix with varying degrees of success, which will depend on the interfacial interaction between the graphene and the polymer, along with the details of the dispersion process. In addition, various graphene forms have also been found to be dispersed within metal and ceramics to achieve enhanced properties. Below is a description of some of the efforts made to disperse graphene in polymers for various applications.

#### 2.7.1 Graphene in acrylonitrile-butadiene-styrene

Graphene was successfully dispersed within an ABS matrix by Dul et al. [102]. ABS is commonly used in 3D printing technology, and therefore, the addition of graphene into ABS was done with the purpose of producing the nanocomposite feed for fused deposition modelling (FDM), also known as fused filament fabrication (FFF), machine. It was concluded that the inclusion of GnP enhanced the elastic modulus and dynamic storage moduli. Although, often undesirable stress and strain characteristics were also observed. The GnP dispersion throughout the ABS matrix was done in two steps, compounding then compression moulding. Compounding involved first melting the ABS in a Thermo-Haake Polylab Rheomix mixer, then adding the GnP in the fifth minute. This was left to process for a further five minutes. The samples then underwent compression moulding for a further ten minutes at 190°C. The
resulting nanocomposite then underwent filament extrusion, after which it was ready for fused deposition moulding. In other work, Aumnate et al. [103] fabricated an ABS/Graphene oxide nanocomposite for FDM 3D printing. In this case, a solvent mixing process was utilized whereby a solution of DMF/GO was sonicated together with a solution of DMF/ABS for 2 hours. Which was then dried to obtain a nanocomposite of DMF/GO. The material then underwent filament extrusion, after which it was suitable for 3D printing. It was found that the 3D printing part had enhanced tensile strength and Young’s modulus, though in some instances, agglomerated GO particles caused the extruder to clog. Singh et al. [104] investigated graphene as a potential filler material in order to enhance the electrical and thermal conductivity in ABS 3D printed parts. Graphene used here was synthesized in situ using a chemical exfoliation method involving an ultrasonic bath and NMP as the exfoliating solvent. The authors compared results with two dispersion methods, which were labelled mechanical mixing and chemical mixing. The chemical mixing process involved mixing the synthesized graphene material with the ABS and acetone, after which it was left to dry then fed into the filament extruder. The mechanical mixing method involved placing the ABS and graphene directly into the filament extruder. Both methods showed an increase in both thermal and electrical conductivity in the 3D-printed parts from that of the ABS with graphene inclusion. Though on average, it was found that the chemically mixed nanocomposite displayed a higher electrical and thermal conductivity. Research shows that graphene can be effectively dispersed throughout ABS to enhance different properties, most of which are for the application of 3D printing. This may come with challenges that can include extrusion clogging, decrease in stress and strain at breaking point and adequate dispersion methods.

2.7.2 Graphene in High density polyethylene

HPDE is another widely used thermoplastic polymer, due to its good processability, low cost and good recyclability. In addition, it possesses high chemical stability and non-toxicity. HDPE is, however, a nonpolar polymer, meaning it is difficult to disperse graphene throughout. Despite this, various research groups have succeeded in doing so [105-107]. Bai and Wei [105] employed a solid-state shear mixing technique to effectively fabricate an HPDE/graphene nanocomposite with good mechanical performance. The process involved first milling the obtained HPDE granules into a fine powder using a pan-mill, then adding graphene powder for further milling. The samples were then mixed in a HAPRO melt mixer at a temperature of 180°C for eight minutes at a rotation speed of 50 rotations per minute. This was then followed by compression moulding. Standard characterization methods, including TEM, SEM. FTIR,
differential scanning calorimetric analysis (DSC) and thermal gravimetric analysis (TGA) were undertaken in order to investigate the morphology and test the performance of the fabricated nanocomposite. The mechanical performance was assessed using an RG-L-10 and impact testing using a ZBC-4B, both according to the international organization for standardization (ISO) standards. It was found that the inclusion of graphene leads to a significant improvement in impact strength, elongation at break and yield strength. This method of dispersion, being solvent-free has great potential for large scale application. In other work, Okan [107] effectively dispersed multilayer graphene oxide in HDPE using a thermokinetic mixing process, reporting an increase in the thermal and mechanical properties from that of pure HDPE. Here a custom made Gelimat mixer was used to mix GO with HDPE at different GO loadings. The mixer was set at a rotation speed of 5500 rpm for 45 seconds, maintaining a temperature of 215°C. Parameswaranpillai et al. [106] fabricated a PP/HDPE/ethylene propylene diene terpolymer (EPDM)/GnP nanocomposite with superior toughness. It was reported that the inclusion of GnP improved the loss modulus, tensile toughness and storage modulus. The fabrication of this nanocomposites involved a melt blending process using a Thermo Haake Polylab system. The PP and HDPE were melt-mixed for two minutes, followed by the addition and mixing of EPDM for another two mins, after which the GnP was added and mixed for another four minutes. There have been various efforts to disperse graphene throughout HDPE in order to improve the mechanical and thermal properties. None of the dispersion methods involved solvents, with the most common utilized process being melt mixing.

2.7.3 Graphene in polypropylene

Various attempts to disperse graphene in PP have been made by researchers [108-111]. One such example includes the work by Parameswaranpillia [106] et al. described above, where a PP/HDPE/EPDM/GnP composite was fabricated via a melt blending process. Another example includes the work by Wang et al. [111], whereby the dielectric properties of an in situ fabricated rGO/PP nanocomposite were characterized. Interestingly this material possessed an ultralow percolation threshold of 0.033%. The fabrication method firstly involved the chemical synthesis of GO following the Hummers method, followed by the dispersion of the dried GO powder in water. The GO powder was mixed with PP in addition to hydrazine, which acted as a chemical reduction agent. Which was then mixed in a water bath for four hours at 95°C. The material was then washed, filtered and dried in order to achieve a rGO/PP nanocomposite. SEM, TEM and XRD were all used to demonstrate the homogeneity of the dispersion. An
Agilent 4294A impedance analyzer was employed to measure the complex permittivity. The measurement took place in a furnace so that the effect temperature had on the dielectric properties could be measured. An Alternating voltage of 1V was applied to measure the response from $10^2$ to $10^7$ Hz. The composite with a filler loading of 0.025 vol.% was found to have a dielectric constant of 23 at $10^2$ Hz, which decreased to 4.5 at $10^7$ Hz. This value was increased with a higher filler loading, showing that the nanocomposite with a 0.04 vol.% exhibited a dielectric constant of up to 1500 in the lower end of the frequency range. The imaginary term in the complex permittivity was used to calculate the AC conductivity. It was found that nanocomposites with loadings above 0.03 vol% exhibited electrical conductivity, which remained steady across the frequency range of $10^2$ to $10^7$. The highest recorded AC electrical conductivity was $10^{-2}$ S/m at $10^7$ Hz. Other efforts to disperse graphene into PP includes the work by Achaby et al. [110] and Huang et al. [108], who both employed melt mixing/melt compounding methods. Later, they were able to characterize the electromagnetic properties of their graphene nanosheet/PP composite, reporting a maximum electrical conductivity of 0.36 S/m and EMI shielding effectiveness of 13dB. In another case, Song et al. [109] dispersed graphene in PP by first coating the graphene in PP latex, followed by melt-mixing into a PP matrix. The obtained nanocomposite demonstrated an increase in both yield strength and Young’s modulus of roughly 74% with a filler loading of 0.42 vol.%. 

2.7.4 Graphene in Epoxy

Epoxy has also been investigated extensively as a matrix material for the dispersion of graphene owing to its outstanding properties [112-114]. Epoxy-based graphene composites were first reported in 2007 [115] where Yu et al. used a multistep approach including acid intercalation, thermal exfoliation, physical separation and dispersion to convert natural graphite into few-layer GnPs. A high shear mixing approach was then applied to achieve a homogeneously dispersed mixture of epoxy and GnPs. As-fabricated composites demonstrated enhanced thermal conductivities (with values up to 1.45 W mK$^{-1}$ at low-volume GnPs loadings ($\approx$ 5 vol%) which significantly outperformed CNT-embedded composites. Chandrasekaran et al. [112] described various graphene incorporated nanocomposites using different types of graphene, including GnP and thermally reduced GO and epoxy as the matrix. investigating the fracture toughness and failure mechanisms of each nanocomposite. The epoxy system used was a three-part epoxy which consisted of a diglycidyl ether of bisphenol A (Araldite LY556), an anhydride hardener (Aradur CH917) and imidazole accelerator (DY070) mixed in weight ratios of 100:90:1 respectively. The dispersion method used here was three-
roll milling, which occurred after mixing in a glove box. The speed of the apron roll was set to 300 rpm, and the roller distance varied from 120 microns to 5 microns. After the milling process went through an appropriate number of cycles, the hardener and accelerator were added, the mixture was then degassed and left to cure. SEM images revealed that that rGO possessed a better dispersion state than the GnP, this was attributed to the oxide groups leftover in rGO after oxidation, which leads to better matrix binding. SEM also revealed failure mechanisms which were either attributed to the separation between graphitic layers, crack pinning or shear failure on fracture surfaces. Fracture toughness tests were carried out following the ASTM E397 standard using a Zwick Roell Z0101, revealing the fracture toughness increase to a GnP filler loading of 1 wt.% and decreased thereafter. King et al. [113] also fabricated GnP/Epoxy composites and measured the mechanical properties. They used aerospace-grade epoxy (EPON 862 with curing agent EPIKURE W) in a high shear mixer to disperse and fabricate samples with varying GnP loading from 1-6%. The mixer was run for 40 minutes at 2500 rpm. An increase in tensile modulus from 2.72 GPa to 3.36 GPa was observed for the nest epoxy and epoxy with 6 wt.% GnP, respectively. In other work, Jia et al. [114] was able to fabricate a 3D graphene foam/epoxy composite with an electrical conductivity of 97 S/m at 0.1 wt.% in addition to a 53% and 38% increase in flexural modulus and strength, respectively, at 0.2 wt.% loading. The graphene foam/epoxy was fabricated in a four-step process. Firstly, the graphene was deposited onto a Ni foam template in a CVD chamber, after which the neat epoxy was impregnated into the foam using an acetone solvent. The solvent was then evaporated, followed by the last step, which was the etching of the Ni. The high electrical conductivity and mechanical properties of this nanocomposite can be attributed to the high-quality graphene that is produced in the CVD Process.

2.7.5 Graphene in Polyvinylidene fluoride

Polyvinylidene fluoride PVDF is a high-performance polymer, which possesses low density and low chemical reactivity to its environment. It has been investigated as a graphene dispersion matrix for various novel applications, which includes but is not limited to piezoelectric nanogenerators [116, 117] and electric heating textiles [118]. Kim et al. [118] fabricated a GnP/PVDF-HFP nanocomposite for the purpose of an electric heating textile. The obtained GnP/PVDF-HFP ink was printed onto untreated flame-retardant cotton fabric in a horseshoe pattern. Fabrication of the nanocomposite ink involved first submerging the PVDF-HFP pellets in acetone, which was followed by adding different loadings of GnP for each sample. This study utilized high GnP loadings ranging from 32 to 64 percent. A digitally
controlled hotplate stirrer was then utilized to stir the solution for longer than a week. A knife-edge method followed by a hot press was then used to apply the nanocomposite onto the cotton fabric. It was found that applying a voltage of 5 V to the fabricated electric heating textile with 64 wt.% GnP loading, output a temperature of roughly 48°C. In other work, Achaby et al. [117] fabricated GO/PVDF films and characterized there piezoelectric properties. It is noted that the crystalline structure in PVDF gives rise to piezoelectric properties. The fabrication method involved GO synthesis via hummers method, after which stirring and sonicating in DMF solvent with the addition of PVDF was utilized in order to achieve a GO/PVDF nanocomposite. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used in order to study the crystalline phase transformation. The occurrence of a β-polymorph crystal formation was identified, which is indicative of a piezoelectric behaviour. Later work by Abolhasani et al. [116] demonstrated the optimization of this nanocomposite system for the application of piezoelectric nanogenerators. The fabrication process involved submerging PVDF in DMF solvent, followed by the addition of graphene at different loadings from 0 to 5 wt.%. This was then put through an electrospinning process which yielded graphene nanofibre/PVDF composites. The electrospinning process was controlled at a spinning voltage of 20 kV, a working distance of 17cm and a feeding rate of 1ml/h. In addition to common characterization techniques (SEM, TEM, FTIR, DSC and XRD), a characterization process was developed for the electrical output of these nanocomposites. It was found that the optimal graphene loading was at 0.1 wt.%, which led to an increase from 3.8V to 7.9V in electrical output compared to that of neat PVDF nanofibres. The fabricated nanocomposite was used in parallel with a rectifier and charged a capacitor, which provided enough power to light an LED for 30 seconds. Graphene/PVDF composites show great novelty in their applications, most of which are fabricated via solvent methods.

### 2.7.6 Graphene in Polyurethane

PU has been used as a graphene dispersion medium for various applications [119-121]. Yao et al. [120] fabricated a graphene/polyurethane sponge for the purpose of a flexible pressure sensor. The fabrication process utilized what they labelled as a fracture microstructure design. The facile and cheap fabrication process involved dip coating a commercially available PU sponge in a solution of highly concentrated graphene oxide, which was followed by centrifugation and drying to remove any unwanted GO solution. The product was then submerged in hot hydrogen iodide in order to chemically reduce the GO. Lastly, to obtain the dense and fractured microstructure for heightened sensitivity, the sponge underwent
hydrothermal treatment followed by strain compression. This yielded a flexible graphene-based sponge with an exceptional sensitivity of 0.26 kPa$^{-1}$ at pressures less than 2kPa and a minimum detectability of 9 Pa. Later on, Yang et al. [121] fabricated a graphene/PU foam for the purpose of oil-water separation. The obtained PU sponge was coated in an in situ fabricated GO dispersion, ferrous ions were then used as a reduction agent, which gave the nanocomposite sponge its magnetic properties. The material demonstrated a high level of hydrophobicity and oleophilicity. Li et al. [119] fabricated three different graphene/PU composites and characterized their applicability as an anticorrosive composite. The composites included GO/PU, mildly reduced graphene oxide (rGO)/PU and functionalized graphene (FG)/PU. Waterborne PU was mixed with each of the graphene types and magnetically stirred for 30 minutes. They were each then coated onto electrogalvanized steel for characterization. Electrochemical impedance spectroscopy was used in order to characterize the corrosion properties. It was noted that all fabricated composites demonstrate good anticorrosive properties, with GO and rGO performing the best due to a better dispersion state.

### 2.7.8 Graphene in Polylactic acid

PLA is becoming more popular as it can be synthesized from renewable sources and is suitable for 3D printing applications. Naturally, various researchers have investigated optimizing PLA’s properties using GnP as a reinforcement. This is exemplified by the work done by Fu et al. [122], whereby functionalized graphene was dispersed in PLA in order to improve the electrical conductivity. Herein, a novel surface functionalization method was developed, which gave control over graphene’s dispersibility. Graphene was functionalized using silane in the presence of an ionic liquid. PLA was then mixed into the solution and compounded using an extruder (HAAKE Rheomex CTW5 minilab II). A screw speed of roughly 150 rpm was used at 180°C for 5 minutes. Compression moulding was then later applied for impedance spectroscopy analysis. The impedance analysis was conducted using A Novocontrol Technologies dielectric impedance analyzer (model Alpha-N) with a voltage of 1V and a $10^{-2}$ to $10^{6}$ Hz frequency range. The reported AC electrical conductivity was on the order of $10^{-4}$ S/m for the composites with 5 wt.%, and the dielectric constant was roughly 18. Prashantha and Roger [123] demonstrated a graphene/PLA nanocomposite in a commercially available FDM 3D printing system and measured mechanical, electrical and EMI shielding properties. The nanocomposite was purchased from a commercial supplier Blackmagic3D Inc., it possessed a graphene loading of 10 wt.%. The graphene type used was identified, though it is marketed as being conductive. The nozzle diameter was 0.4mm and was set to 210°C. The print
bed temperature was set to 60°C. A two-probe system was used to measure the volume resistivity. An impedance bridge was used to measure the dielectric properties, and a vector network analyzer (VNA) attached to a waveguide was implemented to measure the EMI shielding properties. It was found that the volume resistivity in the print plane was 25 ohm/cm while through the print layer was 102 ohm/cm. This was attributed to the alignment of the graphene during the print process. An increase in the dielectric constant from roughly 2.5 to 6.5 was observed in the frequency range of $10^2$ to $10^5$ Hz in comparison to the neat PLA. Lastly, an EMI shielding effectiveness of roughly 16 dB was measured over the x-band (8-12 GHz) frequency range. Paydayesh et al. [124] also investigated PLA as a dispersion medium for graphene. They used a solvent blending method to fabricate GnP/PLA/PMMA nanocomposites, using sulfuric acid, nitric acid and chloroform as the solvents. The samples were dried in Petri dishes and had GnP loadings varying from 0.5 to 4.7 vol.%. Both modelling and experimental techniques were used to characterize the electrical conduction in these materials. The 4-point probe testing was utilized to measure the conductivity, which was roughly 0.5 S/m at a 4.7 vol.% concentration. Various electrical conductivity modelling techniques such as the power-law model, Mumunya model and updated Mamunya model were all utilized, each yielding values ranging from 0.09 to 1.2 for the same material system. Graphene in PLA is already commercially available for 3D printing applications. The reinforced PLA offers heightened mechanical properties and has opened possibilities for low electrical conductivity applications.

2.7.9 Graphene in Polyvinyl alcohol

PVA is a commonly found polymer with good biocompatibility, low toxicity, and water solubility. Graphene has been dispersed in PVA using a range of different processing methods for a various applications. These include but are not limited to anti-flammable materials [125], EMI shielding [126] and humidity sensors [127]. Huang et al. [125] fabricated graphene nanosheet (GnS)/PVA composites and reported that the time to ignition and peak heat release rate (PHRR) had better performance than Sodium Montmorillonite (Na-MMT) and multi-wall carbon nanotube (MWCNT) reinforced PVA. The PHHR of the GnS/PVA nanocomposite with a 3 wt.% loading of GnS displayed a 49% reduction to that of neat PVA. The synthesis of GO was according to the Hummers method. It was then dispersed in a sodium dodecyl sulfate solution under sonication. This was followed by blending PVA pellets with the GO solution and mixing at 90°C for 4 hours. After which, a hydrazine and ammonia solution was then added. The samples were then dried and prepared for cone calorimetry tests. Joshi et al. [126]
were also able to effectively disperse graphene in PVA, yielding a graphene nanoribbon (GnR)/PVA composite that had very high EMI shielding properties. The GnR’s were synthesized via the unzipping of carbon nanotubes, which were formed in a chemical vapour deposition process. The unzipping process occurred in a solution of sulfuric acid and potassium permanganate. The obtained GnR was then dispersed in water at different loadings, followed by the addition of 400 mg of PVA. A VNA was then used to measure shielding effectiveness of up to 60 dB in the X-band with graphene loadings as low as 0.0075 wt.% and samples thicknesses of 0.6 mm.

2.7.10 Graphene in polymethyl methacrylate

Another polymer that is used as a graphene dispersion matrix is (PMMA). This has been explored by various researchers [128-130]. For instance, Tripathi et al. [130] fabricated a reduced graphene oxide/PMMA composites reporting the electrical and mechanical properties. Hummer’s method was used to synthesis GO, after which the GO was reduced using hydrazine hydrate as the reducing agent. The nanocomposites were fabricated using three different dispersion methods, and both were compared. The first involved dispersing the rGO with PMMA using sonication with the addition of Azobisisobutyronitrile (AIBN) as an initiator while also purging nitrogen gas into the system. The second process followed the first, though PMMA beads were added in at a later stage in the process. The third and last method also followed the first method, though a cast moulding process was applied when the prepolymer syrup rGO dispersion was obtained. The casting method demonstrated the best electrical conductivity with a value in the order of $10^{-3}$ at an rGO loading of 2.0 wt.%. It was additionally found that the tensile strength increased to 1 wt.% though decreased thereafter. In other work, Yang et al. [129] applied multiscale analysis in order to further understand the morphological and mechanical properties of graphene/PMMA nanocomposites. The authors used a combination of finite element method (FEM) and dissipative particle dynamics (DPD) to achieve a model that effectively compared the dispersion states of graphene with different functionalization and processing routes. In addition, Young’s modulus and shear modulus of the different simulated nanocomposites could be compared. More recently, Hussien et al. [128] contended that GnP/PMMA composites have potential applicability in optoelectrical, environmental and electronic applications. The fabrication process involved first dissolving the PMMA pellets in chloroform. Afterwards, this solution was left out for the removal of bubbles GnP was added. Which was followed by 5 minutes of sonication at a power of 100 watts. After drying for a day, the samples were characterized using XRD, SEM, double beam spectroscopy
and an LCR meter. The latter two were used to measure the linear optical properties and AC electrical conductivity, respectively. For a photon energy of 5.5 eV the refractive index of the sample with 3.33 wt.% was reported to be rough 12, this may have applications in anti-reflective coatings, solar cells and waveguides. The AC conductivity demonstrated the typical increase with frequency seen across all graphene/polymer nanocomposites. It has been seen that graphene can be dispersed in PMMA using relatively simple dispersion methods. It should be noted that PMMA is a transparent polymer, often used as a replacement for glass. If one wishes to maintain the transparency of PMMA after graphene reinforcement, high-quality graphene must be used, and minimal agglomeration or restacking must occur.

