Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of
the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or
  private study purposes only, and you may not make them available to any
  other person.
- Authors control the copyright of their thesis. You will recognize the
  author's right to be identified as the author of this thesis, and due
  acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material
  from their thesis.

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital
copy of their work to be used subject to the conditions specified on the Library
Thesis Consent Form and Deposit Licence.
Developing an Alternative Composite Material for Electromagnetic Interference Shielding

Pongphat (Patrick) Sittisart

Thesis Submitted in Partial Fulfilment of the Requirements of the Degree of Doctor of Philosophy in Chemicals & Materials Engineering

Department of Chemicals & Materials Engineering
University of Auckland
14 February 2017
Abstract

This research aims to develop a cost-effective and light-weight composite material based on natural fibres for electromagnetic interference shielding. Natural fibres were chosen as they are one of the cheapest forms of fibre, are light-weight and are also a renewable resource.

To shield electromagnetic interference, the shielding material must be electrically conductive. Since natural fibres do not have that property, it is necessary to deposit a conductive coating on natural fibres prior to process them into composites. Nickel was chosen as the material to be used for the conductive coating since it is one of the most effective materials for shielding electromagnetic interference. Electroless plating was chosen as the technique for nickel deposition as it is the most suitable method for the application of a conductive coating on a non-conductive substrate.

The experimental work was split into three stages. The first stage confirmed the possibility of depositing nickel onto natural fibres as a proof of concept. The second stage was the development and optimisation of the nickel coating of cellulose fibres. The final stage was the incorporation of nickel coated cellulose fibres into polypropylene to create an electrically conductive composite with the purpose of shielding equipment from electromagnetic interference. Additionally, composites based on commercially-available stainless steel fibre were fabricated to establish a baseline for comparison. Material properties, such as electromagnetic interference shielding effectiveness, volume resistivity, surface resistivity and flexural strength for both types of composite, were characterised. Furthermore, the 2D and 3D microstructures of these composites were analysed using computer tomography and ImageJ.

The results have indicated that nickel can be successfully deposited onto cellulose fibres, which were then used in fabricating a dense composite. The composite, which contained 50% by weight, of nickel coated cellulose fibres, achieved a satisfactory shielding level, which may be suitable for use in desktop and laptop computers. Additionally, nickel coated cellulose fibre composites are more suitable than stainless steel fibre composites for application where mechanical strength is important. Qualitative and quantitative analysis of SEM images suggests that nickel coated cellulose fibres have shorter effective fibres aspect ratio than SSF because of curved fibres and fines. These are some reasons why stainless steel fibres composite exhibited a lower percolation threshold than nickel coated cellulose fibres composite.
Acknowledgements

I would like to express my deepest gratitude to my supervisor, Prof. Margaret Hyland, for her dedication, guidance and support. This thesis would not have been possible without her help.

I would like to express my appreciation to my co-supervisors, Dr. Michael Hodgson and Dr. Chuong Nguyen for their help and expertise in the aspect of materials and their characterisation techniques.

I would like to thank Scion for providing the raw material for my experiment, lab workspace and equipment for material characterisation. The following Scion researchers and technicians have also contributed to this thesis:

Alan Fernyhough for the idea of developing natural fibres for electromagnetic interference shielding (EMI)

Alan Dickson for help with microscopy technique and ImageJ analysis

Ross Anderson for general help with equipment

Armin Thumm for providing polypropylene fibres and lessons about compression moulding machine

Marie Joo Le Guen for general help and lessons about composite fabrication by vacuum infusion

Donna Smith and Robin Parr for general lessons about equipment in the lab

I would also like to thank Ned Bryant from RTP Company (USA) for performing EMI shielding effectiveness and surface resistivity measurement for my composite materials.