2.7.11 Graphene in Polydimethylsiloxane

PDMS is a silicon-based polymer that has also been explored as a potential dispersion medium for graphene. This has been for the purpose of various novel applications, which includes metacomposites [131], and strain sensors [132, 133]. Wang et al. [133] effectively fabricated GnP/PDMS composites and characterized their gauge factor for the purpose of strain sensing. With a strain range of 2%, a gauge factor of 233 was achieved at a graphene volume concentration of 8.33 vol.%. The fabrication method was described as an evaporation method, whereby tetrahydrofuran was added in order to decrease the viscosity of the polymer, after which it was evaporated in a fume hood. The solution was processed using a sonicator to reach a homogeneous dispersion, then a vacuum chamber in order to remove any unwanted air. In order to characterize the gauge, the piezoresistive properties were measured while the samples were subject to different loadings of elongation. Wu et al. [132] also developed strain sensors using graphene/PDMS composites. The graphene used was a graphene aerogel, it was also reported that the sensitivity could be tailored by controlling the composite’s microstructure. The graphene aerogel was fabricated from GO using what was described as a reduction-induced self-assembly method. The reducing agent chosen was vitamin C. The PDMS was then added using a vacuum infiltration method, whereby the graphene aerogel was submerged in the degassed PDMS during curing for 6 hours. It was found that the microstructure of the composite could be altered by making changes to GO loading or drying conditions. This led to composites of different sensitivity. A more recent and novel application of graphene/PDMS composites includes the work by Sun et al. [131], whereby a metacomposite with negative permittivity was fabricated. This has applications in novel transistors, capacitors, and coil-free resonators. Fabrication involved mixing the polymer precursor, curing agent and heptane in a magnetic stirrer, after which the GnP was added, and the solution was sonicated.
2.7.12 Graphene in Polycarbonate

PC is commonly used building thermoplastic, known for its strength and transparency. Graphene/polycarbonate composites have been developed by various research groups in order to develop new composites with superior mechanical and electrical properties [134-136]. In 2009, Kim and Macosko et al. [134] compared graphite and thermally exfoliated graphene composites fabricated under a melt compounding process. It was concluded that the rGO composites required less filler loading in order to reach percolation and achieve increased rigidity. A year later, Yoonessi and Gaier [135] fabricated thermally exfoliated graphene polycarbonate composites using both emulsion mixing and solution mixing to achieve high electrical conductivity of 51.2 and 22.6 S/m, respectively. Later efforts have been made to achieve electrical conductivities at this level, though reports often show conductivities much lower. For instance, Lago et al. [136] fabricated a graphene polycarbonate composite using single-layer and few-layer graphene via a solution blending method. They reported an electrical conductivity of $10^{-3}$ S/m at a graphene loading of 10 wt.%

2.7.13 Graphene in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

PEDOT:PSS is created by the mixture of two ionomers. It is often used in conductive application as it can carry the charge, it is also transparent. The addition of a graphene filler before curing allows for tuneable properties and leads to novel applications. Some of the applications developed by research groups include transparent solar cell electrodes [137], gas sensors [138], solid-state supercapacitors [139] and transparent photodetector electrodes [140]. Hong et al. [137] demonstrated the fabrication of a graphene PEDOT:PSS composite, which was spin-coated onto indium tin oxide (ITO) substrate in order to make transparent solar cell electrodes. In order to make the graphene/PEDOT:PSS both materials were sonicated together for a 15-minute duration. The spin coating occurred at 7000 rpm for 30 seconds. An energy conversion efficiency of 4.5% was achieved by a solar cell with this material as the counter electrode. Seekaew et al. [138] fabricated graphene/PEDOT:PSS ink which was then used in a commercially available HP Deskjet printer in order to print flexible gas sensors for ammonia detection. The ink was prepared by first dissolving PEDOT:PSS in a mixture of solvents, including dimethyl sulfoxide, ethylene glycol and triton x-100. This mixture was chosen based on its viscosity and printability. It was stirred for 30 minutes at room temperature. A separate solution of chemically synthesized graphene in dimethyl sulfoxide was sonicated for 30 minutes then stirred at room temperature for a full day. The two solutions were then sonicated and stirred together. An ink cartridge from a HP Deskjet 2000 printer was then emptied and
refilled with this ink. The ink was printed onto a transparent and flexible substrate in a particular pattern which effectively acted like a gas sensor. A high ammonia sensitivity of 25-1000 ppm was achieved at room temperature. In other work, Liu et al. [139] developed a solid state flexible supercapacitor using a similar material system. It was noted that the flexible rGO/PEDOT:PSS electrode could be bent without altering the performance. An areal capacitance of 488 mF/cm² was achieved at a scan rate of 10 mV/s. Here, the PEDOT:PSS not only serves as a dispersion medium to prevent graphene agglomeration but serves as a good electrode material due to its excellent electrochemical properties. A bar coating fabrication method was employed, which involved the addition of Ethylene glycol and diethylene glycol dopants, raising the conductivity of PEDOT:PSS from 3.2 S/cm to 230 S/cm. It has been demonstrated that the synergistic combination of graphene and the conductive polymer PEDOT:PSS can lead to various novel applications.

2.8 Graphene’s Environmental Impact
As discussed, graphene and graphene polymer nanocomposites have been prepared and processed using a vast range of synthesis and dispersion methods that potentially impact the environment. Some factors to consider in the processing of graphene composites may include: where is the graphene sourced from? What chemicals and machinery are involved in the synthesis process? What is the impact of the polymer dispersion matrix? How much energy and/or additional chemicals are required during the dispersion process? How sufficiently will the fabricated composite serve its application? In addition to this, there are health risks involved in graphene and a lot of the solvents used in its processing getting into biological systems. Considering this, the full life cycle of graphene polymer composites must be assessed. Various attempts at analyzing the broader impacts of graphene and graphene polymer nanocomposites have been made [141-144], though there is a need to address toxicological and environmental issues before graphene products can be mass-produced [141]. Two specific examples of high impact progression towards environmentally friendly produced graphene include the flash joule heating synthesis of graphene [145] developed by Sun and Hu and the emergence of the sustainable, non-toxic solvent Dihydrolevoglucosenone (Cyrene), which has been identified as an effective solvent for the exfoliation of graphite into graphene [146]. The flash joule heating process is reported to be able to produce graphene from various carbon-containing precursors in a scalable and cost-effective way, requiring 7.2 kJ of energy per grapheme of graphene. While the Cyrene solvent has shown to be more effective at exfoliation than common toxic
organic solvents, including NMP [146], and can additionally be sourced from abundant cellulose.

2.9 Graphene-based disruptive technologies

2.9.1 Graphene Inks and Coatings

Graphene coatings have been utilized for various reasons which, include but not limited to anticorrosion, sensing, EMI shielding and heat management. Glover et al. described the methodology for the development and characterization of an anticorrosion coating to protect iron substrates against cathodic corrosion [147]. GnP was first dispersed in polyvinyl butyral using an ethanol solvent, then applied onto the iron substrate using a bar-cast method, following by room-air drying. Scanning Kelvin probe technique is used to observe and monitor cathodic delamination. It was found that increased GnP volume fractions lead to reduction in the oxygen permeation rates.

Much effort is going into developing graphene-based coatings, which negate the damage on or behind the surface of the substrate due to environmental conditions. These environmental conditions can include heat, UV light, water, oil, physical scratching, microwave or radio waves. Various companies are currently selling graphene coatings for these purposes, including The Sixth Element Materials, Gramor, Graphenano and Electro Conductive Products. One benefit of graphene as coating is that is can be easily painted onto existing structures to enable multifunctional features.

2.9.2 Graphene-enabled Composites

Graphene has been used for research and commercially available composites to introduce a range of structural and functional properties into composites. Graphene composites cover graphene implementation with other materials to optimize properties at spatial scales from the nano to the macro. As one could imagine, the possibilities here are almost endless. Graphene has been used in a range of matrices, including metals ceramics and polymers to develop nanocomposites. Kim et al. [148] fabricated two different types of metal graphene composites by adding monolayer graphene to both copper and nickel, each possessed superior strength. Reports indicate the graphene copper composite, which indicated an ultimate strength of 1.5GPa, while the graphene nickel composite showed even higher strengths of up to 4.0GPa. Both were fabricated by stacking alternat layers of monolayer graphene and metal. Graphene has also been used to enhance the properties of ceramic materials. For instance, walker et al. [149] demonstrated the toughening of silicon nitride ceramics via dispersing and densifying
GnP and silicon nitrite particles using a plasma sintering process. The ceramics fracture toughness is reported to have increased by ~235% with an addition of 1.5% wt/v inclusion of GnP.

2.9.3 Graphene-based Energy Storage Devices

Modern times have seen an increased demand for energy. Renewable energy sources are critical in maintaining a balance in energy harvesting and usage. Another critical step in maintaining this balance is being able to store the energy that has been harvested for later use. Lithium-ion batteries are currently the most utilized technology in this field. Graphene has shown to both be able to boost the performance of these energy storage systems and others. For instance, Yang et al. [150] used what is described as a template-free sol-gel approach to fabricate porous LiFePO$_4$/graphene for superior lithium-ion battery cathodes. The cathode material is reported to have a reversible capacity of 146 mAh/g at 17mA/g after 100 cycles, 42 mAh/g more than the LiFePO$_4$ material without the inclusion of graphene. In addition, this battery is reported to have good tolerance to varied charge and discharge rates. Graphene has also shown to be beneficial in creating high-performance supercapacitors. Supercapacitors are known for having high power density. Zhao et al. [151] demonstrated graphene’s use in supercapacitors, creating polyaniline and reduced graphene oxide supercapacitor electrode that allows for a specific capacitance of 369 F/g.

2.9.4 Graphene Electronics

Another facet of graphene application is in electronics. This includes but is not limited to sensors, antennas, transistors, batteries and circuits. Graphene has the potential to increase the efficiency, flexibility and strength of these devices owing to its high thermal and electrical conductivity, mechanical strength and polymer dispersibility. For example, Graphene sensors have been explored extensively to measure various inputs including electric fields, magnetic fields, chemical, electrochemical, mass and strain [152]. Graphene opens the possibility for novel electronic devices with facile processing methods. Printing of circuits is one example of this, Pan et al. [146] developed an ink that was applied to textile and paper surfaces to achieve an electrical conductivity of $7.13 \times 10^4$ S/m. The technique allowed them to develop an antenna capable of broadcasting and receiving data within the MHz to tens of GHz range.

2.9.5 Graphene-enabled Water Purification

Graphene-based material systems have also shown great promise for application in different water purification systems including semi-permeable membranes for water purification
purposes. Graphene microstructure can be utilized to filter out unwanted salt or contaminants by perforating the nanostructure with tiny holes that allow the flow of water but not the contaminates, additionally graphene can be functionalized to be both hydrophobic and hydrophilic. Due to its high hydrophilicity GO is considered a good candidate over other graphene types for these membranes. Chen et al. [153] used facile and novel methods to create a GO/cellulose hydrogel that was capable of absorbing heavy metals. It was found that the absorption of copper ions (Cu$^{2+}$) increased with an increase in GO loading. More recently, Raghuvanshi et al. [154] have demonstrated the use of GO in filtering out lead ions (Pb$^{2+}$). Interestingly, it was found that wrinkled GO layers led to higher absorption of lead ions.

2.9.6 Graphene Materials for Thermal Management

Adequate thermal management materials are in high demand. This is particularly true in the electronics industry, where high-power portable devices such as tablets and mobile phones require a pathway to exert waste heat. Due to its exceptionally high thermal conductivity, graphene has drawn considerable interest worldwide for heat spreading and dissipation. In 2014, Xin et al. [155] developed lightweight graphene paper using electrospray deposition followed by a rolling process for this particular application. The authors found that the developed graphene film, yielded thermal conductivities in the range of 1238.3-1424 W/mK. The reported values outperformed aluminium and copper at eliminating heat spots. The reported density of the graphene paper was 2.1 g/cm$^3$. It has also been found that graphene can be used to generate electricity from heat. One recent example of such a system, which is able to produce electricity from ambient temperatures is described by Thibado et al. [156]. It uses a specifically designed circuit to harness the energy of out-of-plane fluctuations in graphene at room temperatures.

2.10 Graphene Nanocomposite Applications

Although the focus here is graphene nanocomposite for EMI shielding, applications for these materials are vast and not limited to shielding. The versatile nature of both carbon and composite materials allows for multiscale tuneability in the mechanical, electrical, thermal and chemical properties. This effectively means if the right processing and synthesis conditions can be achieved, graphene may ultimately become immensely ubiquitous. As discussed, graphene nanocomposite materials are heavily sought after as a material in battery and supercapacitor electrodes, thermal management materials, chemical and capacitive sensors, energy harvesting, structural reinforcements, anticorrosive coatings, antennas, printed circuits etc. Below some
discussion and analysis is given on various facets in which graphene polymer nanocomposite EMI shields could replace current technology.

EMI shielding is imperative in aerospace, information technology, automotive, medical and defence industries. Metals remain the most prevalent EMI shielding Material. Metals possess high conductivity, and therefore, low wave impedance which results in significant EMI reflections. On the other hand, metals tend to be heavy, vulnerable to corrosion and difficult to manufacture [8]. Graphene polymer composites offer the possibility for the development of thin, lightweight and easy-to manufacture EMI shields with anticorrosion properties [157]. This ultimately leads to lower life-time costs. Graphene-enabled composites may be applied as a coating or even further embedded into a fibre-reinforced polymer composite system [158]. GRAPHENEST Advanced Nanotechnology- a US-based company- is a provider of graphene-based solutions for advanced composites. The company has recently launched innovative graphene-based EMI Shielding paintable coatings so-called ‘Hexasheild’ that offers customized electrical resistance and wave attenuation levels. Graphene-based EMI shielding composites are anticipated to replace metals in portable devices (which also require high thermal conductivity inherent to these materials) [159], lightning strike protection [160], radar absorption [161] and even provide real-time EM reflection/absorption control [162, 163].

2.10.1 Graphene/Polymers in Defence and Transport Industries

In aviation, global objectives to reduce fuel consumption of aircrafts has led to the use of carbon fibre reinforced plastics as the dominant material in airplane manufacturing, minimizing weight, cost and time of production. In order to achieve heightened SE values, particular for high power lightning strikes, metallic meshes or sheets of copper and aluminum are placed on the outermost layer of carbon fibre. It is found that galvanic corrosion can occur between the metallic mesh and carbon fibre [160, 164]. Corrosion can also be caused by moisture or environmental species [164]. This leads to a degradation of conductivity and the need for routine replacement/maintenance. It has also been reported that these meshes may vaporize under high current lightning strikes [164]. Naturally, carbon-based conductive nanocomposites have been investigated as a potential solution to these problems [165, 166]. Furthermore, it can be seen that these composites allow for facile processing methods [167] and overall lower lifetime costs than metallic meshes. Land, water, and air vehicles are becoming increasingly reliant on electronic communication and control. The proliferation of electronic equipment needs to be met with an increase in consideration of EMI shielding materials that are suited for these applications.
2.10.2 Graphene/Epoxy in Carbon Fibre Composites

Though carbon fibre reinforced plastic (CFRP) possess adequate SE values and good conductivities for general purpose low power EMI shielding [168], utilizing graphene infused resin can lead to multiscale composites with superior mechanical electrical and thermal properties [169]. These materials have novel applications that include but are not limited to structural health monitoring, lightning strike protection and de-icing systems. Here some discussion is given on the fabrication and application of these materials for electronic purposes.

Firstly, epoxy resins are a class of thermosetting polymer often used as an adhesive, coating or carbon fibre matrix material. Its sought after properties include high tensile strength and modulus, resistance to corrosion and good processability [170]. This leads to carbon fibre reinforced epoxy to be prolific across marine, land and aerospace applications. Various epoxy systems can be found for CFRP fabrication with different viscosities and curing regimes. Carbon Fibre acts as a structural reinforcement to negate the intrinsically brittle nature of epoxy.

As mentioned, CFRP possess electrical and thermal conductive properties due to the inclusion of the carbon fibre [171] within the insulating epoxy. Though, it is mainly the anisotropy and inhomogeneity of the composite structure that limits its ability to be used in certain electrical and thermal applications. As an example, the volumetric conductivity of unidirectional CFRP is reported to be 1000 times less than metals, while only 100 times less then metal in the cross-fibre direction [171]. If capacitive effects between fire are not considered, a typical CFRP would have an out-of-plane conductivity zero. Though in reality, ideal manufacturing conditions are not met, and inter-fibre contact points allow some current to flow in the out of the plane direction, given rise to a non-zero out-of-plane conductivity. It Is therefore important to define the volumetric, in-plane and out-of-plane conductivities in anisotropic composites.

There are also found to be large discrepancies in the characterization of the electrical properties of these composites. This is due to un-established standards of electrical characterization equipment for these materials, along with improper or competing mathematical formulations and assumptions surrounding these materials [172]. Munalli et al. [168] reported an electrical conductivity of 10204 S/m for a CFRP made from 4 layers of 2/2 twill weave pattern carbon fabric. In order to determine this value, the SE is first measured using a coaxial transmission line method under the ASTM D4935 standard. From there, the Simon formalism [173] is adopted to mathematically solve for the electrical conductivity from the SE. The Simon formulism operates under the assumption of a good conductor whereby the electrical
conductivity ($\sigma$) is much greater than the angular wave frequency ($\omega$) multiplied by the permittivity ($\varepsilon$), and that the materials involved are non-magnetic ($\mu = \mu_0$). It is given by the following formula:

$$SE_{dB} = 50 + 10\log_{10}(\rho f)^{-1} + 1.7t \left(\frac{1}{\rho}\right)^{1/2}$$

\textit{Equation 1}

Whereby $f$ is the frequency in MHz, $t$ is the thickness of the material in cm and $\rho$ is the volume resistivity expressed in $\Omega$cm.

Various carbon fibre manufacturing processes are well established, some of which include vacuum resin infusion, hand layup and filament winding. Hypothetically, all of which could be adjusted to accommodate nanocomposite resin. In such a situation, the viscosity and curing regime is of importance as the graphene inclusion will influence these parameters, which are vital to the carbon fibre fabrication process. As mentioned, a modified resin will allow for a more homogenous and isotropic conduction pathway throughout the polymer. This will give applicability, including structural health monitoring, lightning strike protection and de-icing.

\textbf{2.10.2.1 Structural Health Monitoring}

A more homogenous conduction pathway will give a better map of currents though the material. Noting points of current discontinuities will signify bending and or fibre breakage points. The addition of GnP allows for tuneability in the current and added capabilities to pinpoint these discontinuities. This may be more suited for fibre laminate which possesses a lower conductivity or distrusted conduction pathways. For example, Müller et al. [174] utilized GnP into a glass fibre-reinforced thermoplastic to achieve structural health monitoring capabilities. Other work includes Balaji and Sasikumar [175] who fabricated strain and damage prediction system for composites via coating glass fibres with \textit{in situ} synthesized rGO. The piezo resistance under deformation was characterized and can now be used to signify deformation or cracking in the composite structure.

\textbf{2.10.2.2 Lightning Strike Protecting}

It is noted that metallic meshes are needed to be placed on top of CFRP that is used in airplanes to achieve a conductive pathway for the high arc power to dissipate. There are various problems associated with these metals, including corrosion, weight, complicated and expensive manufacturing. It can be seen that improving the through-thickness conductivity of CFRP is an effective method of negating structural damage caused by lightning strikes [176]. Kumar et al. [176] used different conductive PANI epoxy resins to increase the out-of-plane conductivity...
varying degrees while noting the change in structural damage under simulated lightning strikes conditions. It was reported that an out-of-plane conductivity of 34 S/m resulted in a composite that was able to retain 73% of its residual flexural strength, while a composite with an out-of-plane conductivity of 110 S/m was able to retain 92%.

Graphene reinforced epoxy nanocomposites were produced to increase the out-of-plane conductivity of CFRP [177]. Though there are limited studies demonstrating this increase. However, it has been demonstrated that using a graphene modified resin results in an increase in volumetric conductivity [169], and assuming a random dispersion of graphene particles means that there must be an increase in the out of the plane direction. Which was explored by Qin et al. [177], who showed that incorporating graphene nanoplatelets into carbon fibre composites leads to an increase in both mechanical strength and electrical conductivity. Herein, a GnP/epoxy suspension was prepared with the assistance of NMP as a solvent utilizing both sonication and centrifugation. Carbon fibres were fabricated with GnP/epoxy as the pre-preg, which was then used in a hand layup process to achieve the final composite. The conductivity was measured using Impedance Spectroscopy (FAS2 Femotostat, Gamry Instruments Inc.) showed a %165 increase in the through the thickness electrical conductivity. A sharp rise was observed for through the thickness electrical conductivity of up to 8 S/m, which is still below adequate levels for lightning strike dissipation. Other methods, such as those reported by Alemour et al. [169] have also been investigated to optimize the conduction properties of carbon fibre. Herein, rGO pastes were used as a coating onto CFRP. Two pastes with 80 wt.% and 90 wt.% of rGO in water were explored. A hot press was used to apply the pastes into the CFRP before curing. It was found that the 90 wt.% rGO paste increased the volumetric conductivity of CFRP from $1.38 \times 10^3$ S/m to $1.12 \times 10^5$ S/m. The electrical conductivity was measured via a four-point probe technique.