John Kennedy from GNS for his advice on the development of this project

Andrew McNaughton (Otago University) for performing micro-CT scan on my composites

ES Plastic for fabricating stainless steel fibres composite

In addition, a special thanks to Product Accelerator and the Department of Chemical and Materials Engineering for 6 months of financial support
Dedication

I would like dedicate this thesis to my grandfather (Sawart Sittisart). I have finally fulfilled a promise that I have made to him. I hope he is proud of me.

A special thanks to my parents (Wittaya and Kotchaphon Sittisart) for their support in my PhD journey. I know how much this means to them and I am very grateful to be able to complete this journey.

I would like to express my deepest gratitude to my lovely wife (Kornkanok Sittisart) for her understanding and support throughout the most difficult time in my life. This thesis would not have been possible without her. Also, thank you my son (Kyrin Sittisart) for motivating me to finish this thesis.

I would also like to thank my elder brother (Surad Sittisart) and sister-in-law (Nantaya Sittisart) for their understanding and support.
Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. Please include one copy of this form for each co-authored work. Completed forms should be included in all copies of your thesis submitted for examination and library deposit (including digital deposit), following your thesis Acknowledgements.

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 6.1 Pages 57 - 58, Chapter 6.2 Pages 59 - 64, Chapters 6.3 and 6.4 Pages 65 - 69

Title of Article: Preparation and Characterization of Electroless Nickel Coated Cellulose Fibres (Published by Springer)

<table>
<thead>
<tr>
<th>Nature of contribution by PhD candidate</th>
<th>Conducted the Research Work</th>
<th>Prepared, Submitted and Revised the Journal Article</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of contribution by PhD candidate (%)</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

CO-AUTHORS

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Margaret Hyland</td>
<td>Provided advice to the research work and revised the journal article</td>
</tr>
<tr>
<td>Dr. Michael Hodgson</td>
<td>Provided advice to the research work and revised the journal article</td>
</tr>
<tr>
<td>Dr. Chuong Nguyen</td>
<td>Provided advice to the research work and revised journal article</td>
</tr>
<tr>
<td>Dr. Alan Fernyhough</td>
<td>Provided advice, raw material and lab space for the research work</td>
</tr>
</tbody>
</table>

Certification by Co-Authors

The undersigned hereby certify that:
- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Margaret Hyland</td>
<td></td>
<td>25/06/2015</td>
</tr>
<tr>
<td>Dr. Michael Hodgson</td>
<td></td>
<td>08/04/2015</td>
</tr>
<tr>
<td>Dr. Chuong Nguyen</td>
<td></td>
<td>30/04/2015</td>
</tr>
<tr>
<td>Dr. Alan Fernyhough</td>
<td></td>
<td>24/04/2015</td>
</tr>
<tr>
<td></td>
<td>Click here</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Click here</td>
<td></td>
</tr>
</tbody>
</table>
This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. Please include one copy of this form for each co-authored work. Completed forms should be included in all copies of your thesis submitted for examination and library deposit (including digital deposit), following your thesis Acknowledgements.

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 7.1 Pages 86 - 87 and 90 - 92, Chapter 7.2 Pages 104 - 106, Chapter 7.3 pages 110 - 111, Chapter 7.4 page 118

Title of Article: Developing a Cost-Effective Composite Based on Electroless Nickel-Coated Cellulose Fibres for Electromagnetic Interference Shielding (Published by Scrivener Publishing LLC)

<table>
<thead>
<tr>
<th>Nature of contribution by PhD candidate</th>
<th>Extent of contribution by PhD candidate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conducted the Research Work</td>
<td>90</td>
</tr>
<tr>
<td>Prepared, Submitted and Revised the Journal Article</td>
<td></td>
</tr>
</tbody>
</table>

### CO-AUTHORS

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Margaret Hyland</td>
<td>Provided advice to the research work and revised journal article</td>
</tr>
<tr>
<td>Dr. Michael Hodgson</td>
<td>Provided advice to the research work and revised journal article</td>
</tr>
<tr>
<td>Dr. Chuong Nguyen</td>
<td>Provided advice to the research work and revised journal article</td>
</tr>
<tr>
<td>Dr. Alan Fernyhough</td>
<td>Provided advice, raw material and lab space for the research work</td>
</tr>
</tbody>
</table>

### Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Margaret Hyland</td>
<td>[Signature]</td>
<td>25/06/2015</td>
</tr>
<tr>
<td>Dr. Michael Hodgson</td>
<td>[Signature]</td>
<td>08/04/2015</td>
</tr>
<tr>
<td>Dr. Chuong Nguyen</td>
<td>[Signature]</td>
<td>30/04/2015</td>
</tr>
<tr>
<td>Dr. Alan Fernyhough</td>
<td>[Signature]</td>
<td>24/04/2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Click here</td>
</tr>
</tbody>
</table>
# Table of contents

Abstract ........................................................................................................................................ii  
Acknowledgements ...................................................................................................................... iii  
Dedication ....................................................................................................................................... iv  
1.0 Introduction ................................................................................................................................. 1  
2.0 EMI, Shielding Theory, Material and Design ............................................................................... 6  
   2.1 Electromagnetic Interference Theory ......................................................................................... 7  
   2.2 Electromagnetic Interference Shielding Theory .......................................................................... 8  
   2.3 Commercial EMI Shielding Materials ....................................................................................... 11  
   2.4 Electromagnetic Interference Shielding Effectiveness of Materials ........................................ 13  
   2.5 Required Material Properties .................................................................................................. 16  
   2.6 Polymers for EMI Shielding ...................................................................................................... 19  
   2.7 Common Fillers for Composites ................................................................................................ 22  
3.0 Factors Affecting the Properties of EMI Shielding Composites ................................................. 27  
   3.1 Percolation Theory and Modelling .......................................................................................... 27  
   3.2 Quantum Tunnelling and Thermal Expansion .......................................................................... 38  
   3.3 Compression Moulding and Injection Moulding – Their Effect on Percolation  
      Threshold and EMI Shielding Effectiveness ............................................................................... 40  
4.0 Electroless Nickel Deposition ...................................................................................................... 44  
   4.1 Electroless Nickel Deposition .................................................................................................. 44  
   4.2 Electroless Nickel Plating of Wood ......................................................................................... 48  
5.0 Research Scope and Directions .................................................................................................. 51
6.0 Developing Nickel Coating on Natural Fibres.................................................................56
6.1 Stage One: Nickel Coating on Filter Paper – Experimental Procedures.......................57
6.2 Stage One: Nickel Coating on Filter Paper – Results and Discussions........................59
6.3 Stage Two: Nickel Coating on Cellulose Fibres – Experimental Procedures................65
6.4 Stage Two: Nickel Coating on Cellulose Fibres – Results and Discussion...................66
7.0 Developing NCCF and SSF Composites ........................................................................86
7.1 NCCF and SSF Composites – Experimental Procedures...............................................86
7.2 Electrical Resistivity of SSF and NCCF Composites.......................................................98
7.3 EMI SE of SSF and NCCF Composites ..........................................................................109
7.4 Mechanical properties of SSF and NCCF Composites................................................115
7.5 Density of SSF and NCCF Composites ..........................................................................127
8.0 Image Analysis, Spatial Analysis and 3-D Microstructure..............................................133
  8.1 Aspect Ratio, Feret Ratio analysis and approximating fibre waviness .........................133
  8.2 Particle distribution analysis .........................................................................................137
  8.3 3-D Object Analysis .....................................................................................................141
9.0 Conclusions and Recommendations ............................................................................148
References...............................................................................................................................151
Appendix – Permission for Reuse.........................................................................................165
List of Figures