2.10.2.3 Self-heating and De-icing

The Joule effect, whereby passing a current through the material to produce heat, is readily observed in graphene/epoxy composites [178, 179]. This has been shown to be utilized in achieving out-of-autoclave curing [178]. Whereby the inclusion of GnP within epoxy facilitated a conducting network throughout the material, allowing the current to be homogeneously dispersed while creating heat due to the Joule effect. Utilizing the homogeneous and isotropic thermoelectric behavior that is enabled by the inclusion of GnP within CFRP is also explored as a de-icing solution. Ice accumulation on aircraft can be a potentially fatal issue, as it may result in a temporary loss of control. It also has adverse effects.
of increasing drag and weight while increasing left and maneuverability. This leads to high fuel consumption. A simple solution can be found by implementing an airplane skin with joule heating capabilities, which would melt the ice at the ice airplane interface allowing the ice block to slide off due to gravity and or wind. Such a joule heating system can be realized by GnP/epoxy carbon fibre composites.

2.10.3 Radar Absorbing Materials

Radar absorbing materials (RAM’s) are implemented in stealth vehicles to minimize the power reflected to the transmitting/receiving antenna. Minimizing the radar cross-section (RCS) can be achieved by reducing reflection via impedance matching. As is shown in Equation 6 on page 60, Impedance matching the material to air can be obtained via raising the permeability. Naturally, much work has been done on decorating graphene with magnetic materials in order to achieve this [180]. He et al. [180] fabricated NiFe$_2$O$_4$/rGO particles which were then mixed into paraffin wax at different weight ratios in order to observe the ranging microwave attenuation properties. It was found that a minimum reflection loss of -42 dB was achieved at 70 wt.% of NiFe$_2$O$_4$/rGO into parrafin wax. He et al. outlined a production method to tune the conductivity, permittivity and permeability of a composite. This can be used to achieve impedance matching conditions, whereby reflection (dB) is as low as possible and absorption is dominant. A similar material system is later explored by Liu et al. [181], who demonstrated a Co$_{0.2}$Ni$_{0.4}$Zn$_{0.4}$Fe$_2$O$_4$/rGO composite used within a double-layer microwave absorber, which achieved a minimum reflection loss of -49.5 dB along displaying excellent broad bandwidth properties. Graphene decorated with magnetic particles and dispersed throughout a polymer matrix show excellent potential as broadband radar absorption materials. This facilitated by the presence of tunability in the permeability in order to achieve impedance matching, then secondary electrically conductive and/or dielectric/magnetic properties in order to turn the absorbed energy into heat [161].

2.10.4 Graphene Foams

Graphene foam composites have shown to be fabricated via either coating a graphene on the desired polymer foam [182-184], coating an existing foam structure in graphene [185], or foaming of a graphene dispersion [186, 187]. Graphene foams are often synthesized via a chemical vapour disposition onto a Ni foam substrate which is then etched off. From there, the foam can be coated in a liquid polymer precursor and cured. Chen et al. [182] fabricated a graphene/PDMS composite foam via this method with a specific EMI SE of 500 dB.cm$^3$/g.
While Wu et al. [183] used a similar method to fabricate a graphene/PEDOT:PSS foam with an exceptionally high specific SE of 3124 dB·cm$^3$/g, they reported this to be the highest among all carbon-based polymer composites. Li et al. [185] reported a unique fabrication method whereby commercially available melamine was first carbonized in a furnace at varying temperatures from 300 °C to 800 °C. The carbon structure was then coated in GO. A reduction process was then utilized to achieve carbonized foam coated in RGO. A vacuum-impregnation process was then used to construct a graphene/epoxy foam. The material achieved a maximum electrical conductivity of 70 S/m. Lastly, a simpler foaming process can be used to achieve graphene polymer foams [186, 187]. In both reported cases, this involves the foaming of a liquid polymer graphene dispersion using CO$_2$ as the foaming agent. Although SE of these materials could be sufficient for some applications, and the fabrication process is facile, specific SE values for these materials were much less than graphene composite foams produced via other methods.

![Image of graphene foam (left), microscopic Image of graphene foam (right) and SE value before and after bending (bottom). Gathered from ref. [182].](image)

2.10.5 Alternative Graphene Shielding Materials
The unique properties of graphene have facilitated many new devices, which does not exclude the field of EMC. For example, Balci et al. [163] demonstrated an electrically switchable radar-
absorbing surface via controlled charge density on the graphene surface. Atomically thin CVD produced graphene sheets are placed on either side of an electrolyte (ionic liquid), a voltage is then applied to either graphene sheet to facilitate a change in charge density on the graphene surface which in turn can be used to control the light-matter interaction through careful interband and intraband engineering. This device showed an excellent control of light-matter interactions over broad frequencies ranging from microwave to visible. These adaptive surfaces are shown to exhibit a minimum reflection loss of 50 dB at and operating voltage of 5 V. A similar approach can be found by Salihoglu et al. [162], whereby a similar material system was used to create an adaptive thermal camouflage. Both devices are flexible and easily workable, whereby the main manufacturing difficulty lies in the CVD process. Both devices demonstrate the ground-breaking and vast engineering capabilities that are enabled by graphene.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>FABRICATION METHOD</th>
<th>FILLER LOADING</th>
<th>RELATIVE PERMITTIVITY</th>
<th>RELATIVE DIELECTRIC LOSS</th>
<th>RELATIVE PERMEABILITY</th>
<th>RELATIVE MAGNETIC LOSS</th>
<th>DC CONDUCTIVITY [S/M]</th>
<th>REFLECTIVITY (R) [DB]</th>
<th>ABSORPTION (A) [DB]</th>
<th>SHIELDING EFFECTIVENESS (SE) [DB]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMICALLY REDUCED GRAPHENE (CRG) AND THERMOPLASTIC POLYURETHANE (TPU)</td>
<td>Sonication with TPU matrix using N,N-dimethylformamide (DMF) as a solvent</td>
<td>20 wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>$1.7 \times 10^{-4}$</td>
<td>5.07 at 15 GHz</td>
<td>13.8 at GHz</td>
<td></td>
</tr>
<tr>
<td>THERMALLY REDUCED GRAPHENE (TRG) AND (TPU)</td>
<td>Sonication blended with TPU matrix using DMF as a solvent.</td>
<td>10 wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>$3.1 \times 10^{-2}$</td>
<td>3.7 at 15 GHz</td>
<td>26.1 at GHz</td>
<td></td>
</tr>
<tr>
<td>TPU/TRG</td>
<td>Sonication blended with TPU matrix using DMF as a solvent.</td>
<td>5.5 vol. %</td>
<td>$\approx 28.6$</td>
<td>$\approx 25.0$</td>
<td>-----</td>
<td>-----</td>
<td>$3.1 \times 10^{-2}$</td>
<td>3.7 at 15 GHz</td>
<td>26.1 at GHz</td>
<td></td>
</tr>
<tr>
<td>GRAPHENE/POLY(ETHYL SILICONES) (PDMS) FOAM</td>
<td>Template-directed chemical vapor deposition (CVD)</td>
<td>$\approx 0.8$ wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>200</td>
<td>4</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>GNP/EPOXY</td>
<td>Solvent swelling method.</td>
<td>0.02 wt.%</td>
<td>$\approx 10.25$</td>
<td>$\approx 0.6$</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>NIFE$_2$O$_4$/RGO MIXED INTO PARAFFIN WAX.</td>
<td>Hydrothermal treatment followed by mixing into polymer.</td>
<td>70 wt.% of NiFe$_2$O$_4$/r-GO filler.</td>
<td>$\approx 8$ to 5 decreasing with frequency.</td>
<td>$\approx 4$ to 1.5 decreasing with frequency</td>
<td>$\approx 0.9$ to 0.11</td>
<td>$\approx 0.1$ to 0.3</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>GNP/EPOXY</td>
<td>Sonicated with acetone as solvent.</td>
<td>15 wt.%</td>
<td>$\approx 8$ across the whole frequency range.</td>
<td>$\approx 0.5$ to 1.5 across the whole frequency range</td>
<td>-----</td>
<td>-----</td>
<td>$1.3 \times 10^4$</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>PMMA/TRG foam</td>
<td>Solution blending and melt compounding</td>
<td>1.8 vol.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>3.11</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>PS/RGO</td>
<td>Stirring and sonication</td>
<td>3.47 vol.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>43.5</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
</tbody>
</table>

2.11 Meta-analysis of EMI shielding graphene/polymers

Table 1 outlines the relevant values for EMI shielding based on the materials and fabrication method used. Of the seven methods, the highest conductivity reached was by the (CVD)
graphene/PDMS foam. Shielding effectiveness of 23dB was reached at thickness 1mm for the material. This result can be attributed to the high intrinsic conductivity of CVD graphene and the foam structure, which induces further internal reflections. All reported SE values reached adequate levels except for the GnP/epoxy [188] and PMMA/TRG foam [186]. Higher graphene loadings, thicker shields or better processing conditions may be needed to raise the conductance for adequate shielding, particularly at lower frequencies. The highest SE value featured in
Table 1 was by PS/rGO at 45.1 [189]. The high level of shielding can be attributed to the compression moulding process, which resulted in a more structured percolation pathway. Magnetic effects are often not featured as the values for permeability, and magnetic loss are mostly insignificant unless the graphene has been magnetically functionalized as with the
NiFe$_2$O$_4$/r-GO [180]. Absorption is the dominant mechanism for shielding, which is common at the reported frequencies as per Figure 17. Chemically and thermally reduced graphene have both shown adequate shielding values; however, the thermally-reduced graphene (TRG) outperformed the chemically-reduced graphene (CRG) at half the loading [71]. This is due to the larger surface area of the TRG, which gives rise to longer percolation paths and less inter-platelet junctions which block charge transport. Interestingly, CRG outperformed TRG at higher loadings, which can be attributed to agglomeration, nonuniform dispersion, and restacking that often occurs with larger surface areas [71]. It can be seen that although GnPs can be produced efficiently in bulk, reaching adequate losses in GnP reinforced epoxies remains a challenge. Further investigation into aspect ratio and dispersion methods is required to achieve optimal SE values in GnPs/epoxy composites.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>FABRICATION METHOD</th>
<th>FILLER LOADING</th>
<th>RELATIVE PERMITTIVITY</th>
<th>RELATIVE DIELECTRIC LOSS</th>
<th>RELATIVE PERMEABILITY</th>
<th>RELATIVE MAGNETIC LOSS</th>
<th>DC CONDUCTIVITY [S/M]</th>
<th>REFLECTIVITY (R) [DB]</th>
<th>ABSORPTION (A) [DB]</th>
<th>SHIELDING EFFECTIVENESS (SE) [DB]</th>
<th>FREQUENCY</th>
<th>THICKNESS</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMICALLY REDUCED GRAPHENE (CRG) AND THERMOPLASTIC POLYURETHANE (TPU)</td>
<td>Sonication with TPU matrix using N,N-dimethylformamide (DMF) as a solvent</td>
<td>20 wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>1.7x10^-4</td>
<td>5.07 at 15 GHz</td>
<td>13.8 at 15 GHz</td>
<td>18 to 24</td>
<td>12.4-18 GHz</td>
<td>-----</td>
<td>[71]</td>
</tr>
<tr>
<td>THERMALLY REDUCED GRAPHENE (TRG) AND (TPU)</td>
<td>Sonication blended with TPU matrix using DMF as a solvent</td>
<td>10 wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>3.1x10^-2</td>
<td>3.7 at 15 GHz</td>
<td>26.1 at 15 GHz</td>
<td>26 to 32</td>
<td>12.4-18 GHz</td>
<td>-----</td>
<td>[71]</td>
</tr>
<tr>
<td>TPU/TRG</td>
<td>Sonication blended with TPU matrix using DMF as a solvent.</td>
<td>5.5 vol %</td>
<td>≈28.6</td>
<td>≈25.0</td>
<td>-----</td>
<td>-----</td>
<td>3.1x10^-2</td>
<td>3.7 at 15 GHz</td>
<td>26.1 at 15 GHz</td>
<td>26 to 32</td>
<td>12.4-18 GHz</td>
<td>-----</td>
<td>[190]</td>
</tr>
<tr>
<td>GRAPHENE/POLY(DIETHYL SILoxANE) (PDMS) FOAM</td>
<td>Sonication blended with TPU matrix using DMF as a solvent. template-directed chemical vapor deposition (CVD)</td>
<td>≈0.8 wt.%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>200</td>
<td>4</td>
<td>19</td>
<td>≈23</td>
<td>8-12 GHz</td>
<td>≈1 mm</td>
<td>[182]</td>
</tr>
<tr>
<td>GNP/EPOXY</td>
<td>Solvent swelling method.</td>
<td>0.02 wt.%</td>
<td>≈10.25</td>
<td>≈0.6</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>1 MHz</td>
<td>0.5 cm</td>
<td>[191]</td>
</tr>
<tr>
<td>NIFE2O4/RGO MIXED INTO PARAFFIN WAX.</td>
<td>Hydrothermal treatment followed by mixing into polymer.</td>
<td>70 wt.% of NiFe2O4 ( \times ) GO filler.</td>
<td>≈ 8 to 5 decreasing with frequency.</td>
<td>≈ 4 to 1.5 decreasing with frequency</td>
<td>≈ 0.9 to 0.11</td>
<td>≈ 0.1 to 0.3</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>2-18 GHz</td>
<td>≈2mm</td>
<td>[180]</td>
</tr>
<tr>
<td>GNP/EPOXY</td>
<td>Sonicated with acetone as solvent.</td>
<td>15 wt.%</td>
<td>≈ 8 across the whole frequency range.</td>
<td>≈ 0.5 to 1.5 across the whole frequency range</td>
<td>-----</td>
<td>-----</td>
<td>1.3 x 10^-4</td>
<td>-----</td>
<td>-----</td>
<td>≈ 4 to 14 across frequency.</td>
<td>8-20 GHz</td>
<td>-----</td>
<td>[188]</td>
</tr>
<tr>
<td></td>
<td>Solution blending and melt compounding</td>
<td>PMMA/TRG foam</td>
<td>1.8 vol%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>3.11</td>
<td>-----</td>
<td>-----</td>
<td>13–19</td>
<td>8–12 GHz</td>
<td>2.4 mm</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------</td>
<td>---------------</td>
<td>---------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>PS/RGO</td>
<td>PS/RGO</td>
<td>3.47 vol%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>43.5</td>
<td>-----</td>
<td>-----</td>
<td>45.1</td>
<td>8.2–12.4 GHz</td>
<td>2.5 mm</td>
</tr>
</tbody>
</table>

*Table 1 – Important values relating to EMI shielding for different graphene/polymers.*
2.12 Modelling of Graphene nanocomposites for EMI Shielding.

2.12.1 Electromagnetic Responses of Materials

Materials fall under being dielectric, conductive, or magnetic depending on the response of the bound and free electrons within a material to electromagnetic radiation (EMR) and consequentially which of the constitutive parameters dominate [192]. An in-depth understanding of the responses of materials to EMWs enables us to design and fabricate shielding materials with optimal properties. Equations 2 to 4 define an EMR’s interaction with matter [192]:

\[ D = \varepsilon E \]  \hspace{1cm} \textit{Equation 2}
\[ B = \mu H \]  \hspace{1cm} \textit{Equation 3}
\[ J = \sigma E \]  \hspace{1cm} \textit{Equation 4}

Wherein E and H represent the electric and magnetic field intensity vectors, respectively and D, B and J represent the electric flux density, magnetic flux density and electric current density vectors, respectively.

Permittivity denoted by \( \varepsilon \), is a measure of a material’s electric polarizability, as determined from the summation of the electric dipoles within it. In a conventional homogenous material, these polarities can be either dipole, Ionic or electronic, (ref. Figure 14) depending on the structure of the material and the incident wave frequency. An EMW incident on any dielectric material will cause polarizations which align with the applied field. Dipole polarizations refer to the alignment of permanent dipole structures, whereas ionic polarizations refer to the displacement of ions. Electronic polarization describes the displacement of electron orbitals. Composite materials may also possess space charge polarities owing to interfacial charge accumulation which also contributes to permittivity, which will be discussed in detail in section 0.
Table: Types of Electric Polarizations

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>No Applied Field</th>
<th>Applied Field</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole (or orientational)</td>
<td></td>
<td></td>
<td>Some molecules (such as water) have permanent dipole moments which tend to align to an applied electric field ($E_a$).</td>
</tr>
<tr>
<td>polarization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic (or molecular)</td>
<td></td>
<td></td>
<td>Some materials possess bonded positive and negative ions that tend to displace themselves under an applied electric field.</td>
</tr>
<tr>
<td>polarization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electronic polarization</td>
<td></td>
<td></td>
<td>This polarization occurs due to electron orbitals of an atom perturbed in the direction of an applied electric field relative to the nuclear centre.</td>
</tr>
</tbody>
</table>

**Figure 14 - An explanation of some common types of electric polarizations in a material. Adapted from [192].**

Similar to permittivity, permeability denoted as $\mu$ is a measure of a material’s magnetic polarizability. EMWs incident on magnetic materials influences magnetic dipoles in the form of electron orbitals, electron spins and nuclear spins. Lastly, electrical conductivity, which is represented by $\sigma$, describes a material’s ability to conduct an electric current due to the presence of unbound electrons moving throughout the material. Even though EM shielding does not wholly rely upon conductivity, reflection, and absorption are both strongly dependent on conductivity (as evident in Figure 17). Good conductors generally serve as good reflectors of EMWs.

Although electrical conductivity, magnetic permeability and permittivity are the basis for defining a materials electromagnetic response, further modifications must be made to these constitutive parameters if necessary. These adjustments include frequency dependence, anisotropy, non-linearity, and inhomogeneity. The anisotropy of the conductive inclusion can be handled by defining the constitutive values as tensors. While the frequency dependent nature of materials is often handled by defining the key parameters as complex numbers. In this case, $\varepsilon$, $\mu$ and $\sigma$ are denoted by $\varepsilon'$, $\mu'$ and $\sigma'$ while the role of imaginary components of $\varepsilon''$, $\mu''$ and $\sigma''$ are also considered. Resulting in the following: $\varepsilon = \varepsilon' - i\varepsilon''$, $\mu = \mu' - i\mu''$ and $\sigma = \sigma' - i\sigma''$. The imaginary terms represent a phase lag between the applied AC field and the response of the material. Imaginary conductivity was found to be negligible at frequencies below 300 GHz [193] and thus, disregarded here. Imaginary permittivity and permeability are associated with dielectric and magnetic polarization losses. Resistance in the polarization process is known as dielectric and magnetic loss. This energy will often propagate throughout the material.
as heat. This heat is often indistinguishable from DC conductivity. Thus, AC conductivity is often defined, which includes both types of energy propagation. In addition, the proposed composite models are assumed to have a linear response to the applied field strength, as evident in equations 2 to 4.

### 2.12.2 Electromagnetic Interference Shielding

Figure 15 - Schematic of a shielding material (green) under incidence from an electromagnetic plane wave positioned in air. depicts a shielding component (green) positioned in the air under far-field plane wave radiation ($E_i$ and $H_i$), whereby, the far-field radiation is defined at a distance $r > \frac{\lambda}{2\pi}$ with $\lambda$ referring to radiation wavelength. When an EMW encounters the shield, the EMW is then broken into reflected ($E_r$ and $H_r$), internal ($E_1$ and $H_1$), internally reflected ($E_2$ and $H_2$) and transmitted ($E_t$ and $H_t$) components.

Figure 15 - Schematic of a shielding material (green) under incidence from an electromagnetic plane wave positioned in air.

An EMW comprises of magnetic (H) and electric (E) components. With Figure 15 - Schematic of a shielding material (green) under incidence from an electromagnetic plane wave positioned in air., they are at right angles to each other and the direction of propagation (Z). Considering that the shield is positioned in the far-field, SE is attainable from either E or H fields, which will return the same value [5]. Therefore, only the electric field is considered here. SE is defined as the ratio of transmitted and incident power, or otherwise as to the sum of reflection (R),
absorption (A) and multiple reflections (M). It is often expressed in dB, as shown in Equation 5 below:

\[ SE_{db} = 20\log_{10}\left|\frac{E_i}{E_t}\right| = R_{db} + A_{db} + M_{db} \quad \text{Equation 5} \]

SE below 20dB is considered minimal, between 20dB-80dB is average and between 80dB-120dB is above average. Anything above 120dB is unattainable with cost-effective methods [194]. Reflection, absorption, and multiple reflection contributions are depicted in Figure 16. These can be represented in terms of the bulk material properties - \( \varepsilon \), \( \mu \) and \( \sigma \) as explained below.