Figure 2.1: Electromagnetic spectrum showing common shielding range. Reprinted with permission from [1].................................................................6
Figure 2.2: Three essential components for EMI. Reprinted with permission from [1]...........7
Figure 2.3: The wave impedance measures the relative strength of electric and magnetic fields. It is a function of source structure. Reprinted with permission from RFCafe.com [26] 8
Figure 2.4: Illustration of Faraday’s cage, showing the distribution of electrical changes on conducting enclosure under applied electric field. Redrawn based on original by [29]...........9
Figure 2.5: Illustration of the interaction between magnetic field and material with good permeability. The magnetic field generally remains on the surface of the material since it provide a path of low reluctance. Thus, magnetic field strength is less inside the enclosure. Redrawn based on original by [30].................................................................10
Figure 2.6: Illustration of eddy current generated inside an electrically conductive material under an alternating magnetic field. This produces an opposing magnetic field which reduces the strength of incident magnetic field. Redrawn based on original by [25]......................10
Figure 2.7: Representation of shielding phenomena for electromagnetic waves passing through a homogeneous barrier. Reprinted with permission from [1].................................13
Figure 2.8: “Surface Resistivity,” RTP Company technical brochure 2009-01-14, Surface Resistivity illustration provided as a courtesy by RTP Company [45].................................17
Figure 2.9: Shielding effectiveness vs. volume resistivity. Reprinted with permission from Interference Technology [11] ..................................................................................20
Figure 3.1: Schematic sketch of the resistivity of a composite as a function of filler concentration for isotropic particles (full line) and carbon black (dashed line) concentration. Reprinted with permission from [112].................................................................31
Figure 3.2: Effect of filler aspect ratio on the critical filler concentration needed to induce bulk conductivity (or attaining percolation threshold) in a filled polymer. Reprinted with permission from [113]..................................................................................................................32
Figure 3.3: Geometry of curved fibre. Reprinted from [116] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry. ............33
Figure 3.4: Comparison of critical concentration (volume fraction) predictions from Monte Carlo and excluded volume models. Reprinted with permission from the author of [93]......37
Figure 3.5: An illustration of a system of metallic particles which are embedded in an insulating matrix. The particles are not connected geometrically but via tunnelling, electrically. Reprinted with permission from [126].................................................................39
Figure 3.6: Typical graph of resistivity as a function of temperature. Reprinted with permission from [6]........................................................................................................................................39
Figure 3.7: Schematic of injection moulding. Reprinted with permission from [128].........40
Figure 3.8: Photomicrograph showing fibre orientation in compression moulded SSF composite. Reprinted with permission from [129].........................................................................................41
Figure 3.9: Fibre orientation in injection moulded SSF composite A) sidewall skin, B) sidewall core, C) centreline skin and D) centreline core. Reprinted with permission from [129] ..............................................................42
Figure 3.10: Conductivity curves for composite containing aligned and randomly oriented flakes. Reprinted with permission from [115].................................................................42
Figure 3.11: Shielding effectiveness versus flake loading for composites containing and randomly oriented flakes. Reprinted with permission from [115].........................................................43
Figure 4.1: Correlation between electrical resistivity and phosphorus content of nickel coating on steel substrate. Reprinted with permission, courtesy of Nickel Institute [136]..........48
Figure 6.1: a) SEM image and b) EDS spectra of uncoated filter paper .................................59
Figure 6.2: EDS spectra of cellulose fibres .............................................................................60
Figure 6.3: a) SEM image and b) EDS spectra of filter paper coated for 2.5 minutes at 84 °C .................................................................................................................................................................60
Figure 6.4: a) SEM image and b) EDS spectra of filter paper coated for 20 minutes at 84 °C61
Figure 6.5: XRD graph of coated and uncoated filter paper ..................................................63