![Figure 16 – Schematic showing the different contributions to EMI shielding.](image)

2.12.2.1 Reflection

Reflection (R) refers to surface reflections at the first air-shield interface caused by an intrinsic impedance mismatch between the shield and surrounding air. In order to achieve a lower impedance than air, the shielding material must be conductive. Therefore, metals make good reflectors of EMWs. As metals are the most commonly used EMI shielding material, reflection is the most common mechanism of EMI shielding.

The definition of intrinsic impedance (\( \eta \)) is \( \eta = \frac{E}{H} \) in units of ohms \([\Omega]\). The general solution for this in terms of bulk materials properties is given by equation 6 as below.

\[ \eta = \sqrt{\frac{\omega \mu i}{\sigma + \omega \varepsilon i}} \quad \text{Equation 6} \]
where \( \omega \) [rad/s] represents the angular frequency of the wave and \( i \) - indicates the imaginary unit. \( \varepsilon \) [F/m], \( \mu \) [H/m] and \( \sigma \) [S/m] signify the bulk material properties, as explained previously. Conductivity is dictated by the mobility and density of unbound charge carriers (electron and holes), while the other terms characterize all possible magnetic and dielectric material polarizations along with the friction involved in the polarization process. Reflection can be determined via Equation 7 [195] where \( \eta_{\text{air}} \) is the intrinsic impedance of air and \( \eta_e \) is the intrinsic impedance of the shielding material.

\[
R_{dB} = 20 \log_{10} \left( \frac{(\eta_{\text{air}} + \eta_e)^2}{4\eta_e\eta_{\text{air}}} \right) \quad \text{Equation 7}
\]

### 2.12.2.2 Absorption

Absorption refers to electromagnetic energy that is absorbed into the shielding material and dissipated as heat. This heating can be caused by Ohmic losses in induced currents, or otherwise by losses involved in magnetic (\( \mu'' \)) and/or dielectric (\( \varepsilon'' \)) polarization process. The propagation constant (\( \gamma \)) has real and imaginary components which dictate the attenuation (\( \alpha \)) given in [Np/m] and phase (\( \beta \)) given in [rad/m] of a travelling wave. The attenuation in terms of bulk properties is given in Equation 8 as below:

\[
\alpha = \text{Re}\left[\gamma\right] = \text{Re}\left[ \sqrt{i\omega\mu(\sigma + i\omega\varepsilon)} \right] \quad \text{Equation 8}
\]

Absorption is then given using the following equation where \( t \)[m] is the thickness of the shield, \( \beta_{\text{air}} \) is the phase constant of air and \( \gamma_e \) is the propagation constant of the shielding material [195].

\[
A_{dB} = 20 \log_{10} \left| e^{-i\beta_{\text{air}}t} e^{\gamma_et} \right| \quad \text{Equation 9}
\]

### 2.12.2.3 Multiple Reflections

Another shielding mechanism similar to that of reflection and absorption is the multiple reflections, which describes the process of reflections at different surfaces or interfaces within the shielding material. The multiple reflection factor (M) is given by Equation 10 as follows:

\[
M_{dB} = 20 \log_{10} \left( 1 - \frac{(\eta_{\text{air}} - \eta_e)^2}{(\eta_{\text{air}} + \eta_e)^2} e^{-2\gamma_et} \right) \quad \text{Equation 10}
\]

The multiple reflection loss is often negligible when the distance between reflecting surfaces or interfaces is significantly larger than the skin depth (\( \delta \)), where \( \delta = \frac{1}{\alpha} \) [5].
2.12.2.4 EMI Parameters

Figure 17 (a-e) shows the dependence of SE, R, A and M on conductivity (a), frequency (b), permittivity (c), thickness (d) and permeability (e). The plots are based on solutions to the equations outlined above [192]. For each of the plots, all variables (except the x-axis) are kept fixed at $\sigma = 1$, frequency = 5 GHz, relative permittivity = 5, thickness = 1cm and relative permeability = 1. Increased conductivity results in a large increase in absorption and a small increase in reflection. The increase in absorption can also be seen through Equation 8 and 8, where an increase in the attenuation constant is facilitated by losses present in the material. Reflection is increased because of an increase in the impedance difference between the material and air. An increase in frequency shows little effect on the total SE beyond 4 GHz. Below this, absorption increases steadily, while reflection decays rapidly. This occurrence is due to changes in both the propagation constant and impedance values. It should be noted that conductivity and permittivity are frequency-dependent for graphene composites. Despite this,
for now, we have assumed fixed values for the sake of simplicity. Permittivity is shown to slightly affect SE owing to changes in the propagation constant and impedance values. As expected, absorption increases steadily with thickness. It was also observed that increasing the permeability will increase absorption. Notably, a zero point for reflection can always be observed in the permeability plot, that is the point at which the impedance matches that of air.
Figure 17 – Plots demonstrating the dependence SE, R, A and M have on conductivity (a), frequency (b), permittivity (c), thickness (d) and permeability (e).
An alternative approach to the analytical derivation of Maxwell’s equations outlined above [195] is to implement a numerical solution. This practice is often necessary for the field of EMI shielding as obtaining an analytical solution or even an experimental value for large complexly shaped 3D parts is often unachievable.

2.12.3 Numerical Methods for EMI Simulation

Numerical solutions are essential in the modelling of electromagnetic waves, all modern simulation software currently relies on numerical solutions. This includes but is not limited to Finite Element Methods (FEM), Finite Volume Methods (FVM), Finite Difference Time Domain (FDTD) and Finite integration Technique (FIT). A brief comparison of each of these methods as applied to electromagnetic propagation problems is discussed.

Various software packages are available including but not limited to ANSYS, CST microwave studio and COMSOL Multiphysics which possess graphical user interfaces (GUIs) developed to run numerical solutions. These may involve an algorithm based on any of the aforementioned approaches.

2.12.3.1 Finite Difference Time Domain (FDTD)

Finite Difference Time Domain (FDTD) is a simple yet favored methodology for EMI problems due to it being time domain, meaning one simulation can resolve a wide range of frequencies using a Fourier transform. All FEM, FVM, FDTD and FIT methods involve grid discretization, whereby continuous Maxwell equations are broken into discrete algebraic counterparts which can then be solved across the whole grid. Kane Yee [196] was the first to propose the FDTD algorithm in 1966, which solved Maxwell’s curls equations across grids staggered in space and time. The differential operators in Maxwell’s equations are replaced with finite differences by means of a Taylor expansion. A leapfrog approach is implemented which solves magnetic and electric field values based on one another at different space and time steps. Consequently, any material can be defined on the grid if its conductivity, permittivity and permeability are known.

2.12.3.2 Finite Element Method (FEM) & Finite Volume Method (FVM)

Finite element method is one of the more well-known numerical approaches, this may be mainly attributed to its applicability across a wide a wide range of disciplines [197]. Which includes problems involving heat transfer, fluid dynamics and structural mechanics. FEM only deals with harmonic fields, not time varying fields. Due to this, Computational time will be
exceedingly large for a large amount of frequencies, consequentially FEMs are often avoided in modelling of electromagnetic shielding material performance.

FVM is similar to that of FEM, though there are subtle differences in the discretization process which can be seen here [198]. FVM is also not well suited to EMI shield modelling as significant computational time and algorithmic complexity is needed to resolve a wide range of frequency responses.

2.12.3.3 Finite Integration Technique (FIT)
The key difference that defines the finite integration technique is that it discretizes the integral form of Maxwells equations as appose to the differential form. This leads a collection of theoretical, numerical and algorithmic advantages [199]. Much like FDTD, FIT is found to work well in both frequency and time domain also showing stability across a variety of mesh types. FIT has proven to be both an efficient and accurate tool for the modelling of electromagnetic waves.

2.12.4 Multiscale Modelling
Graphene, being a nanomaterial is quite small in comparison to the macroscopic EMI shielding composite behavior. A simulation of the electromagnetic behavior which possess features at the nano and macroscopic scale would require sophisticated algorithms along with immense computing power. The computational cost of numerical solutions becomes increasingly expensive with the use of smaller grid sizes. Multi-scale modelling techniques can be implemented in order to resolve electromagnetic effects at different spatiotemporal scales. There are various multiscale modelling approaches, some of which are further discussed later in this thesis. A common theme between all of them is to first homogenize the material. In the case of electromagnetism an effective conductivity, permittivity and permeability is found via an average over a representative volume element. These effective values are used to then define the homogenized material properties.

Physically, the graphene/polymer can be treated as macroscopically homogenous if a good dispersion is achieved and the wavelengths of interest are sufficiently larger than the graphene inclusion. Homogenized (or effective) bulk properties can also be theoretically predicted via knowledge of the heterogeneous microscopic interactions between the graphene and polymer matrix. Below a comprehensive description of all the electromagnetic behavior at the micro scale is given. This is described under an analytical continuum-based model eventually leading
into a theoretical electromagnetic graphene/polymer homogenization model based on Bruggeman’s effective medium theory [200].

2.12.5 Micromechanics of Graphene Nanocomposites

Conductive GnP-integrated polymer composites preserve the advantages of lightness, low-cost, design flexibility and ease of processing of polymers. Incorporating conductive fillers circumvent the intrinsic transparency of polymers through interactions between the EMWs and conductive fillers. The SE of GnP-integrated polymer composites mainly depends on the graphene filler’s intrinsic conductivity, permittivity, permeability and aspect ratio. Percolation, tunnelling and hopping are regarded as three critical mechanisms of conduction [31] in GnP-polymer nanocomposites, which are outlined below. In conjunction, the presence of agglomeration altering the aspect ratio and an imperfect interface affecting both conductivity and permittivity is also discussed below. Understanding the micromechanical phenomena over a range of frequencies will further assist in a comprehensive and accurate model that can determine the bulk material properties based on the intrinsic properties of both the GnP and polymer. Which then can be used as comprehensive tool to analyze and predict the electromagnetic properties of the material up to roughly 12 GHz, thus the SE can be found via analytical or numerical methods previously discussed.

2.12.5.1 Percolation

The critical conductive filler content is referred to as the percolation threshold, the point at which the filler forms an interconnected network [201]. One can observe a drastic increase in the conductivity of the polymer at this critical filler concentration point. Above the percolation threshold, an insulating polymer would allow the flow of current through the conductive network established by conductive fillers. The sharp insulator-conductor transition is seen to be more emphasized in situations of high contrast; that is, where the difference in the constituent properties of the composite is significant [202]. The percolation threshold is purely governed the level of agglomeration and the filler inclusion geometry [31, 202] (characterized by the aspect ratio). It can be directly derived from the micromechanical modelling [203]. Although due to aspect ratio degradation during processing, higher percolation thresholds are often found than theoretical values predicted by these models [204].

Graphene’s flat sheet microstructure offers substantial advantages over conventional carbon fillers due to its extreme aspect ratio values which give rise to a low percolation threshold. This feature means graphene makes a desirable filler as it will exert high conductivity with minimal
loading, if appropriately dispersed. The conductivity of epoxy was found to be $\sim10^{-14}$ S/m [164], whereas adequate conductivity for shielding applications is reported to be 10 S/m [164].

Table 2 – Summary of electrical conductivities for GnP-loaded polymer composites at various loadings outlines the electrical conductivity values of GnP/epoxy composites with various loadings and dispersion methods. Although percolation was reached, any of the previously reported composites did not achieve sufficient shielding conductivity. The highest electrical conductivity of $7 \times 10^{-1}$ S/m was achieved by the direct mixing of GnPs at 5 wt. % into epoxy, followed by the sonication method [179]. It is also worth noting that while increasing the loading would enhance the electrical conductivity, this will also promote agglomeration. As a result, longer mixing time or high-pressure dispersion techniques will be needed. This practice may degrade the aspect ratio of GnPs, leading to the drop in ultimate conductivities. Maintaining graphene’s large surface area throughout the dispersion process is the key to achieving high electrical conductivities at low percolation thresholds.

Table 2 – Summary of electrical conductivities for GnP-loaded polymer composites at various loadings

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Dispersion Method</th>
<th>Polymer Type</th>
<th>Percolation Threshold</th>
<th>Electrical Conductivity at percolation threshold [S/m]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GnPs</td>
<td>Sonication</td>
<td>Epoxy</td>
<td>0.1 vol%</td>
<td>$1.02 \times 10^{-3}$</td>
<td>[94]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Three-roll milling</td>
<td>Epoxy</td>
<td>1 wt%</td>
<td>$2 \times 10^{-6}$</td>
<td>[12]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Direct mixing and sonication</td>
<td>Epoxy</td>
<td>5 wt%</td>
<td>$7 \times 10^{-1}$</td>
<td>[179]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Three-roll milling and sonication</td>
<td>Epoxy</td>
<td>0.52 vol%</td>
<td>$2.5 \times 10^{-3}$</td>
<td>[101]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Three-roll milling and mechanical stirring</td>
<td>Epoxy</td>
<td>1.5 wt%</td>
<td>$1 \times 10^{-7}$</td>
<td>[204]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Three-roll milling</td>
<td>Epoxy</td>
<td>0.3 wt%</td>
<td>$3 \times 10^{-5}$</td>
<td>[205]</td>
</tr>
<tr>
<td>Graphene nanosheets (GnSs)</td>
<td>Sonication</td>
<td>Epoxy</td>
<td>1 wt%</td>
<td>$1 \times 10^{-5}$</td>
<td>[206]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Sonication with solvent</td>
<td>Epoxy</td>
<td>1 wt%</td>
<td>$1 \times 10^{-6}$</td>
<td>[207]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Three-roll milling</td>
<td>Epoxy</td>
<td>0.52 vol%</td>
<td>-----</td>
<td>[91]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Sonication with acetone solvent</td>
<td>Epoxy</td>
<td>8.5 wt%</td>
<td>(8 \times 10^{-7})</td>
<td>[178]</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------</td>
<td>--------</td>
<td>---------</td>
<td>-----------------</td>
<td>------</td>
</tr>
<tr>
<td>GnPs</td>
<td>Sonication</td>
<td>Epoxy</td>
<td>5 wt%</td>
<td>-----</td>
<td>[208]</td>
</tr>
<tr>
<td>GnPs</td>
<td>Sonication with isopropyl alcohol solvent</td>
<td>Epoxy</td>
<td>0.75 wt%</td>
<td>-----</td>
<td>[209]</td>
</tr>
</tbody>
</table>

### 2.12.5.2 Electron Tunneling

The electron tunneling phenomenon can be understood in terms of the probabilistic nature of quantum particles wherein the particles penetrate a potential energy barrier with a height larger than the total energy of the particles. Based on this occurrence, electron’s probability distribution will be non-zero on the other side of a potential which is classically forbidden. Thus, electrons travel through the graphene network with higher conductivity than otherwise expected. Electron tunneling was observed in carbon-nanofibre composites using conductive-tip atomic force microscopy (AFM) [210]. The authors claimed that this phenomenon has a minimal effect at low loadings, growing stronger after that. Due to its complex quantum mechanical nature, the phenomenon is difficult to analyze [202]. Xia et al. [211] effectively employed Cauchy’s probabilistic function to describe the random tunneling process in graphene polymer composites, which increases considerably at the percolation threshold, followed by a continuous increase thereafter due to a reduction in inter-particle distance.

### 2.12.5.3 Agglomeration

The dispersion state of graphene fillers throughout the polymer matrix has major impacts on the resulting nanocomposite properties. Along with higher loadings needed to reach percolation and inhomogeneous properties, agglomerated particles alter the desirable intrinsic properties of the nanoparticles. Agglomeration is known as the assemblage of particles in the matrix which can occur due to strong van der Waals forces between GnPs inclusions. Atif et al. [212] explores some of many causes and potential production pathways to limit agglomeration in both graphene an CNT polymer composites. Here the synthesis method used, geometry of the filler, surface chemistry and type of polymer matrix used are listed as some of critical factors which affect the dispersion state. Some of the findings included - the carbon filler synthesis method often yields the filler in entangled form, which will affect the dispersion, higher volume fractions are more likely to agglomerate, solvents and surfactants can be used to achieve better dispersions, and close attention to the production parameters is key in achieving a good dispersion. The details of graphene polymer nanocomposites fabrication are provided earlier.
in this thesis (page 22). However, modelling the effect of agglomeration has not yet been discussed.

Modelling such a complex material system can be undertaken by separating the filler rich section (agglomerates) which possess a higher filler concentration, from the non-percolating filler poor section. The effective (or homogenized) property is then determined for each section. Secondly, the total nanocomposite effective property is then determined from the summation of these two sections [211, 213]. This two-scale approach is also known as ‘selective localization’ [31]. Figure 18 illustrates selective localization wherein two phases are present. The rich section with higher graphene concentration contains agglomerates while the poor section holds low concentrations of graphene.

![Figure 18 - Schematic depiction of a highly agglomerated graphene nanocomposite. Image produced by author](image)

The aforementioned modelling technique relies on the correct assumption of the level of agglomeration, that is essentially the volume fractions of the filler rich and filler poor sections. This assumption can be assisted by microscopy techniques such as scanning electron microscopy (SEM) which give insight into the micro morphology. Additionally, software such as Image J can be used to characterize particle size distribution etc. Although no software available can directly determine the level of agglomeration. It can also be noted that an average particle after dispersion could also be used and agglomeration modelling can be avoided. Agglomeration serves as the biggest cause as to why theoretical modelling and experiment values of graphene nanocomposites yield different results [214].

### 2.12.5.4 Imperfect Interface & Nanocapacitance

As with many particulate composites, a thin layer intervenes between the GnPs/polymer boundaries. The interfacial layer possesses different properties to that of the matrix and filler alone, consequently altering the effective GnP/polymer conductivity and permittivity. Thus, an
accurate model must account for this, so that values will match experimental observations. The
Imperfect interface problem has a long history in composite research, as suitable bonding
between filler and matrix is necessary for a good dispersion. Xia et al. [211] effectively handled
it by treating the inclusion as if it has a thinly coated isotropic layer around it. By doing this, a
subsequent modification is then made on the permittivity, permeability, and conductivity of the
graphene inclusion to that of a graphene inclusion with a thinly coated layer. Which is described
as the Mori-Tanaka approach [215]. With the correct assumption of the interlayer properties,
the coating method is shown to be effective.

An additional requirement that a thorough model needs to consider is known as
‘nanocapacitance’. Nanocapacitance happens due to the Maxwell-Wagner-Sillars (MWS)
polarization effect, which describes the ability of two materials with different conductivities to
create polarizations [216]. Electron conduction through the percolating network will move
positive charges in the polymer matrix towards them, and thus charges will accumulate at the
surface interface creating polarization. An in-depth exploration of this phenomenon is
performed by Yousefi et al. [216], while looking at the EMI properties of graphene polymer
composites. This process, which is theoretically identical to a traditional macroscopic
 capacitor, will cause the permittivity to be continuously increased above its percolation
threshold. The random nature of this occurrence has motivated Xia et al. [211] to investigate
the use of Cauchy’s cumulative distribution function to adjust the permittivity.

2.12.5.5 Frequency-Dependent Conductivity and Permittivity
Electron hopping is a phenomenon in which electrons are excited into free delocalized states,
thereby conducting charge. In 2018, the equation \( \sigma(T) = \sigma_0 e^{-\left(\frac{T}{T_0}\right)^\gamma} \) was suggested Marsden et al. [31], which dictates electron hopping as dependent on temperature (T). Dyre’s hopping
model as presented by Xia et al. [13] may be a more suitable approach for the estimation of
SE, Since the adjustment of conductivity can be made in terms of frequency, instead of
temperature, as shown in Equation 11;

\[
\sigma(\omega) = \sigma_{\text{static}} p(\omega) \quad \text{Equation 11}
\]

where \( p(\omega) \) is Dyre’s hopping function that could be calculated using Equation 12 as follows.

\[
p(\omega) = \frac{\omega\tau_0(tan^{-1}(\omega\tau_0))^2}{[0.5ln(1+(\omega\tau_0)^2)]^2+(tan^{-1}(\omega\tau_0))^2} \quad \text{Equation 12}
\]

where \( \tau_0 \) is the characteristic time of electron tunneling, and \( \omega \) is the angular frequency.
In consequence of electron hopping, there will be less interfacial charge accumulated at higher frequencies. Nanocapacitive affects, therefore, become less prominent as electron hopping increases with frequency under an AC loading. This system can be modeled by a network of capacitors, as depicted in Figure 19. It, therefore, becomes necessary to implement the frequency-dependent Debye relaxation for the interfacial permittivity [13, 31] (Equation 13).

\[ \varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_{\text{static}} - \varepsilon_\infty}{1 + \omega^2 t_\varepsilon^2} \]  

Equation 13

\( \varepsilon_\infty \) represents the dielectric permittivity of the interlayer at \( \omega \to \infty \) and \( t_\varepsilon \) is Debye’s relaxation time that represents the MWS effects.

Figure 19 - Schematic of Maxwell-Wagner-Sillars effects due to the formation of numerous nanocapacitors in the graphite-polymer composites; Reproduced with permission from Ref. [13].