Figure 6.6: Surface resistivity of nickel coated filter paper at plating temperatures of 72 and 84 °C.........................................................................................................................................................64
Figure 6.7: SEM images of nickel coated cellulose fibres (12% nickel, 15 minutes plating time) ..................................................................................................................................................67
Figure 6.8: SEM images of nickel coated cellulose fibres (Plating time: 5(a), 10(b), 15(c), 20(d), plating temperature = 72 °C).................................................................70
Figure 6.9: SEM images of nickel coated cellulose fibres (Refresh: 1(a), 2(b), 3(c) and 4(d), 15 minutes plating time, plating temperature = 72 °C).........................................................71
Figure 6.10: SEM images of nickel coated cellulose fibres (12%(a), 18%(b), 24%(c) and 30%(d), 15 minutes plating time, plating temperature = 72 °C)..............................................72
Figure 6.11: SEM images of nickel coated cellulose fibres a) refresh once, 10 minutes, 72 °C, b) refresh once, 10 minutes, 84 °C and c) refresh once, 15 minutes, 72 °C).........................73
Figure 6.12: SEM images of nickel coated cellulose fibres a) pre-treatment solution = 20 ml, 12% nickel, 15 minutes, 72°C, b) pre-treatment solution = 100 ml, 12% nickel, 15 minutes, 72°C and c) pre-treatment solution = 20 ml, 18% nickel, 15 minutes, 72°C)..............................75
Figure 6.13: SEM images of nickel coated cellulose fibres (pre-treatment solution = 20 ml, 12% nickel, 15 minutes, 72°C, refresh once)........................................................................75
Figure 6.14: SEM images of nickel coated cellulose fibres (pre-treatment solution = 20 ml, 12% nickel, 15 minutes, 72°C, refresh twice).................................................................76
Figure 6.15: SEM images of nickel coated cellulose produced with scaled up conditions .....77
Figure 6.16: XRD graph of coated and uncoated cellulose fibres .........................................................78
Figure 7.1: Porosity of compression moulded Original NCCF composite ........................................87
Figure 7.2: SEM image of cross-section of compression moulded Original NCCF composite. (bright areas indicate nickel coated cellulose fibres) .........................................................90
Figure 7.3: Illustrations of the characterization process of the NCCF and SSF composites...93
Figure 7.4: “Coaxial Transmission Line Test,” RTP Company technical presentation 2014-09-05, Spectrum Analyzer/Tracking Generator illustration provided as a courtesy by RTP Company [160] ..................................................................................................................94
Figure 7.5: Selecting an area of interest (left) and subsequently cropping the section for analysis (middle) and subsequently thresholding the region of interest to distinguish between matrix (black) and fibres (white). This was done on 50 wt% best Optimised NCCF ..........98
Figure 7.6: Surface resistivity of injection moulded SSF composite at different loading ......99
Figure 7.7: Volume resistivity profile of injection moulded SSF composite at 8 wt% loading .................................................................................................................................100
Figure 7.8: Volume resistivity profile of injection moulded SSF composite at 16 wt% loading .................................................................................................................................100
Figure 7.9: Volume resistivity profile of injection moulded SSF composite at 4 wt% loading .................................................................................................................................101
Figure 7.10: EMI SE of SSF composites and their respective surface resistivity ..............102
Figure 7.11: Surface resistivity of compression moulded Original NCCF composite at
different loading ........................................................................................................104
Figure 7.12: Volume resistivity profile of compression moulded Original NCCF composite at
40 wt% loading ........................................................................................................105
Figure 7.13: Volume resistivity profile of compression moulded Original NCCF composite at
50 wt% loading ........................................................................................................106
Figure 7.14: Volume resistivity profile of compression moulded Original NCCF composite at
20 wt% loading ........................................................................................................106
Figure 7.15: Surface resistivity of the compression moulded Optimised NCCF composite at
different loading ........................................................................................................107
Figure 7.16: Volume resistivity profile of the compression moulded Optimised NCCF