2.12.5.6 Thermal Conductivity Modelling

Although the thermal conductivity of graphene polymer composites does not fall under an electromagnetic property, similar modelling approaches can be used to determine a graphene polymer composite thermal conductivity [217]. Therefore, some discussion is given on the construction of this model. Much like the case for electromagnetism the theory can be broken up into three parts: filler, matrix and interface. A coated graphene or more formally a Mori-Tanaka [218] approach is also taken, whereby the filler is modified to a coated filler which accounts for any interfacial effects. The thermal conductivity at the interlayer is determined by a weighted summation of contributions from filler to matrix (F-M) and filler to filler (F-F) contacts. F-M contact decreases with an increase in filler loading, while F-F increases. These trends can be modelled with Cauchy’s cumulative distribution function. If the thermal conductivity at both the F-M and F-F contacts are well defined, then the interfacial thermal conductivity as a function of filler loading can be found. Much like the electromagnetic model this can be used to define the properties of a coating modified filler, then finally the properties of the homogenized composite.
2.12.6 Effective Medium Theory for EMI

Both analytical and numerical solutions of Maxwell’s equations for EMI shielding properties are reliant on knowing the conductivity, permeability, and permittivity of all present materials. Determining these values can also be done by experimental characterization techniques. Alternatively, a theoretical approach can be adopted, which determines the composite properties based on the properties of its constituent parts. Putting all the micromechanical phenomena of electron transport in GnPs/epoxy samples together into a standard homogenization model allows for an effective conductivity, permeability and permittivity to be determined [13, 211].

A first step for determining the electronic properties of nanocomposites can be taken by adopting classical percolation theory (see Equation 14) [31].

\[ \sigma_e = \sigma_0 (c_1 - c_1^*) \]

*Equation 14*

where \( \sigma_e \) is the effective conductivity, while \( c_1 \) and \( c_1^* \) represent the filler concentration and percolation threshold, respectively. \( \sigma_0 \) and \( t \) denote the empirical curve fitting parameters. Although Equation 14 is a commonly-used empirical model (e.g. Bauhofer and Kovacs [219]) which can provide a useful curve fit to experimental data, it does not offer any insights into the underlying micromechanics.

More complex computer-based modelling and simulation (CMS) approaches have shown to be useful in uncovering the physical nature, performance and applications of graphene composites [220]. This may include Quantum Chemistry approaches (QC) [221] Molecular Dynamics (MD) [222, 223] and Monte-Carlo (MC) [224] simulation techniques. Unfortunately, all these approaches are computationally expensive and therefore, not particularly suited for continuum problems involving a larger number of atoms. Other models which were developed from the framework of micromechanics have shown to handle relevant parameters, such as filler concentration, shape and orientation in an intuitive and computationally inexpensive manner [202, 225]. Exhaustively covering all modelling techniques for nanocomposites is an ambitious task and out of the scope of this review. Instead, some discussion on commonly used techniques will be provided.

Micromechanics employs traditional continuum-based mechanics to describe the behavior of features in the scale of microns, whereas nanomechanics deals with QC, MD, and continuum atomistic-based modelling. Macromechanics refers to models constructed with disregard for the underlying micro/nanomechanics, which includes MC simulations and resistor-based
networks [226]. Further discussion on some of these methods as applied to graphene and graphene composites is provided below.

2.12.6.1 Quantum Chemistry
Quantum chemistry (QC) approaches are based on the solution to Schrödinger’s equation [227]. The computational expense of solving this equation grows rapidly with the number of particles. The two of the most found approaches to solving the Schrödinger equation are density functional theory and the wavefunction based approach. QC solutions are an essential tool if one wishes to calculate the density of states or band structure of graphene. Liu and Shen [228] used a quantum chemistry density functional theory approach in order to compare the effectiveness of different bandgap engineering strategies. The strategies compared included surface bonding, isoelectronic codoping and alternating the electrical and/or chemical environment. Through density functional simulation it was concluded that alternating the chemical environment and isoelectronic codoping were two effective strategies for altering the bandgap structure of graphene. Here, Quantum chemistry has been used as tool to analyze the structure of graphene and make predictions that are now only require the engineering solution in order to achieve such results.

2.12.6.2 Molecular Dynamics
Molecular dynamics (MD) is a commonly used simulation tool that models the dynamics of a material system at the molecular scale by treating each atom as a node is the system that exerts a force on one another. For MD computation, the initial position and velocity along with boundary conditions must be set. MD simulation can be used to analyze and explore graphene and graphene-based nanostructures. For instance, Pie et al. [229] was able to predict the mechanical properties of graphene that had been functionalized with hydrogen using a molecular dynamics approach. The tensile strength, Young’s modulus and fracture strain were all able to be calculated at hydrogen functionalization levels from 0 to 100%. It was reported that 100% hydrogen coverage of graphene lead to a 30% decrease in Young’s modulus and roughly 65% decrease in both fracture strain and tensile strength. Evidently, molecular dynamics has provided to be a useful tool in analyzing the properties of graphene nanocomposites under different conditions. This was achieved much faster than what can be understood by empirical methods.
2.12.6.3 Monte-Carlo Simulation

Monte-Carlo simulation (MC) are a commonly found computation tool that is used to increase computation time. In contrast to MD which focuses on the dynamics of the systems atoms at all points in time, MC only focuses on the equilibrium or final conditions. This inevitably cuts out a large amount of computation time. One example of the utilization of MC methods to simulate graphene behavior includes the work by Fasolino et al. [224] which analyzed the intrinsic ripples present in monolayer graphene. Another example includes the work by Mostaani et al. [230] which analyzed and compared the binding forces between graphene layers stacked in an AA or BB structure.

2.12.6.4 Image Processing

Image processing is a unique approach in which microscopic images which were taken by either atomic force microscopy (AFM), scanning electron microscopy (SEM) or optical microscopy methods are analyzed based on a binary digit system that suggests whether a particular spot belongs to the conductive or the insulating phase, depending on its brightness. A computer algorithm is then employed to determine the effective composite conductivity. This method is limited by only being two dimensional and highly dependent on the image contrast [226].

Recently, Taherian [226] described 36 mathematical-analytical approaches to model the conductivity of composites. He also expounded a broader range of micromechanical and macromechanical models along with some discussion on image processing techniques. Further overlapping categories of composite modelling comprise empirical methods (i.e. mixing theory), percolation-based methods, bounding methods (place upper-lower bounds on the response of material), effective medium approximations, asymptotic homogenization, fractional calculus and many other strategies in the growing field of multi-scale modelling.

2.12.6.5 Effective Medium Approximation

The effective medium approximation (EMA) - which was later extended into the self-consistent method, is used to describe macroscopic properties of microinhomogeneous materials. This work can be seen as an extension of the work performed by Eshelby [231] on the strain-stress relationship of an ellipsoidal inclusion in a surrounding elastic solid. Effective medium approximations benefit from being simple, accurate, and computationally inexpensive and if applied well, micromechanically descriptive. These features make this approach suitable for graphene polymer nanocomposites [13]. A fundamental limitation of the effective medium approximation is...
approximation is that the wavelength must be significantly larger than the filler inclusion size [13]. Ganguly et al. [193] suggest the Maxwell Garnet method as it is a simple and well established EMA for determining the electromagnetic values of composites. Koledintseva et al. [232] employed the Maxwell-Garnet approach for the assessment of EMI shielding properties of different composites and concluded that the method could be only used for low filler concentrations below the electrical percolation threshold. In this study, McLachlan’s equation was needed to be used near and above the percolation threshold.

Likewise, Bruggeman’s effective medium-approach which was first introduced in 1953 [200] has shown to be able to accurately determine the electrical conductivity, permittivity, and permeability of graphene nanocomposites. Additionally, it can be incorporated as the backbone of a model which features further exploration into some of the micromechanical features affecting the SE. These traits include percolation, agglomeration, imperfect interface, nanocapacitance, electron tunneling, frequency-assisted electron tunneling, and dielectric relaxation. The proposed model, as constructed by Xia et al. [13] has shown to be in agreement with experimental results up to 12 GHz. Here, the anisotropic behavior of graphene nanocomposite is handled by taking the orthogonal average and therefore viewing the homogenized nanocomposite material as isotropic. The demonstrated model provided a simple analytical framework for predicting composite bulk properties along with the percolation threshold. Reflection, absorption, shielding effectiveness, conductivity, permittivity, permeability, and percolation threshold could then be plotted against experimental variables including incident radiation frequency, filler aspect ratio and filler concentration. These may then be further used to tailor nanocomposites to meet specific technological applications.

\[
\begin{align*}
    c_0 \frac{k_0-k_e}{k_e+k_0-k_e} + c_1 \left[ \frac{2(k_1-k_e)}{k_e+S_{11}(k_1-k_e)} + \frac{(k_3-k_e)}{k_e+S_{33}(k_3-k_e)} \right] &= 0 \quad \text{Equation 15}
\end{align*}
\]

Equation 15 above is known as the Bruggeman’s effective medium equation [200]. It is best presented here with three terms. One for the polymer properties, and one each for the in-plane and out-of-plane graphene properties. Once the interfacial effects are defined, namely, electron tunnelling, electron hopping, nano-capacitance the interfacial conductivity can be used to determine the properties of a coated filler. Equation 15 can then be used to solve for filler rich and filler poor regions of the inhomogeneous composite, then lastly for the properties of the total nanocomposite.

Here \( k_i \) represents the material property of interest (e.g. electrical conductivity, thermal conductivity, permittivity, permeability etc.) of the \( i \)th phase, with 0, 1, 3 and e meaning the
matrix, filler in-plane, filler out-of-plane and effective medium phases. $C$ denotes the volume concentrations, while $S_{11}$ and $S_{33}$ represent components of the Eshelby tensor in the in-plane and out-of-plane directions, respectively. The Eshelby tensor \cite{231} defines the ellipsoidal geometry as determined from the aspect ratio.

The derivation of Equations 15 present by Wang & Weng \cite{202} is summarized as follows. Maxwell’s far-field matching \cite{1} is adopted to solve the effective conductivity tensor. The filler geometry is idealized to be ellipsoidal, and therefore, the wave scattering tensors are defined accordingly. A new effective medium is then defined, which under the conditions of Maxwell’s far-field matching will possess the same volume averaged scattered field as the scattered field determined from the material’s constituents at a far distance. Lastly, by assuming a random filler orientation, an orientational average can be taken which resolves the existing tensor equation into Equation 15.

2.13 Experimental Characterization of GnP/Epoxy Composites for EMI Shielding

There are several methods available for determining the electromagnetic shielding and bulk electromagnetic properties of nanocomposites. SE, permittivity, permeability, and loss can all be determined from measured reflection and transmission coefficients which is a regular practice in the field of electromagnetic compatible nanocomposites \cite{11}. Furthermore, several analysis tools have been employed for the understanding of the physicochemical properties relating to the filler or dispersion state and its effect on SE. Some of the reputable techniques assessing the physical, morphological, and functional properties of nanocomposites and their constituent elements are summarized and discussed below.

2.13.1 Characterization of Graphene Flakes and Dispersions

Firstly, some discussion is given on the methods used to characterize graphene flakes and dispersions. Then later discussion is provided on methods used for characterization of the electromagnetic properties.

Several widely available scientific instruments have been used to characterize graphene in different forms. Microscopy for one, is a ubiquitous tool used across many scientific disciplines; graphene science is no exception. The following sections outline the importance of being able to microscopically observe graphene flakes, dispersions and composites along with some methods used to so.
2.13.1.1 Morphological Properties

As discussed previously achieving a uniform dispersion is key in creating a conductive pathway throughout a non-conductive polymer. The shape and size of this pathway is therefore of great interest.

2.13.1.1.1 Particle Size and Aspect Ratio Characterization

The electrical characteristics of nanocomposites are highly dependent on the size of the filler particles, often characterized by the aspect ratio [233]. There are several reports conducted on the effect graphene aspect ratio has on polymer composite properties. The effect of functionalized GnP aspect ratios on mechanical properties was reported by Chong et al. [234]. They showed that the reinforcement effects of GnPs are significantly decreased by agglomeration as this alters the aspect ratio. Furthermore, the impact of GO aspect ratio on the properties of polyvinyl alcohol nanocomposites was investigated [66], the authors concluded that increasing the aspect ratio would enhance Young’s modulus. The effect of aspect ratio on Young’s modulus was also in agreement with the Halpin-Tsai model. On the other hand, there is a limited number of studies on the development of epoxy matrices reinforced with thin graphene sheets (or stacks of several graphene sheets) with particular regard to the calculation of the aspect ratio of the filler.

Generally, dynamic light scattering methods (DLS) are used to measure the size and size distribution of nano/microparticles. This method relies on the assumption that the filler nanoparticles are spherical shaped. Due to the planar 2D shape of GnP's, other alternative methods may be required for GnP's. Corcione et al. were probably first to successfully calculate an average value of the aspect ratio - the ratio between the in-plane average dimension and the thickness of the reinforcement, based on measurements of thermal and electrical properties [191]. Authors have reported an aspect ratio ranging between 1250 and 1550 which suggests the formation thin graphite platelets characterized by a thickness in the order of a few tens of nanometres, which were dispersed in the epoxy matrix through sonication. Also, Bharadwaj model was used to predict the average orientation of graphene stacks, using the average aspect ratio calculated from macroscopic properties of nanocomposites. Ravindran et al. [235] have recently suggested pairing microscopy and image processing techniques/software such as ImageJ in order to determine particle size distribution. Conventional microscopy techniques for resolving submicron imagery are outlined below.
2.13.1.1.2 Microscopical Observation
A large number of microscopic methods including but not limited to optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) have been extensively utilized to investigate the morphology of graphene fillers and dispersions [236-238]. These may be categorized into three main subcategories of optical microscopy, scanning probe microscopy and electron microscopy methodologies.

2.13.1.1.2.1 Optical Microscopy
The optical absorbance of pristine graphene (i.e. mechanically exfoliated graphene) has been found to be 2.3% per single layer in the visible range [239]. Although it is possible to acquire optical images of suspended graphene sheets under bright field transmitted light, the observation of single-layer graphene materials using an optical microscope remains tricky. This hindrance becomes particularly important when graphene is deposited on a substrate that increases the background absorption, which could impede the identification of graphene flakes on a substrate. Compared to graphene, GO has much paler colour and even weaker optical absorbance [240], which prohibits its direct optical observation under bright field illumination. Other optical methods including interference-based techniques [241, 242], imaging ellipsometry [243] and polarization (parameter) indirect microscopic imaging (PIMI) [244] were employed to image graphene and GO deposited dielectric-coated silicon wafers. It is though worth mentioning that thicker graphene flakes can be imaged with an optical microscope under reflective illumination.

2.13.1.1.2.2 Scanning Probe Microscopy
Scanning probe microscopy techniques have been extensively used to image graphene-based materials since its high resolution allows accurate height measurement at the nanometre scale. Among these, AFM has become an essential instrument for research in the graphene area. The first reported isolation of graphene was confirmed via AFM [245]. Figure 20 (b) and (c) depict a single layer of crystalline graphite (graphene) and a micrograph of graphene sheets deposited onto a mica respectively, which were both obtained via AFM. More recently, AFM has been used to characterize and directly observe GnPs [246].

It is common to use the following equation to determine the number of layers (N) for the measured single-layer graphene thickness via AFM [247]

\[
N = \frac{(t_{\text{measured}} - 0.4)}{0.335} 
\]

Equation 16
However, careful inspection of the current literature reveals that AFM has been an inaccurate and unreliable method for N determination, particularly for single-layer graphene with reported values of thickness in the literature ranging from 0.4 to 1.7 nm [248].

Scanning tunnelling microscopy (STM) uses tunnelling electrons to produce three-dimensional real-space images of the surfaces of materials which is often used for imaging graphene materials when an atomic-scale resolution is needed. The major disadvantage of scanning probe techniques is their low-throughput, making it costly and time-consuming for large-area sample examination. Therefore, these measurements may not adequately represent and ignore the inevitable distributions in particle size. In addition, they need to operate on a low-vibration platform, and the samples need to be deposited on a surface possessing low roughness such as Si wafer, freshly cleaved mica, or quartz.

2.13.1.2.3 Electron Microscopy

SEM creates an image of the surface of a sample by detecting reflected or knocked off electrons. This method is useful in imaging the sample surface morphology and can also be used to uncover GnP particle size distribution within different polymer matrices [235]. SEM is a common characterization technique and is often used to observe many graphene-based materials. For example, Hernandez et al. demonstrated the analysis of thin graphite flakes with fewer than five layers made with a liquid-phase exfoliation using SEM [249] and Cote et al. observed monolayer GO using SEM [250]. Later examples show SEM being used for GnP observation [251].

Transmission electron microscopy (TEM) can uncover the inner structure of a sample on the submicron scale enabling the quantitative analysis of the GnP size. It relies on the transmission of electrons through the material to create an image. This method is useful for investigating the GnP dispersion state within the epoxy. The in-plane carbon-carbon bond distance in graphene is 0.142 nm, which was considered too small to be resolved in most conventional TEMs. However, the development of aberration-corrected TEMs enabled the direct observation of the atomic structure of graphene-related carbons [252].
Figure 20 - (a) bright field images taken by the modulated polarization parameter imaging system using 100x objective of a chemically prepared graphene overlapped to 1 to 6 layers on a glass slide, reproduced with permission from Ref. [244]. (b) Single-layer crystallites of graphite on top of an oxidized Si wafer visualized by AFM (scale bars: 1 μm.), reproduced with permission from Ref. [245]. (c) Micrographs of an AFM image of graphene sheets deposited onto a mica substrate from an aqueous dispersion, reproduced with permission from Ref. [109]. (d) STM topographic images of a single layer of graphene where a honeycomb structure is observed, reproduced with permission from Ref. [253]. (e) SEM images of a graphite flake sample, reproduced with permission from Ref. [254]. (f) A representative TEM image of graphene sheets deposited onto a mica substrate from an aqueous dispersion, reproduced with permission from Ref. [109].

Perhaps one of the most important early papers on TEM of carbon was a 1952 study of catalytically grown carbon filaments by the Russian scientists Radushkevich and Lukyanovich [255]. Their TEM images which are now recognized as the first observation of the structures known as CNTs clearly showed that the filaments were tubular. Over the past 60 years, understanding the structure and properties of graphite became a priority for the nuclear industry, mainly since radiation effects on graphite may have played a role in the Windscale reactor fire of 1957. Consequently, much fundamental work was carried out on the structure of
graphite using conventional bright and dark field TEM during the 1960s [256-258]. In 2007, Kazu Suenaga et al. published one of the earliest TEM images in graphene area [259]. Gong et al. have conducted a comprehensive analysis of defects in single-layer and bilayer graphene [260]. In consideration for digital image analyses, Ravindran et al. [235] note that the ultramicrotomy process involved TEM would result in significant time being spent stitching several TEM micrographs together, and thus SEM is favoured.

2.13.1.1.3 Raman Imaging
The number of graphene layers can be estimated using optical techniques such as Rayleigh imaging and Raman spectroscopy [261, 262]. Rayleigh imaging relies heavily on interferometric contrast between graphene and the underlying substrate upon white light illumination. The obtained contrast can provide valuable information on the thickness of the graphene sheet. However, it is not able to accurately determine layer number, particularly for \( N > 6 \) [261]. Nonetheless, Raman spectroscopy has proven to be the technique of choice for determining \( N \), since particular features of the Raman spectrum are highly dependent upon \( N \) [248]. The most noticeable changes occur at around \( \sim 2600-2700 \text{ cm}^{-1} \) known as the 2D band which alters in shape and changes position and intensity with changes in the number of layers. Raman spectroscopy, though limited to high-quality graphene with very few structural defects, is much more reliable for few-layer (\( N < 4 \)) samples than for thicker samples which are generally much more prevalent.

2.13.1.1.4 X-Ray Diffraction
X-rays diffraction patterns can be used to determine the intermolecular spacing of crystalline materials. This method can help confirm the existence of graphene [263], and characterization of graphene composites [264]. For instance, Kashi et al. [264] compared the x-ray diffraction patterns from polymers with and without GnP inclusion noting the effect that GnPs may have on the crystallinity of both polylactide and polybutylene adipate-co-terephthalate. Determining the number of graphene layers is much more difficult with x-ray diffraction then other methods, as x-ray diffraction data is not highly dependent on the number of layers. More complicated models are needed if one wishes to do so [265].

2.13.2 Testing Methods for the Measurement of EMI Parameters
The process for determining the dielectric and magnetic properties of materials is often undertaken by an experimental setup which measures the amount of power transmitted through and reflected by the material. SE can be determined from these reflection and transmission values, while the bulk properties can also be determined via conversion methods. Conventional
conversion methods include Nicholson-Ross-Weir (NRW), NIST Iterative, New non-iterative or Short circuit line (SCL) [266]. It is important to note that for some semiconductive materials, Ohmic and dielectric losses are often indistinguishable. In other words, for non-magnetic materials, $\varepsilon^\prime$ can also be represented as $\sigma_{ac}$ in S/m where both terms constitute both Ohmic and dielectric losses.