composite at 20 wt% loading ....................................................................................108
Figure 7.17: Volume resistivity profile of the compression moulded Optimised NCCF
composite at 40 wt% loading ....................................................................................108
Figure 7.18: Volume resistivity profile of the compression moulded Optimised NCCF
composite at 50 wt% loading ....................................................................................109
Figure 7.19: EMI shielding effectiveness of injection moulded composite panels with
different loading of SSF at different frequency .........................................................110
Figure 7.20: EMI shielding effectiveness of compression moulded composite panels with
different loading of Original NCCF at different frequency .......................................111
Figure 7.21: EMI shielding effectiveness of the compression moulded composite panels with
different loading of Optimised NCCF ........................................................................112
Figure 7.22: Volume resistivity profile of the compression moulded Original and Optimised
NCCF composite at 50 wt% loading ........................................................................114
Figure 7.23: Maximum flexural strength of injection moulded SSF composite at different
loading ..........................................................................................................................116
Figure 7.24: Young’s modulus of injection moulded SSF composite at different loading ...117
Figure 7.25: Maximum flexural strength of compression moulded Original NCCF composite
at different loading .....................................................................................................118
Figure 7.26: Fracture surface of compression moulded Original NCCF composite at 40 wt%
loading .......................................................................................................................121
Figure 7.27: Fracture surface of compression moulded uncoated cellulose fibres composite at
40 wt% loading at 200x magnification .......................................................................122
Figure 7.28: Fracture surface of compression moulded uncoated cellulose fibres composite at 40 wt% loading at 800x magnification .............................................................. 123
Figure 7.29: Young’s modulus of compression moulded Original NCCF composite at different loading ........................................................................................................ 124
Figure 7.30: Maximum flexural strength of compression moulded Optimised NCCF composite at different loading ................................................................. 125
Figure 7.31: Young’s modulus of compression moulded Optimised NCCF composite at different loading ............................................................................................ 126
Figure 7.32: Density of injection moulded SSF composite at different loading ............ 128
Figure 7.33: Density of compression moulded Original NCCF composite at different loading ........................................................................................................... 129
Figure 7.34: Density of compression moulded Optimised NCCF composite at different loading ............................................................................................................. 130
Figure 8.1: Aspect ratio and Feret ratio of NCCF composites .................................... 135
Figure 8.2: Aspect ratio and Feret ratio of SSF composites ...................................... 135
Figure 8.3: SEM image of NCCF 10 at 200x magnification ...................................... 136
Figure 8.4: SEM image SSF 4 at 200x magnification ............................................. 136
Figure 8.5: Waviness ratio of NCCF ...................................................................... 137
Figure 8.6: Illustration and explanation about the characteristic of the F-function and G-function [190] .......................................................................................... 138
Figure 8.7: An example of a graph for the F function. Reprinted with permission from the author [191] ........................................................................................................... 139
Figure 8.8: F-function for NCCF 10 ................................................................. 140
Figure 8.9: G-function for NCCF 10 ................................................................. 141
Figure 8.10: Number of 3D objects found in SSF, Original and Optimised NCCF composite at various loadings ............................................................... 142
Figure 8.11: Number of voxel found in the major cluster in SSF, Original and Optimised NCCF composite at various loadings ........................................... 145
Figure 8.12: Example of 50 wt% NCCF composite stacks (left, 2089 total images) and 12 wt% SSF composite stacks (right, 2085 total images) ......................... 146
List of Tables