There are various experimental methods including but not limited to; transmission/reflection line methods, open-ended coaxial probe methods and free space methods, these are detailed below. All these methods rely on the use of a network analyzer (NA), which are further classified as scalar network analyzer (SNA) and VNA. The function of SNA is to gauge the amplitude of electrical signals only, while the VNA is used to gauge both the phases as well as magnitudes of the different signals. Despite the high cost incurred in VNA, it is the most preferred and commonly used instrument because of the inability of SNA to assess complex signals such as complex permittivity ($\varepsilon^*$) and complex permeability ($\mu^*$). Figure 33 and Figure 32 both provide an image which features a VNA.

2.13.2.1 Transmission/Reflection Line Methods

Transmission/Reflection line methods are suited for measuring both the permittivity and permeability of samples using either a coaxial line or waveguide. A solid planar material is placed in a specialized holding unit, and the power reflected and transmitted is compared to that of reference material. This method works well for samples with medium to high loss [96]. The accuracy is limited by air-gap effects, and when the sample length is a multiple of one-half the wavelength [266]. This method is widely understood as the preferred method, mainly due to its standardization, meaning comparable results can be easily achieved in different laboratories [267]. Al-Hartomy et al. demonstrate the use of the coaxial line method in determining the SE of GnP and CNT filled natural rubber composites across a frequency range of 2-12 GHz [268]. Furthermore, waveguide techniques have been demonstrated to be suitable for graphene foams which possess superior shielding properties [186, 269]. This method is by far the most prevalent in current EMI materials research. A Typical waveguide setup is featured below in Figure 21 - Waveguide attached to a Vector Network Analyzer. Gathered from ref. [270]. Here, two coaxial waveguide adapters are connected to the two waveguide components which meet at the middle where the sample is held.
2.13.2.2 Open-ended coaxial probe methods

Open-ended coaxial probe methods are like coaxial line methods although the coaxial line stops at the sample, meaning only the reflection is measured. As a result, the permeability cannot be determined [266]. However, Open-ended coaxial probe methods benefit from being able to determine reflections from liquids, biological specimens and semi-solids. Inaccuracies can arise from air gaps between the sample and the solid [266]. Figure 22 features an image of a VNA attached to a dielectric probe which is positioned up against the sample. Note the cable and sample are tilted held using the clamp/stand this is essential as any small movement will lead to drastic changes in the results.
2.13.2.3 Free space method

Free space methods have also been used to determine the SE and bulk properties of various materials [267], which is done so by placing an antenna and receiver in a room with the shielding material. This method benefits from being suitable to a wide choice of materials ranging from solids to gases. The test takes place in an open space that is often designed to simulate the normal usage conditions and is therefore commonly used as a final product test. Inaccuracies from this method can arise from unwanted diffraction of the signal and multiple reflections occurring between the antenna and material surface [266]. Figure 23 is a schematic depiction of a typical free-space EMI measurement system which features a VNA along with antennas and a system to hold them. It additionally features a two dielectric lenses, which ensure which ensure plane wave incidence on the material under test (MUT).

![Figure 23- schematic of a typical open-space EMI measurement. Gathered from ref. [272].](image)

In some situations, it may be impossible to reduce the amount of ambient noise in an area, significantly. Therefore, a shielded room may be needed. The technique usually involves at least two shielded rooms with a wall between them, through which sensors can be run. The testing device and testing equipment are placed in one room, and sensor arrays in the other. Shielding leads are often included to reduce the potential for measuring errors caused by external signals.

Alternative methods may also include the shielded box method and resonant method. The shielded box method is much less prevalent due to drawbacks caused by difficulties in achieving good contact between the shielding material and box along with a limited frequency range (roughly up to 500 MHz) [267]. The resonant method benefits from being highly accurate and able to measure small samples, although it relies on a high-frequency resolution.
VNA and is limited to a small bandwidth [266]. Al-Hartomy et al. utilized this technique to determine the permittivity of GnP and CNT filled natural rubber composites.

2.13.2.4 Measurement/Calculation of bulk material properties

The above methods all measure the S-parameters, which is a common way of describing power transmission and reflection ratios. These S-parameters can be used to solve for the SE of a given material. Alternatively, conversion methods (described below) can be used to determine the bulk material properties from these S-parameters.

As the permittivity calculated in these methods is the complex permittivity which defines both the permittivity and loss, the loss term can be used to determine the ac conductivity, $\sigma_{ac}$. Herein, it is assumed that the material under test is non-magnetic, as with GnP/epoxy. Although it may be possible to extrapolate $\sigma_{ac}$ down to zero hertz to determine $\sigma_{dc}$, it may be necessary to measure $\sigma_{dc}$ directly. This can be achieved using specific test equipment.

2.13.2.5 Conversion Methods

Common conversion methods include Nicholson-Ross-Weir (NRW), NIST Iterative, New non-iterative or short circuit line (SCL) [266]. Each of which may be suitable depending on the task at hand. A description of each is provided below.

**Nicholson-Ross-Weir (NRW)** – A method suitable for both coaxial and waveguide measurements, that is computationally simple and fast. Though it is not suitable for low loss materials and is inaccurate when the material length is a multiple of half the wavelength.

**NIST Iterative** – This method is more complicated than NRW though is accurate across the whole frequency range and can be used for both high loss and low loss materials. It is also in incapable of measuring permeability.

**New Non-Iterative** – A method that is similar to the NRW, though is accurate across all frequencies and can’t calculate permeability. It is however a more sophisticated and computationally expensive algorithm.

**Short Circuit Line (SCL)** – This method is based on a one port measurement. It cannot calculate permeability and is iterative, meaning more sophisticated algorithms are needed.

Conversion methods are particularly important in measurements such as waveguide measurements, whereby the materials are tested without a TEM wave mode present. If the Shielding effectiveness were to be calculated from directly from the s-parameter file obtained from a waveguide measurement, this would not be describing the plane wave TEM condition.
under which the SE is often characterized. If conversion methods are used first this means the bulk material properties can be determined prior to the SE calculation. The SE can then be calculated under any conditions, meaning varying materials shape, size and varying incident wave conditions.

2.13.1.6 Direct Measurement

Electrical conductivity measurements are often achieved by either a two-point or four-point probe method whereby the resistivity is measured from applying either a voltage or current across the sample. Some important considerations to be made for this method are; good electrical contact between the probes, lighting or heating altering the sample’s conductivity, the impedance of the electrical probing equipment, calibration, and the non-Ohmic (non-linear) relationship between the current and the applied voltage. All conductivity values featured in Table 2 were achieved using either a four-point or two-point method [12, 91, 94, 101, 178, 179, 204-209].

![Figure 24](image)

**Figure 24** - (a) Two-point probe schematic. (b) Four-point probe schematic. Gathered from ref. [273]

Direct measurement techniques for permeability and permittivity are limited. Though it should be clear that whether categorized here as a direct measurement of S-parameter measurement all material measurements rely on sending a signal through the material and measuring the feedback. It is only the experimental setup that varies.
Chapter 3

Research Design

The research design can be broken up into three components: (1) sample fabrication, (2) experimental characterization and (3) theoretical modelling. The outcomes of this research project include characterization of the electromagnetic properties of in situ fabricated GnP/epoxy nanocomposites, GnP/polyvinyl alcohol nanocomposites films and GnP/epoxy/carbon fibre composites. In addition, a micromechanical model which predicts the bulk electromagnetic properties was constructed along with software that calculates the electromagnetic propagation through materials with said properties. Lastly, SEM, Waveguide Measurements & Dielectric probe measurements were undertaken in order to experimentally characterize the materials and compare them against theoretical predictions.

Figure 25 – An outline of the procedure taken in characterization of GnP/Epoxies. shows the critical steps taken in the theoretical and experimental determination of SE for the fabricated materials. SEM was chosen as it was readily available and suitable for the magnification scale of interest. With modifications made based on the micromechanics discussed, Bruggeman’s effective medium theory was then used to determine the effective conductivity and permittivity. A HP 85070A dielectric probe kit attached to HP 8752C Network analyzer was used to characterize the fabricated materials over the 0.3-6 GHz range. The provided software measures S-parameters, then converts them to the bulk material properties. In order to investigate higher frequencies, a ROHDE and SCHWARZ ZNB-40 VNA attached to a WR-90 waveguide was utilized. The measurements for this setup were conducted over the frequency range 8.2-12.4 GHz. For this, various conversion methods where explored, the NRW method was then chosen over others based on the criteria of robustness, simplicity and adequacy for this measurement. Code for which can be found here liam-anderson-l12/NRW-conversion: NRW conversion (github.com).

Lastly, reflection, absorption, multiple reflection, transmission and SE can be determined from both theoretical and experimental results of the bulk material properties by use of Maxwell’s equations. It should be noted that magnetic permeability was not measured as any of the matrix or filler material used did not possess significant magnetic properties. Relative permeability of 1 was assumed, which is in agreeance with predictions made by the model.

It is the intention that the research design adequately matches the research goals and outcomes.
3.1 Sample Fabrication

Various GnP/epoxy samples were fabricated, which were then characterized and contrasted against the micromechanical model predictions. GnP/epoxy/carbon fibre composites and GnP/PVA films were also fabricated and characterized. The fabrication process for each is outlined below.

3.1.1 GnP/Epoxy Sample Preparation

32g of PrimeTM 20LV epoxy resin was sonicated for a minimum of six hours at 30°C with the inclusion of GnP. 8g of PrimeTM 20 slow hardener was then added, maintaining a resin/hardener ratio of 100:26. Grade M GnP was purchased from XGSciences with an average particle diameter of 5 and 25 microns. Both 5- and 25-micron samples were prepared at different loadings of 0.5, 1, 2, 3 and 5 wt.%. Samples were left to cure at ambient temperature for 48 hours, then placed in an oven for post-curing at 80°C for 4 hours. The samples were then cut into appropriate sizes for analysis. Multiple pieces were made for each GnP loading in order to analyse the consistency of results.
3.1.1 GnP/Epoxy Fabrication difficulties and findings
Long sonication times were needed due to the fabrication method being solvent-free. In addition, there was still the presence of agglomerates even after long sonication times, particularly for large loadings. In future, it may be beneficial to treat the sample after sonication with centrifugation and filtering. Various moulds were also investigated, ultimately arriving at a silicon rubber mould with mould release wax being the most suitable. This was based on reusability, ease of removal and eliminating the need to cut samples to size after fabrication.

3.1.2 GnP/epoxy/carbon fibre composites Sample Preparation
Carbon fibre fabric was cut to 30cm x 30cm squares. The infusion mesh and vacuum bag were also cut to shape. Resin dispersion was prepared. This included degassing in a vacuum, where care was taken to slowly alter the vacuum pressure to ensure the resin air bubbles did not burst too suddenly.

The mould surface was prepared, a peel-ply layer was added, carbon fibre fabric was placed on top, and the infusion mesh was added. Vacuum bagging tape was applied, resin feed spiral and vacuum bag were positioned (Figure 26). Lastly, the resin feed hose and vacuum feed hose were attached along with the resin feed pot, catch pot and vacuum pump. The infusion process ran until carbon fibre was fully saturated. The pressure was applied during the infusion process to ensure the adequate spreading of resin across all of the carbon fibre layers.

![Figure 26 - Images of the carbon fibre epoxy resin infusion process.](image-url)

Figure 26a is an image of the infusion mesh being positioned. Figure 26b shows the complete setup prior to infusion, the vacuum bag, vacuum tape and resin inlet can be seen. Care was taken to ensure no leaks were present in the bag.
Samples were prepared with plain epoxy (PrimeTM 20LV with PrimeTM 20 slow hardener) and GnP loaded epoxy. Both 25 and 5-micron GnP at 2 wt.% was used to create two different samples. Carbon fibre samples were then cut into the desired size for the dielectric probe and waveguide analysis.

3.1.1.2 GnP-reinforced carbon fibre fabrication difficulties and findings

It was noted that the addition of GnP accelerated the exothermal epoxy curing process, leading to a large peak exotherm temperature. The curing sample began to exert smoke and melt the plastic container in which it was held. This meant that care must be taken to ensure that (1) the resin has enough time to infuse throughout the carbon fibre laminates before curing and (2) the container in which the resin is held must have enough thermal stability to be able to handle the high peak exotherm temperature. In order to handle these issues, a glass beaker lined with aluminium foil was used as the feed pot, and the infusion was set to a slightly higher rate. An additional problem encountered involved the degassing, where it was found that rapid bubbling caused the resin to splutter everywhere. This was eventually accounted for by ensuring progression towards the vacuum condition happened at a slow rate. That way, smaller, less energetic bubbles were formed.

3.1.3 GnP/PVA films

Firstly, a Polyvinyl Alcohol (PVA) solution was made by mixing 10wt.% of dry PVA with water. Different wt.% of GnP was then added into the solution. A degassing process was then employed to ensure there were no air bubbles were present. In order to adequately disperse GnPs this was then placed in a high shear mixer at 20000 rpm.

3.2 Modelling and Software Design

Majority of the software was written from scratch in MATLAB or python. EMI shielding equations, as outlined in section 2.12.2 Electromagnetic Interference Shielding were used to design an EMI shielding GUI in Python. In addition, a FDTD software tool was written in MATLAB, which can visualize and determine the EMI shielding behaviour of different structures. Micromechanical models which predict the nanocomposites electromagnetic properties based on their constituents’ properties were also created. MATLAB code for the NRW conversion method is also supplied.

The constructed software tools are available on my Github account here: liam-anderson-l12 (github.com).
Herein some discussion is given on the development of these software tools and the models upon which they are based. There also some discussion on peripheral software tools, which were essential in the completion of this work. A full list of the software is given below:

- EMI Shieling GUI for a plane wave incident on a flat surface.
- Preliminary FDTD algorithm which calculates EMI shielding properties.
- Micromechanical modelling software outputs the percolation trends of electrical conductivity, permittivity, magnetic permeability and thermal conductivity of graphene/polymer nanocomposites.
- xFDTD (established electromagnetic FDTD solver)
- S-parameter toolbox to convert S-parameters obtained from VNA into workable data format [274].
- NRW Software was written to convert S-parameters into bulk material properties.

3.2.1 Micromechanical Model Construction

All the micromechanical models were developed in Python using the Microsoft Visual Studio integrated development environment (IDE), they are based on the literature discussed in sections 2.12.5 Micromechanics of Graphene Nanocomposites and 2.12.6 Effective Medium Theory for EMI. The construction of these models is outlined below. The Python packages used here include but are not limited to: numpy, sympy and pandas.

An Algorithm was written in Python, which took the following form: Inputs were defined, concentrations for rich and poor sections were defined, as were Eschelby tensor’s for both the GnP and Agglomerates. At this point, the percolation threshold can be solved. Next, the GnP inclusion was modified to be treated as a “coated” inclusion which handles the interfacial effects, including electron tunnelling, nano-capacitance, electron hopping and Debye’s relaxation. The Bruggeman equation could then solved, first for GnP and epoxy within agglomerates (filler-rich section) and GnP and epoxy outside agglomerates (filler-poor section), then lastly for agglomerates within the filler poor section. It was initially planned to develop this model into a GUI, although it is not practical at this stage due to a long code run time (> 2:30 mins on 64-bit Intel core i7 (2.2 GHz) 8 GB RAM). Nonetheless, the details of this work are outlined below.

3.2.1.1 Electrical Conductivity Model

After importing the relevant Python packages, the following variables were defined.

- Graphene volume concentration vector (C1)
- Epoxy volume concentration vector (C0 = 1 – C1)
- Graphene density (ρg)
- Graphene aspect ratio (αg)
• Graphene thickness (Gthick)
• In-plane graphene electrical conductivity ($\sigma_g|$)
• Out-of-plane graphene electrical conductivity ($\sigma_g\perp$)
• Polymer density ($\rho_p$)
• Polymer electrical conductivity ($\sigma_p$)
• Agglomerate aspect ratio ($\alpha_a$)
• $a$ and $b$ agglomeration parameters ($a$, $b$)
• Interfacial thickness (Ithick)
• Interfacial electrical conductivity ($\sigma_i$)
• Electron tunnelling scaling parameter ($\gamma_0$)
• Incident wave angular frequency ($\omega$)
• The characteristic time of electron hopping ($t_{\text{hop}}$)

In addition to assigning a numerical value to each of these parameters, selective localized areas must be defined in order to account for agglomeration. This involves defining a filler rich ($C_R$) and filler poor ($C_P$) region along with both graphene ($C_{1R}$, $C_{1P}$) and polymer concentrations ($C_{0R}$, $C_{0P}$) in each region. The appropriate definition of $a$ and $b$ represents the ratio of graphene in the rich region out of the total amount of graphene and the dependency $C_{1R}$ has on $C_1$, respectively. This is made evident by the following equations [202].

$$a = \frac{C_{1R} \cdot C_1}{C_1}$$

$$C_{1R} = b + c_1(1 - b) \quad \textit{Equations 17}$$

Accurate selective location also requires that the following conditions must be met.

$$C_1 + C_0 = 1$$

$$C_R + C_P = 1$$

$$C_{1R} + C_{0R} = 1$$

$$C_{1P} + C_{0P} = 1 \quad \textit{Equations 18}$$

This implies that the total filler and matrix concentrations must satisfy the following.

$$C_1 = C_{1R} \cdot C_R + C_{1P} \cdot C_P$$

$$C_0 = C_{0R} \cdot C_R + C_{0P} \cdot C_P \quad \textit{Equations 19}$$

Using the parameters $a$ and $b$, it is now possible to define the dependency $C_R$ and $C_{1P}$ have on $C_1$ using the following equations [202].
\[ C_R = \frac{a}{b + C1(1 - b)}C1 \]
\[ C1 = \frac{(1-a)(b+C1(1-b))}{-C1+a+(b+C1(1-b))}C1 \]  

Equations 20

This completes the modelling of agglomeration effects.

The next step was to define the Eschelby tensor of both the graphene and graphene agglomerate. This was so done using the following equation:

\[ S_{11} = S_{22} = \begin{cases} \frac{a}{2(1-a)^{3/2}}[\arccos \alpha - \alpha(1 - \alpha)]^{1/2}, & \alpha < 1; \\ \frac{a}{2(1-a)^{3/2}}[\arccos \alpha - \alpha(1 - \alpha)]^{1/2}, & \alpha > 1; \end{cases} \]

Equation 21

\[ S_{33} = 1 - 2S_{11} \]  

Equation 22

This equation is taken from Xia et al. [211]. The Eschelby tensor is purely dependent on the aspect ratio. This equation is used to determine the Eschelby tensor of both the graphene filler and agglomerate.

At this point, the percolation threshold can be determined using the following equation [211]:

\[ c_1' = \frac{9S_{33}(1-S_{33})}{-9S_{33}^2 + 15S_{33} + 2} \]  

Equation 23

Where \( c_1' \) is the percolation threshold. Here, the Eschelby tensor \( S \) used is that of the agglomerate. This is due to the fact that in order for the entire composite to reach percolation the agglomerates must be touching, and this condition is harder to meet than the percolation state achieved from high surface area graphene filler [202].

The next steps involve defining the interlayer volume, electron tunnelling and electron hopping. This allows for the filler to be then modified to a “coated” filler, following the Mori-Tanaka [218] approach. Firstly, the interlayer volume is given by the following equation.

\[ C_{int} = 1 - \frac{G_{thick}}{2} \left( \frac{G_{thick}}{2 \alpha_g} \right)^2 \left( \frac{G_{thick}}{2 \alpha_g} + I_{thick} \right) \left( \frac{G_{thick}}{2 \alpha_g} + I_{thick} \right)^2 \]  

Equation 24

An electron tunnelling modified electric conductivity at the interlayer is given by [13]:

\[ \sigma_i^{static} = \sigma_i / \tau(C1, C1', \gamma_d^{static}) \]  

Equation 25

The “static” implies that the value is frequency independent. The \( \tau \) function is defined as follows [13]:
\[ \tau(C_1, C_1', \gamma) = \frac{F(C_1') - F(C_1, C_1')}{F(1, C_1') - F(0, C_1')} \]  

Equation 26

Where \( F \) is Cauchy’s cumulative probabilistic function defined below:

\[ F(C_1, C_1', \gamma) = \frac{1}{\pi} \arctan \left( \frac{C_1 - C_1'}{\gamma} \right) + \frac{1}{2} \]  

Equation 27

In order to account for the onset of electron hopping Dyre’s hopping model [275] is utilized, which involves the following equations.

\[ \sigma_i^{freq} = \sigma_i^{static} * p \]  

Equation 28

Where:

\[ p = \frac{\omega t_{hop}(\arctan(\omega t_{hop}))^2}{0.5 \ln(1+(\omega t_{hop})^2 + (\arctan(\omega t_{hop}))^2)} \]  

Equation 29

Now that an interlayer conductivity that accounts for electron tunnelling and electron hopping is defined (\( \sigma_i^{freq} \)), this can be used to obtain the conductivity of the coated filler (\( \sigma_c \)) using the following equation.

\[ \sigma_c = \sigma_i^{freq} \left[ 1 + \frac{(1 - C_{int})(\sigma_g^{\parallel} - \sigma_i^{freq})}{C_{int} S_{11}(\sigma_g^{\parallel} - \sigma_i^{freq}) + \sigma_i^{freq}} \right] \]  

Equation 30

The above equation can be used to solve for the in plane (\( \sigma_c^{\parallel} \)) and out-of-plane (\( \sigma_c^{\perp} \)) coating modified filler. These values can then be used in the following Bruggeman effective medium equation [13] to solve for the effective electrical conductivity (\( \sigma_e \)).

\[ \mathbf{C_0} \frac{\sigma_p - \sigma_e}{\sigma_e + (\sigma_p - \sigma_e)/3} + \frac{c_1}{3} \left[ \frac{2(\sigma_g^{\parallel} - \sigma_e)}{k_e + S_{11}(\sigma_g^{\parallel} - \sigma_e)} + \frac{(\sigma_g^{\perp} - \sigma_e)}{\sigma_e + S_{33}(\sigma_g^{\perp} - \sigma_e)} \right] = 0 \]  

Equation 31

Solving the above polynomial for \( \sigma_e \) and neglecting negative or imaginary solutions allows for the effective electrical conductivity of a graphene polymer nanocomposite to be determined. In order to solve equation 31, polynomial simplification steps were needed to be taken.