Table 2.1: Electrical conductivity relative to copper and relative permeability of selected materials. Modified from [37]......................................................................................................................... 18
Table 2.2: Skin depth of common materials calculated at 30 MHz.................................................. 18
Table 2.3: EMI shielding effectiveness Studies on PANI – PTSA/CMC and PAn– CSA/CMC Reinforced conducting E-Glass Fabric. Reprinted with permission from [16] ....................20
Table 2.4: EMI shielding effectiveness results of PANI composites. Reprinted with permission from [16].......................................................................................................................... 21
Table 2.5: EMI shielding effectiveness of various PPY/fabric complexes at 1 GHz. Reprinted with permission from [16] ........................................................................................................ 21
Table 2.6: EMI shielding effectiveness results of PPY composites. Reprinted with permission from [16]........................................................................................................................................ 22
Table 2.7: Typical properties of vapour-grown carbon nanofibres, single-walled carbon nanotubes, multi-walled carbon nanotubes and carbon fibres. Modified from [17]...........23
Table 2.8: EMI shielding effectiveness value of nickel-coated carbon fibre composite. Reprinted with permission from [16]............................................................................................................. 26
Table 2.9: Stainless steel fibre filled thermoplastic for resin type-7% stainless steel fibre. Modified from [90] ................................................................................................................................. 26
Table 3.1: Probability of cluster formation in two and three dimensional lattices. Permission to reprint obtained from the author. Modified from [93] .............................................................. 28
Table 3.2: Calculated values of critical exponent in two and three dimensions. Permission to reprint obtained from the author. Modified from [93] ........................................................................... 29
Table 3.3: Experimental values of percolation theory variables. Permission to reprint obtained from the author. Modified from [93] ............................................................................................................ 30
Table 3.4: Predictions from two dimensional Monte Carlo simulation (values are reported as critical area fraction). Permission to reprint obtained from the author. Modified from [93] ..34
Table 3.5: Predicted and experimental value of percolation threshold for various systems. Permission to reprint obtained from the author. Modified from [93].................................36
Table 4.1: Summary table of factors affecting the kinetics of electroless nickel deposition...47
Table 6.1: Composition of nickel plating solution (for filter paper).......................................57
Table 6.2: ImageJ analysis of the coverage of nickel on filter paper ......................................62
Table 6.3: Composition of nickel plating solution (for cellulose fibres).................................66
Table 6.4: Table of trials to determine the optimal electroless plating conditions to uniformly deposit nickel onto cellulose fibres with good coverage ........................................69
Table 6.5: Table of trials to determine the optimal electroless plating conditions to uniformly deposit nickel onto cellulose fibres with good coverage and improved EMI shielding capability ..................................................................................................................82
Table 7.1: Table of trials to determine the optimal compression moulding conditions to fabricate a porosity-free Original NCCF composite ..............................................88
Table 7.2: Summary of composite of conducting fillers and conventional polymers ........115
Table 7.3: Summary of the average values for EMI SE, electrical resistivities, mechanical properties and density of composites ..............................................................................132
Table 8.1: Analysis of F-function and G-function graph for SEM images ....................140
Table 8.2: summary of 3D objects detected in SSF and NCCF composite at various filler loading................................................................................................................................143
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Absorption</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>B</td>
<td>Multiple reflection</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon Fibres</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Skin depth</td>
</tr>
<tr>
<td>dB</td>
<td>Decibels</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>Permittivity of free space</td>
</tr>
<tr>
<td>( \varepsilon_r )</td>
<td>Real part of dielectric constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Electric field intensities incident on the shield</td>
</tr>
<tr>
<td>$E_1$</td>
<td>Transmitted electric field though the shield</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>E-Field</td>
<td>Electric Field</td>
</tr>
<tr>
<td>EMC</td>
<td>Electromagnetic Compatibility</td>
</tr>
<tr>
<td>EMI</td>
<td>Electromagnetic Interference</td>
</tr>
<tr>
<td>EMI SE</td>
<td>Electromagnetic Interference Shielding Effectiveness</td>
</tr>
<tr>
<td>ESD</td>
<td>Electrostatic Discharge</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>FCC</td>
<td>Federal Communications Commission</td>
</tr>
<tr>
<td>GHz</td>
<td>Gigahertz</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$H_0$</td>
<td>Magnetic field intensities incident on the shield</td>
</tr>
<tr>
<td>$H_1$</td>
<td>Transmitted magnetic field though the shield</td>
</tr>
<tr>
<td>H-Field</td>
<td>Magnetic Field</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>ICPs</td>
<td>Intrinsically Conductive Polymers</td>
</tr>
<tr>
<td>kHz</td>
<td>Kilohertz</td>
</tr>
</tbody>
</table>
\( \lambda \)  
Wavelength