The Python code for this model can be found here https://github.com/liam-anderson-l12/Graphene-Nanocomposite-Properties.

3.2.1.2 Permittivity Model

The permittivity of a graphene polymer nanocomposite can also be determined using Equation 31. In order to do so, the following additional parameters must first be defined:

- In-plane graphene permittivity (\( \varepsilon_{g^{\parallel}} \))
- Out-of-plane graphene permittivity (\( \varepsilon_{g^{\perp}} \))
• Interfacial permittivity at the static state ($\varepsilon_i^{\text{static}}(0)$)
• Interfacial permittivity at the high-frequency state ($\varepsilon_i^{\text{high-freq}}(0)$)
• Scaling parameter for the formation of nanocapacitors at the static state ($\gamma_{\text{static}}^a$)
• Scaling parameter for the formation of nanocapacitors at the high-frequency state ($\gamma_{\text{high-freq}}^a$)
• The relaxation time of Debye theory ($t_e$)

Similar to the case of electron tunnelling in the electrical conductivity model, Cauchy’s cumulative distribution function is used to model the effect of nanocapacitance [211]. Nano capacitive modified interfacial permittivity ($\varepsilon_i$) is firstly found for the static state and then for the high-frequency state via subbing in $\varepsilon_i^{\text{static}}(0)$ and $\varepsilon_i^{\text{high-freq}}(0)$ into Equation 25, respectively.

Secondly, Debye’s relaxation function featured below is used to calculate the frequency-dependent nano capacitive modified interfacial permittivity.

$$\varepsilon_i^{\text{freq}} = \varepsilon_i^{\text{high-freq}} + \frac{\varepsilon_i^{\text{static}} - \varepsilon_i^{\text{high-freq}}}{1 + \omega^2 \tau_e^2}$$  \hspace{1cm} \text{Equation 32}$$

A coated modified filler permittivity can then be found for the in-plane and out-of-plane direction via subbing $\varepsilon_i^{\text{freq}}$ into Equation 30. Then lastly the effective nanocomposite permittivity can be found via solving Equation 31.

The

3.2.1.3

If the magnetic permeability of the polymer, graphene (in both in-plane and out-of-plane directions) and interlayer are known, then it is possible to determine the effect on nanocomposite permeability. This achieved through the application of $C0\sigma P - \sigma_e \sigma_e + (\sigma_p - \sigma_e)/3 + \frac{c1}{3} \left[ \frac{2(\sigma_g - \sigma_e)}{k_e+s_{11}(\sigma_g - \sigma_e)} + \frac{(\sigma_g - \sigma_e)}{\sigma_e+s_{33}(\sigma_g - \sigma_e)} \right] = 0$ \hspace{1cm} \text{Equation 31 and 31.}$

3.2.1.4

Similar methods can be used to determine the effective thermal conductivity ($k$) of graphene polymer composites [217]. This again involves solving $C0\sigma P - \sigma_e \sigma_e + (\sigma_p - \sigma_e)/3 + \frac{c1}{3} \left[ \frac{2(\sigma_g - \sigma_e)}{k_e+s_{11}(\sigma_g - \sigma_e)} + \frac{(\sigma_g - \sigma_e)}{\sigma_e+s_{33}(\sigma_g - \sigma_e)} \right] = 0$ \hspace{1cm} \text{Equation 31 and Equation 31.}$ The thermal conductivity of the interlayer is determined from the Kapitza resistance (g-p) (which refers to graphene-polymer contact resistance) and graphene-graphene (g-g) contact resistance. This is made evident through the following equation.

$$k_{\text{int}} = k_{g-p}[1 - \tau(c_1, c_1', \gamma)] + k_{g-p} * \tau(c_1, c_1', \gamma)$$  \hspace{1cm} \text{Equation 33}$$

99
The equations outlined in section 2.12.2 Electromagnetic Interference Shielding describe the analytical model which a Python GUI was built upon. $R_{dB} = 20 \log_{10} \left( \frac{\eta_{air} + \eta_e}{\eta_e \eta_{air}} \right)^2$  \hspace{1cm} \text{Equation 7}

$\gamma_{dB} = 20 \log_{10} \left| e^{-t \beta_{air} t} e^{\gamma_{air} t} \right|$  \hspace{1cm} \text{Equation 9}  

$M_{dB} = 20 \log_{10} \left| 1 - \left( \frac{\eta_{air} - \eta_e}{\eta_{air} + \eta_e} \right)^2 e^{-2 \gamma_{air} t} \right|$  \hspace{1cm} \text{Equation 10}

Equation 10 were used to plot the reflection, absorption and multiple reflection values of an electromagnetic plane wave incident on a flat surface as a function of frequency. Within the GUI, the user must define the material properties, including conductivity, permittivity, permeability and thickness. A screenshot of the GUI is given below (Figure 27 – Screenshot of Shielding Effectiveness GUI).

Development of this GUI involved the import of the tkinter, matplotlib and numpy Python packages. Tkinter was utilized to develop the GUI, which is controlled by the mentioned equations. There were difficulties in translating the GUI into a standalone .exe file that runs without Python installed on the user’s computer. Therefore, as it stands, Python must be installed on the user’s computer in order to run the GUI.

The Python code for this GUI can be found here [https://github.com/liam-anderson-l12/Shielding-Effectiveness](https://github.com/liam-anderson-l12/Shielding-Effectiveness).
3.2.3 Numerical Model of Shielding Effectiveness Construction

As explained previously, a numerical solution may be needed for more complex geometries than what is depicted in Figure 15 - Schematic of a shielding material (green) under incidence from an electromagnetic plane wave positioned in air. For this reason, numerical solution algorithms were explored in MATLAB. An Ab initio one-dimensional FDTD was written in MATLAB. FDTD was chosen over the other methods due to its simplicity, prevalence throughout the computational simulation community and EMI Shielding relevance.

A screenshot of three different time steps for the FDTD algorithm is provided below (Figure 28). This can be used to calculate reflection, absorption and transmission values through a defined material. Details of constructing the model are outlined below.

Firstly, the following parameters were defined and saved in a MATLAB function.

- Permittivity is a three-column vector that defines the permittivity of the material along with the permittivity of the surrounding medium on either side of it.
- Permeability, also a three-column vector which defines the material and surrounding medium.
- Conductivity, again a three-column vector defining the material and surrounding medium conductivity.
- The material positioning and size in one dimension. A four-column vector.
- The cell resolution
- The wavelength resolution
- The feature resolution
- Incident wavelength bandwidth

The user can numerically define any of these values, which are then used to further define other variables, including but not limited to the cell size, the number of cells, time steps, incident
wave etc. The source chosen here is a gaussian source, though this can be modified. At this point, the grid resolution, time step, source and coefficients to equations that go in the loop should all be defined, and the field E and H fields should be initialized.

The main loop consists of an iteration though each time step. Within this loop, there are two sub loops which consist of iterations through space, whereby the H field is updated from the E field, then vice versa.

Given that the system described conserves energy, it should maintain that \( R+T+A=1 \). Frequency-based reflection and transmission data can be found via a Fourier transform placed before and after the shielding material. Care must be taken to filter out the source field. Given the energy conservation relation, the easiest way to determine absorption due to any lossy effects present in the material would be using the following equation \( A = 1-R-T \). Though this relies on the assumption that energy has conversed, the algorithm behaves as it should, and R and T are accurately defined. There are alternative ways to calculated absorption, which mainly focus on integration over the conducting region.

Figure 29 shows example plots of reflection, absorption and transmission values calculated from a gaussian wave incident upon a material with a conductivity of 5 S/m, relative permittivity of 2.25 and the relative permeability of 1.
Figure 29 - Example $R,A,T$ plots from the FDTD model constructed in MATLAB

The MATLAB code for this model can be found here https://github.com/liam-anderson-l12/FDTD-MATLAB.

3.2.4 Further Numerical Modelling of Shielding Effectiveness

In order to further investigate numerical simulation techniques and the FDTD approach, established software “xFDTD” was used to investigate 3D wave propagation as an incident on an aeroplane with specified shielding material properties.

The material properties for the airplane depicted in Figure 30 consist of permeability of 1, the relative permittivity of 25 and conductivity 10 S/m. The excitation was a plane wave at 10 V/m. The goal here was to give a preliminary example of wave propagation upon a common object in 3D. A more realistic situation would have different parts of the airplane with different materials properties. The run time for the simulation at realistic airplane dimensions exceeded any workable amount, therefore for this example, the length was shrunk to 18cm.
3.2.5 NRW Conversion Method Construction

The NRW method was chosen as the conversion method of choice due to robustness, simplicity, and adequacy for this particular measurement. The conversion resulted in the values of the materials under the test’s permittivity and electrical conductivity. These values could then be used to calculate the electromagnetic shielding effectiveness. A MATLAB file for the conversion was created; an outline of the construction of the file and the NRW process is given below.

1. The S-parameter files are read in MATLAB.
2. The reflection coefficients are calculated from the S-parameters.
3. The transmission coefficient is calculated from the S-parameters.
4. The permeability is calculated from the reflection coefficient, free space wavelength and waveguide cut-off wavelength.
5. The complex permittivity is calculated from the permeability, free-space wavelength, waveguide cut off wavelength and material length.
6. Electrical conductivity is calculated from the imaginary term in complex permittivity.

The GitHub repository for this work can be here: liam-anderson-l12/NRW-conversion: NRW conversion (github.com).
3.3 Experimental Characterization Processes

In order to measure the electrical conductivity, permittivity, reflection, absorption, and SE of each of the samples, they all underwent dielectric probe and waveguide testing. The dielectric probe analysis was completed first, and due to the frequency limitations of this setup, a different VNA and with a waveguide was chosen for a second round of testing. In addition, some samples were investigated with a scanning electron microscope in order to get an idea of the underlying morphology. The characterization processes are therefore categorized into (1) SEM, (2) Dielectric Probe and (3) Waveguide.

3.3.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a commonly used nanocomposite characterization technique. SEM was used to further investigate the micromechanical structure of GnP/Epoxy. In particular, the agglomeration, interfacial thickness and general morphology can further be understood by the use of SEM. Figure 31 is an SEM image of GnP/Epoxy with 1 wt. % loading and 5-micron sheet size GnP. The percolation path is contained within the dark areas. The scale here is on the order of 100 microns, further magnification will be needed to resolve individual GnP particles.

Figure 31 – SEM image of GnP/epoxy.
3.3.2 Dielectric Probe
An open-ended coaxial probe method (Figure 32) was used to determine the complex permittivity of prepared samples from 300 MHz to 6 GHz.

![Dielectric Probe Setup](image)

*Figure 32 – HP 85070A dielectric probe kit attached to HP 8752C Network analyzer.*

The probe and VNA measure the S-parameters, the software provided then converts these values into complex permittivity outputting both $\varepsilon'$ and $\varepsilon''$. Using the equation $\varepsilon'(\omega) = \frac{\sigma_{ac}}{\omega}$, a frequency-dependent conductivity can then be obtained. It is important to note that as GnP/Epoxy possesses both ohmic and dielectric losses, the terms $\varepsilon''$ and $\sigma_{ac}$ represent contributions from both types of loss as this system is incapable of distinguishing between the two. The details of the S-parameter to dielectric properties conversion are unknown as this information was not provided by the supplier.

3.3.3 Waveguide Analysis
As mentioned, the upper-frequency spectrum for the dielectric probe setup was limited between 0.3 and 6 GHz. It is commonly found that modern electronic equipment relies on transmission of frequencies that go above 6 GHz. Therefore, it is essential to measure the fabricated material’s properties above these frequencies. In order to do so, the following setup was constructed.
Figure 33 features a ROHDE and SCHWARZ ZNB-40 VNA, which was attached to a WR-90 waveguide. The materials were cut to fit into the waveguide, ensuring there were no air gaps. The system was calibrated using the VNA’s de-embedding function. The materials center was placed in the middle of the waveguide. S-parameter files for each material were gathered over the frequency range of 8.2 to 12.4 GHz.

Post-processing of the S-parameter data was undertaken using the NRW method. The allowed for AC conductivity and permittivity to be determined.
Chapter 4

Results/Finding

An outline of the sample preparation and characterization methods were given above (page 87). This section provides the results and discusses the findings determined by the dielectric probe and waveguide measurements. The dielectric probe measurement provides the SE, AC electrical conductivity and complex permittivity of the GnP/epoxy and GnP/epoxy/carbon fibre samples over a frequency band of 0.3 GHz to 6 GHz. While the waveguide measurements provide the AC electrical conductivity and permittivity of the GnP/PVA, GnP/epoxy and GnP/epoxy/carbon fibre over a frequency range of 8.2 to 12.4 GHz. Unfortunately, the SE was not determined over this frequency range due to inaccurate results, this will be discussed further. Additionally, predictions made by the constructed models are also produced and contrasted with experimental values.

4.1 Dielectric Probe Results

Various GnP/epoxy and GnP/epoxy/carbon fibre composites samples underwent dielectric probe testing. The results, along with theoretical predictions, are provided here.

4.1.1 GnP/Epoxy Dielectric Probe Results

The end of the coaxial probe effectively acts as an antenna. Once placed up against the material, the energy received back through the coaxial cable is measured by the VNA. Thus, it is the volume conductivity that is being measured here. The HP dielectric probe kit came with software for the S-parameter to bulk material properties conversion. The details of which method was used were not provided. Here, four samples of each material at a specific loading were tested in order to ensure the precision of the test equipment and the dispersion variance across samples. The value determined from the software gave the complex permittivity: $\varepsilon(\omega) = \varepsilon' + i\varepsilon''$ where the AC electrical conductivity was determined from $\sigma = \omega\varepsilon''$. Table 3 - Permittivity and AC Electrical Conductivity of GnP/Epoxy at 0.3 GHz and Table 4 - Permittivity and AC Electrical Conductivity of GnP/Epoxy at 6 GHz show the permittivity and ac conductivity of GnP/epoxy at 0.3 and 6 GHz, respectively. Neat epoxy conductivity and permittivity are not featured in tables 3 and 4 though they remained at values of roughly 0 and 3 across the whole frequency range.

<table>
<thead>
<tr>
<th>5-micron GnP</th>
<th>25-micron GnP</th>
</tr>
</thead>
</table>

Table 3 - Permittivity and AC Electrical Conductivity of GnP/Epoxy at 0.3 GHz
<table>
<thead>
<tr>
<th>GnP wt.%</th>
<th>Relative Permittivity</th>
<th>Conductivity [S/m]</th>
<th>Relative Permittivity</th>
<th>Conductivity [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.23</td>
<td>2.96*10^{-3}</td>
<td>4.84</td>
<td>1.42*10^{-3}</td>
</tr>
<tr>
<td>1</td>
<td>4.33</td>
<td>1.92*10^{-3}</td>
<td>4.30</td>
<td>2.00*10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>4.12</td>
<td>3.62*10^{-3}</td>
<td>7.19</td>
<td>6.63*10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>8.05</td>
<td>4.17*10^{-3}</td>
<td>7.10</td>
<td>5.59*10^{-3}</td>
</tr>
<tr>
<td>5</td>
<td>10.5</td>
<td>7.78*10^{-3}</td>
<td>7.08</td>
<td>5.59*10^{-3}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GnP wt.%</th>
<th>Relative Permittivity</th>
<th>Conductivity [S/m]</th>
<th>Relative Permittivity</th>
<th>Conductivity [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-micron GnP</td>
<td></td>
<td></td>
<td>25-micron GnP</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>6.39</td>
<td>0.229</td>
<td>4.78</td>
<td>0.134</td>
</tr>
<tr>
<td>1</td>
<td>4.29</td>
<td>0.109</td>
<td>4.06</td>
<td>0.109</td>
</tr>
<tr>
<td>2</td>
<td>4.11</td>
<td>0.125</td>
<td>6.41</td>
<td>0.234</td>
</tr>
<tr>
<td>3</td>
<td>7.39</td>
<td>0.135</td>
<td>7.15</td>
<td>0.346</td>
</tr>
<tr>
<td>5</td>
<td>11.2</td>
<td>0.656</td>
<td>6.67</td>
<td>0.346</td>
</tr>
</tbody>
</table>

Table 4 - Permittivity and AC Electrical Conductivity of GNP/Epoxy at 6 GHz

Variances in results were observed across samples with the same loading. This was attributed to agglomeration/non-uniform dispersion and poor contact between the probe and sample. 5-micron GnP at 5 wt.% showed to have both the highest relative permittivity at 11.2 and conductivity at 0.66 [S/m]. It could be expected that 25-micron GnP would achieve the highest permittivity and conductivity values, although it is known that larger sheet sizes at higher loadings are more likely to agglomerate [71]. This likely the case here. There is a clear trend that increasing loading increases both conductivity and permittivity. However, agglomeration and poor probe contact result in imprecision and inaccuracy, with the two main outliers being...
5-micron GnP at 0.5wt. % and 2 wt. %. A clear increase in conductivity with increasing frequency can be observed. This is in agreement with the model and can be understood in terms of the onset electron hopping. A decrease in permittivity across frequency was expected but not observed here. However, broader frequency ranges then 0.3 – 6 GHz may be needed to observe these effects.

Figure 34 shows the AC conductivity of all the prepared GnP/epoxy samples between 0.3-6 GHz as a function of frequency. It can again be seen that 5-micron GnP at 5% performed the best as this material possessed the highest conductivity and therefore would provide the best shielding. As shown, none of the GnP/epoxy samples reached the benchmark value for shielding of 10 S/m.

is a clear indicator of how electrical conductivity increases with frequency, as explained by the onset of electron hopping. This, along with the higher operating frequencies of most modern devices, was the motivation to explore higher frequencies in order to investigate the upper limits of these effects.
The SE, Reflection (R), Absorption (A) and Multiple Reflection (M) versus the frequency range of 0.3 to 6 GHz are shown in Figure 35 for GnP/epoxy nanocomposites containing 5-micron GnP at 5 wt.% loading and 1 cm thickness. This material was chosen as it yielded the highest conductivity. A SE of 3.2 dB was found at 0.3 GHz, which increased to 7 dB at 6 GHz. Both reflection and absorption are seen to increase with frequency. It is common for absorption to increase with frequency in most materials, as seen in Figure 17. However, a decrease in reflection is more commonly expected. As previously explained, due to the composite structure of GnP/Epoxy, interfacial electron hopping occurs, which will increase the conductivity at higher frequencies. This increase in conductivity results in larger than expected reflection values at higher frequencies. Due to limitations of the VNA and dielectric probe used, we were unable to obtain values at frequencies higher than 6 GHz, although it is expected that SE values will continue to grow with frequency. This will be explored under the waveguide measurement section. As it stands, 5-micron GnP/Epoxy with a loading of 5 wt. % under 6-7 hours sonication has not reached adequate EMI SE of 20 db. However, SE values may be increased with better
processing methods. It may also be considered that incorporating GnP/Epoxy with existing structural materials with already existing SE values in the same order, for example, carbon fibre, may ultimately lead to adequate SE.

Figure 35 - EMI Shielding of 5-micron GnP/Epoxy at 5wt.%.

4.1.1.1 Model Validation

Herein, the described micro-scale homogenization model will be compared with dielectric probe results. 25-micron GnP loaded epoxy with an incident wave of 6 GHz was chosen as the reference. Figure 36 and Figure 37 show the measured and theoretical values of electrical conductivity and relative permittivity, respectively. While Table 5 and Table 6 show some of the values that were input into the constructed model.

Table 5 - Input Parameters for GnP/Epoxy electrical conductivity model.

<table>
<thead>
<tr>
<th>Input Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GnP Aspect ratio</td>
<td>1.26 x 10^{-3} (5-micron GnP)</td>
<td>[217]</td>
</tr>
<tr>
<td></td>
<td>2.54 x 10^{-4} (25-micron GnP)</td>
<td></td>
</tr>
<tr>
<td>GnP thickness</td>
<td>6.3 x 10^{-9}</td>
<td>[217]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>In-plane GnP conductivity</td>
<td>$10^7$ [S/m]</td>
<td>XG sciences GnP - grade M datasheet</td>
</tr>
<tr>
<td>Out-of-plane GnP conductivity</td>
<td>$10^2$ [S/m]</td>
<td>XG sciences GnP - grade M datasheet</td>
</tr>
<tr>
<td>Epoxy conductivity</td>
<td>$10^{-14}$</td>
<td>[164]</td>
</tr>
<tr>
<td>Agglomerate aspect ratio</td>
<td>0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration scaling parameter a</td>
<td>0.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration scaling parameter b</td>
<td>0.05</td>
<td>N/A</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>$12 \times 10^{-9}$</td>
<td>[217]</td>
</tr>
<tr>
<td>Interlayer conductivity</td>
<td>$6 \times 10^{-7}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Electron tunneling scaling parameter</td>
<td>0.00025</td>
<td>[211]</td>
</tr>
<tr>
<td>Characteristic time of electron hopping</td>
<td>$1.1 \times 10^{-8}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Relaxation time of Debye theory</td>
<td>$2 \times 10^{-10}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Frequency</td>
<td>6 GHz</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The theoretical curve shows clear signs of percolation. The experimental values fail to do, which may be attributed to the dielectric probes and/or the conversion method used to work with low loss materials. Nonetheless, the plots show a solid match between theory and experiment after percolation. Additionally, there is a dip in the experimental results at higher loadings. This is particularly accentuated in Figure 37. This is a clear sign of agglomeration. The move away from the theoretical curve is due to the higher levels of agglomeration at higher loadings. In contrast, the agglomeration levels were kept constant across all loading in the modelling, leading to discrepancies.
Figure 36 – AC electrical conductivity of GnP/Epoxy at 6 GHz.
Table 6 - Input parameters for GnP/Epoxy permittivity model.

<table>
<thead>
<tr>
<th>Input Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GnP Aspect ratio</td>
<td>1.26 x 10⁻³ (5-micron GnP)</td>
<td>[217]</td>
</tr>
<tr>
<td></td>
<td>2.54 x 10⁻⁴ (25-micron GnP)</td>
<td></td>
</tr>
<tr>
<td>GnP thickness</td>
<td>6.3 x 10⁻⁹</td>
<td>[217]</td>
</tr>
<tr>
<td>In-plane GnP relative permittivity</td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td>Out-of-plane GnP relative permittivity</td>
<td>0.67 * (In-Plane Value)</td>
<td>[13]</td>
</tr>
<tr>
<td>Agglomerate aspect ratio</td>
<td>0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration parameter a</td>
<td>0.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration parameter b</td>
<td>0.05</td>
<td>N/A</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>12 x 10⁻⁹</td>
<td>[217]</td>
</tr>
<tr>
<td>Epoxy Permittivity</td>
<td>2.42</td>
<td>[211]</td>
</tr>
<tr>
<td>Interlayer relative permittivity at 0 Hz</td>
<td>3</td>
<td>[13]</td>
</tr>
<tr>
<td>Interlayer relative permittivity at infinite Hz</td>
<td>0.01</td>
<td>[13]</td>
</tr>
<tr>
<td>Nanocapacitance scaling parameter at 0 Hz</td>
<td>10⁻⁶</td>
<td>[211]</td>
</tr>
<tr>
<td>Nanocapacitance scaling parameter at infinite Hz</td>
<td>10⁻⁵</td>
<td>N/A</td>
</tr>
<tr>
<td>Debye relaxation time</td>
<td>2.10⁻¹⁰</td>
<td>N/A</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>12 x 10⁻⁹</td>
<td>[217]</td>
</tr>
<tr>
<td>Frequency</td>
<td>6 GHz</td>
<td>N/A</td>
</tr>
</tbody>
</table>

In order to predict the nanocomposites permittivity, the values shown in Table 6 were input into the described model. The model predicted much higher values of permittivity at lower frequencies close to 0 Hz. However, both theory and experiment show much lower permittivity values across the experimental test range of 0.3-6 GHz. This can be attributed to Debye relaxation effects. Figure 37 shows an increase in permittivity at roughly 2wt.%. The increase is sharper in the measured values than in the theoretical curve. As reliable data on the permittivity of XG sciences’ grade M GnP was unattainable, a semi-empirical approach was taken whereby the permittivity value that gave a good fit was chosen. Higher values of GnP permittivity would have made for a sharper increase at the percolation threshold. However, the reality of higher values was in question. Lastly, as mentioned, the dip in permittivity at higher loadings shown in the measured values can be attributed to agglomeration.
The theoretical and experimental data for the calculated SE is depicted in Figure 38, which is at a frequency of 6 GHz and a GnP loading of 5 wt.% with a 5-micron flake size. Here we can see a good fit between experiment and theory.
4.1.2 GnP/epoxy/carbon fibre composite Dielectric Probe Results

Dielectric probe data from the prepared carbon fibre composites samples are shown in Table 7 and Table 8. As with the GnP/Epoxy nanocomposites, values were averaged across multiple samples in order to account for any inaccuracies due to agglomeration or poor sample contact. Again, as HP did not supply it, the details of the conversion method are unknown. It should also be noted that varying conductivities are reported across the literature for carbon fibres. The conductivity measured here more closely resembles the volume conductivity, which is much lower than the often reported in-plane conductivity.

Table 7 – Permittivity and AC electrical conductivity of GnP/epoxy/carbon fibre composites at 0.3 GHz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Permittivity</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Fibre Composites</td>
<td>27.0</td>
<td>0.00985</td>
</tr>
<tr>
<td>Carbon Fibre Composites with 2wt.% 5-micron GnP</td>
<td>29.7</td>
<td>0.00697</td>
</tr>
</tbody>
</table>
Table 8 – Permittivity an AC electrical conductivity of GnP/epoxy/carbon fibre composites at 6 GHz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Permittivity</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Fibre Composites</td>
<td>27.6</td>
<td>0.925</td>
</tr>
<tr>
<td>Carbon Fibre Composites with 2wt.% 5-micron GnP</td>
<td>29.7</td>
<td>0.623</td>
</tr>
</tbody>
</table>

The inclusion of 2 wt.% of 5-micron GnP into the CFRP matrix resulted in an increase in permittivity and decreased volume conductivity over the 0.3-6 GHz range. This implies that a GnP percolating network was not formed throughout the volume of the material. Though further studies will be required to explore the dispersion state of GnP here, these results are suggestive that alternate processing conditions may be needed to achieve higher volume conductivities. As seen in Figure 39, permittivity stays constant across frequency, while an increase in AC conductivity is observed.

![Graphs showing permittivity and AC conductivity](image)

Figure 39 - Permittivity and AC electrical conductivity of GnP reinforced carbon fibre.

4.2 Waveguide Results
The results gathered by the ROHDE and SCHWARZ ZNB-40 Vector Network Analyzer and WR-90 waveguide system are presented below. The experimental results were compiled in S-
parameter form. These were then converted into bulk material properties using the NRW method. As described below, there were errors involved in this experimental setup which unfortunately led to inaccurate and imprecise results.

4.2.1 GnP/Epoxy Waveguide Results

Figure 40 shows the Permittivity and AC conductivity of GnP/Epoxy with a 3 wt.% loading of 5-micron GnP across the X-band. The results presented here are invalid and more work needs to be done in order to achieve accurate results. In order to identify that the inaccuracies were due to experimental errors and not the NRW conversion technique. The NRW conversion method used was tested with materials with known properties. The Permittivity plot of ABS is shown below.
Figure 41 shows that the relative permittivity of ABS is roughly 2.43 across the X-Band. Although there is noise in the data an accurate value and trend is determined proving the developed NRW conversion’s method stability. It can therefore be concluded that the issue lies in the experimental setup.

Table 9 and 10 show the AC conductivity and relative permittivity of 5-micron and 25-micron GnP filled epoxy respectively, averaged across the x-band frequency range. It is clear here that the values inaccurate due to negative values etc., there is no distinguishable trend with GnP loading. The experimental setup has yielded both inaccurate and imprecise values.

Table 9 - Relative Permittivity and AC Conductivity of 5-micron GnP/Epoxy averaged over the X-band.

<table>
<thead>
<tr>
<th>GnP Loading (wt.%)</th>
<th>Relative Permittivity</th>
<th>AC conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.04707</td>
<td>-0.02792</td>
</tr>
<tr>
<td>0.5</td>
<td>0.082202</td>
<td>0.07977</td>
</tr>
<tr>
<td>1</td>
<td>-0.12821</td>
<td>-0.07144</td>
</tr>
<tr>
<td>2</td>
<td>-1.20527</td>
<td>-0.70248</td>
</tr>
<tr>
<td>3</td>
<td>-0.31341</td>
<td>-0.17555</td>
</tr>
<tr>
<td>5</td>
<td>-1.01714</td>
<td>-0.60228</td>
</tr>
</tbody>
</table>

Table 10 - Relative Permittivity and AC Conductivity of 25-micron GnP/Epoxy averaged over the X-band.

<table>
<thead>
<tr>
<th>GnP Loading (wt.%)</th>
<th>Relative Permittivity</th>
<th>AC conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.12007</td>
<td>-0.06791</td>
</tr>
</tbody>
</table>
Table 11 shows the relative permittivity and AC conductivity of GnP/PVA with different loadings of GnP averaged across the X-band frequency range. Negative values of permittivity and conductivity are non-physical. It is, therefore, evident that the experimental setup has yielded unreliable results.

<table>
<thead>
<tr>
<th>GnP Loading (wt.%)</th>
<th>Relative Permittivity</th>
<th>AC conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.28941</td>
<td>-0.16254</td>
</tr>
<tr>
<td>1</td>
<td>-0.76991</td>
<td>-0.44487</td>
</tr>
<tr>
<td>5</td>
<td>-1.69153</td>
<td>-0.96605</td>
</tr>
<tr>
<td>10</td>
<td>-1.60328</td>
<td>-0.90529</td>
</tr>
<tr>
<td>30</td>
<td>-3.78071</td>
<td>-2.16384</td>
</tr>
<tr>
<td>50</td>
<td>-3.80241</td>
<td>-2.1912</td>
</tr>
</tbody>
</table>

Due to invalid results, it was impractical to calculate SE values between the X-band frequencies for the GnP/PVA.

4.2.3 GnP/epoxy/carbon fibre composites Waveguide Results

Table 12 shows the results as determined by the experimental waveguide setup. Unfortunately, the results were unreliable due to an inaccurate and imprecise experimental setup.

<table>
<thead>
<tr>
<th>GnP Loading</th>
<th>Relative Permittivity</th>
<th>AC conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFRP</td>
<td>-3.36483</td>
<td>-1.92538</td>
</tr>
<tr>
<td>CFRP w/ 2wt.% 5-micron GnP</td>
<td>-3.1011</td>
<td>-5.40082</td>
</tr>
<tr>
<td>CFRP w/ 2wt.% 25-micron GnP</td>
<td>-3.52197</td>
<td>-2.00869</td>
</tr>
</tbody>
</table>
Due to invalid results, it was impractical to calculate SE values between the X-band frequencies for the GnP reinforced carbon fibre.

4.2.4 Explanation of inaccuracies in the Results

The NRW conversion method used was tested against a material of known properties (ABS), as shown in Figure 41. This leaves the explanation of inaccuracies down to errors in the experimental setup. The following possible causes for such errors are explained below.

- The cables attached to the sample holder should not move after calibration. Any slight movement after calibration can induce phase changes. As the NRW conversion method is particularly sensitive to phase changes, this served as a big issue. This could be avoided by instead of placing the material inside the waveguide, building a sample holder. The sample holder would be removable and placed between two waveguides. The waveguides would be fixed, as would the coaxial to waveguide connectors and coaxial cables. This would mean that the sample could be replaced without moving the experimental setup.

- The sample holder should be of the same length as the sample. The means that calibration is referenced at the right electrical length.

- The samples should be flat to avoid any unwanted reflections. Unwanted reflections due to an unsmooth surface would be seen as intrinsic material properties after the NRW conversion when, in reality, they would be due to the samples physical structure/shape.

- Placing the sample inside the waveguide does not guarantee that the sample is completely parallel to the waveguide cross-section. The means that there could be unwanted air gaps, leading to unwanted reflections and/or transmission. It also means that the sample surface is not orthogonal to the wave vector.

To summarize, possible issues include airgaps, flat and misaligned surfaces, unwanted movement inducing phase changes and ambiguous calibration reference planes. These all could be avoided by building a sample holder and placing it between two waveguides. The sample holder would have to be the same thickness as the sample. This means that the fabricated
samples would all need to be the same thickness, avoiding the issue of having to make many sample holders and calibrating before every test.

4.2.5 Theoretical Prediction of GnP/epoxy properties within the X-band.
Although the experimental values made by the waveguide setup were deemed unreliable in this case, the following shows that theoretical predictions across this frequency range yielded results that were much more realistic. A 5wt.% loading of 5-micron GnP was selected as an example material, the results for which are displayed in table 13. Observation of this table shows a peak conductivity of 0.56 S/m at 12 GHz. It is important to note that as the constructed model has agglomeration scaling parameters at a=0.8 and b=0.05, higher conductivity values may be physically available. The inputs for the model were kept consistent with previous modelling work and are reported in table 14.

Table 13 - Values of 5-Micron GnP/Epoxy at a loading of 5 wt.% for different frequencies within the X-band. As predicted by the micromechanical model.

<table>
<thead>
<tr>
<th>Frequency (GHz)</th>
<th>Relative Permittivity</th>
<th>AC conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6.38</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>5.26</td>
<td>0.48</td>
</tr>
<tr>
<td>12</td>
<td>4.61</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 14 below shows the inputs used to calculate the values presented in table 13 above.

Table 14 - Input Parameters for X-band GnP/Epoxy electrical conductivity model.

<table>
<thead>
<tr>
<th>Input Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GnP Aspect ratio</td>
<td>1.26 x 10^{-3} (5-micron GnP)</td>
<td>[217]</td>
</tr>
<tr>
<td>GnP thickness</td>
<td>6.3 x 10^{-9}</td>
<td>[217]</td>
</tr>
<tr>
<td>In-plane GnP conductivity</td>
<td>10^7 [S/m]</td>
<td>XG sciences GnP - grade M datasheet</td>
</tr>
<tr>
<td>Out of-plane GnP conductivity</td>
<td>10^2 [S/m]</td>
<td>XG sciences GnP - grade M datasheet</td>
</tr>
<tr>
<td>Epoxy conductivity</td>
<td>10^{-14}</td>
<td>[164]</td>
</tr>
<tr>
<td>Agglomerate aspect ratio</td>
<td>0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration scaling parameter a</td>
<td>0.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Agglomeration scaling parameter b</td>
<td>0.05</td>
<td>N/A</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>12 x 10^{-9}</td>
<td>[217]</td>
</tr>
</tbody>
</table>
The results for the micro-mechanical model over the x-band frequencies are shown in table 13. The relative permittivity declines from 6.38 to 4.61 over the 8 to 12 GHz range, while the AC conductivity increases from 0.4 S/m to 0.56 S/m over the same range. Earlier in this thesis, the micromechanics of graphene nanocomposites (section 2.12.5 Micromechanics of Graphene Nanocomposites was discussed in detail. Frequency-dependent permittivity and conductivity were identified. It was noted that electron hopping, a mechanism whereby electrons hop into free delocalized states, occurs increasingly often at higher frequencies. This is the explanation for the increase in AC conductivity with frequency observed here. Nano capacitance is also noted as a micromechanical phenomenon whereby the charge is built up at the graphene-polymer interface due to Maxwell-Wagner-Sillars (MWS) polarization effect. The electrons that are involved in the nano capacitive effect are the same ones that participate in the hopping process. Therefore, the nano capacitive effect is less prevalent at higher frequencies. Following this, the permittivity should become smaller with larger frequencies.

In addition to percolation behavior, it can be concluded that the constructed micromechanical model shows trends of electron hopping and nano-capacitive Debye relaxation in the X-band. These are all confirmed phenomena present in graphene/polymer nanocomposites, which are characterized by a rise in electrical conductivity and a decrease permittivity with increasing frequencies.
Chapter 5

Conclusion and Recommendation

5.1 Conclusion
The search for next-generation EMI shielding materials can be met by carbon polymer nanocomposites. The need for lighter weights, cost reduction and corrosion resilience, particularly in the aerospace and defence industries, influence the move away from metals and towards carbon polymer composites. Here, GnP was chosen as the carbon filler as it can be processed cheaply in bulk, as was epoxy due to its wide usage and superior electrical and mechanical properties. As it stands, meeting adequate electrical conductivity in GnP reinforced epoxy composites is challenging, therefore thick shields or novel nano and/or macrostructures/morphologies may be needed to meet shielding requirements. In order to achieve this, further investigating different processing routes of these materials is needed. Such processing considerations may include longer sonication times or alternative dispersion methods. As understood through the literature review introducing solvents, surfactants, exfoliants and or modified polymers, along with all valid processing options can lead to higher conductivities and EMI shielding values. Although more work is needed to confirm this fabricated material system’s adequacy for EMI applications, an apparent rise in electrical conductivity and EMI shielding effectiveness was identified via the inclusion of GnP into the epoxy matrix. Additionally, percolation behaviour was experimentally identified and theoretically confirmed. Insight was given into the conducting mechanism via theoretical approaches, which were then identified via experiment. This was particularly exemplified by the confirmation of the electron hopping mechanism, which was observed via an increase in electrical conductivity at higher frequencies. Prospects for GnP reinforced epoxy applications were also demonstrated through the fabrication of CFRP with GnP modified epoxy resin.

Neither GnP nor Epoxy possesses significant magnetic permeability to enhance the SE. It is anticipated that a magnetic carbon filler (pyrolytic carbon) may allow for enhanced SE. It was seen that although larger GnP sheet sizes give rise to lower percolation thresholds, they are more likely to agglomerate during the dispersion, and it is ultimately the agglomeration and aspect ratio that dictates the percolation threshold. This means that at higher loadings, 5-micron GnP showed larger composite conductivity and permittivity than 25-micron GnP.

Some discrepancies existed between the experimental data and theoretical predictions over the 0.3-6 GHz range. This was mainly attributed to poor agglomeration fitting. It may be possible
in future to resolve SEM images that show levels of agglomeration in each sample, allowing for better agglomeration fitting.

Measurements taken over larger frequencies may be needed to uncover decreases in permittivity with frequency as predicted by Debye relaxation. Larger bandwidths and higher frequencies will also be beneficial in gaining a better understanding of general EMI shielding properties of the material under test. Unfortunately, X-band measurements were inadequate, and time permits that this thesis must be submitted before consolidated results can be provided.

Although an FDTD algorithm was constructed, analytical solutions will suffice for now as no 3D large scale EMI shielded part that will not fit into standard EMI material characterization equipment has been fabricated.

Lastly, it was observed that the carbon fibre samples with 2 wt. % inclusion experienced a decrease in conductivity and an increase in permittivity over the 0.3-6 GHz. This implies a conductive network throughout the composite was not formed. However, further modelling and experimental characterization will be needed in order to uncover this counterintuitive behaviour.

5.2 Recommendations for Future work

Some recommendations for future work are outlined below.

1. **Optimized dispersion process and/or material selection.** Perhaps the next best step in improving the dispersion process would involve using centrifugation and filtering after sonication in order to remove leftover agglomerates. It is also likely that further exfoliation may be needed to ensure adequate dispersion and high enough conductivities for EMI shielding applications. The next step may be to introduce specifically engineered microstructures, which are tuned to capture electromagnetic energy of certain wavelengths. Another feasible option to explore may be to replace the GnP with pyrolytic carbon particles, which would give control over the composite’s magnetic permeability. Permeability control not only allows for an increase in EMI shielding but would open the possibility of developing a radar-absorbing material through impedance matching.

2. **Further SEM imaging.** Further SEM imaging would be beneficial in understanding the nanocomposite morphology. This can lead to a better understanding of the filler
particle size distribution and shape. Therefore, a comprehensive understanding of agglomeration and hence dispersion could be met.

3. **Optimized X-band EMI characterization process.** As explored, there were some issues with the waveguide measurement, which were intended to measure the X-band EMI and bulk material properties. The needed improvement included developing a sample holder, which would ensure the cable and waveguide do not have to move after calibration. The sample holder would need to be roughly the same thickness as the samples; therefore, it would be best to make many samples with the same thickness, which would avoid re-calibration after each sample measurement.

4. **Further modelling.** Further modelling work could include (1) development of the multi-scale model into a user-friendly GUI, which would include all the modelling work into one. Allowing the user to easily predict macro-scale behavior based on micro/nano-scale inputs. (2) Accounting for the inclusion of carbon fibre into the model, effectively allowing for higher phase composites with different filler geometries. (3) Developing the FDTD model to be able to map higher spatial dimensions.
References


ce%20the%20final%20GNP%20product.


161. Ahmad, H., et al., Stealth technology: Methods and composite materials—A review. Polymer Composites. 0(0).


183. Liu, P., et al., Microwave absorption properties of double-layer absorbers based on Co0.2Ni0.4Zn0.4Fe2O4 ferrite and reduced graphene oxide composites. Journal of alloys and compounds, 2017. 701: p. 841-849.