MCP  
Metal Coated Plastic

MHz  
Megahertz

\( \mu \)  
Magnetic Permeability

\( \mu_0 \)  
Permeability of free space

MWNT  
Multi-Walled Carbon Nanotubes

NCCF  
Nickel Coated Cellulose Fibres

OD  
Oven-Dried

\( \Omega \)  
Ohm

\( \sigma \)  
Conductivity

\( P_0 \)  
Power intensities incident on the shielding

\( P_1 \)  
Transmitted power though the shield

PA  
Polyacetylene

PANI  
Polyaniline

PC  
Polycarbonate

PE  
Polyethylene

PET  
Polyethylene Terephthalate

PP  
Polypropylene

PPV  
Poly(p-phenylene-vinylene)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PTH</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PCB</td>
<td>Print Circuit Board</td>
</tr>
<tr>
<td>R</td>
<td>Reflection</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SE</td>
<td>Shielding Effectiveness</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SSF</td>
<td>Stainless Steel Fibres</td>
</tr>
<tr>
<td>S/m</td>
<td>Siemens per meter</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>t</td>
<td>Thickness of material</td>
</tr>
<tr>
<td>tan δ</td>
<td>Dielectric loss or loss tangent</td>
</tr>
<tr>
<td>v</td>
<td>Speed of light in vacuum</td>
</tr>
<tr>
<td>VGCNF</td>
<td>Vapour Grown Carbon Nanofibres</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>Z₀</td>
<td>Characteristic impedance of air</td>
</tr>
<tr>
<td>Z₁</td>
<td>Impedance of the electromagnetic wave propagating domain</td>
</tr>
<tr>
<td>Z₉</td>
<td>Impedance of incident magnetic field</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Zs</td>
<td>Impedance of shielding material</td>
</tr>
<tr>
<td>Zw</td>
<td>Wave impedance</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Electromagnetic interference (EMI) refers to a process by which electromagnetic radiation interferes with the performance of electronic devices. This process can cause the degradation or even the malfunction of electronic equipment. Therefore it is essential for electrical systems and electronic devices to be able to operate at a desired level of performance under the influence of EMI. This performance is also known as the electromagnetic compatibility of a system [1].

EMI is an on-going concern which affects electronic systems and devices ranging from commercial products to military activity and space exploration [1]. All electronic devices emit electromagnetic radiation as a by-product of their electrical or magnetic activity. Not only does EMI interfere with the performance of electronic devices but it also has a negative impact on human health. Prolonged exposure to electromagnetic radiation may cause insomnia, nervousness and headaches [2].

Although electromagnetic waves at any particular frequency are capable of causing EMI, most problems occur in the radio frequency region. The aim of this project then is to develop a light composite fibre system to provide a cost-effective and simple solution for shielding EMI. The frequency range of interest in this study is 300 MHz – 1.5 GHz, as this is where EMI interferes with radio communications. Generally, a minimum shielding effectiveness value of 30 dB is considered satisfactory for most commercial applications as it corresponds to a 99.9% reduction of the interference signal [3].
Shielding EMI generally refers to the process where shielding materials are used to partially or fully enclose either the EMI source or the receptor. This process reduces the amount of electromagnetic radiation leaving the source of electromagnetic energy or entering the susceptible receptor.

To shield EMI, the shielding material will need to be electrically conductive [1]. There are several options available for EMI shielding, including metals, conductive coatings and conductive plastic compounds (or conductive composite) [4-6]. Bulk metal sheets and conductive coatings on non-conductive base materials have been used to achieve satisfactory EMI shielding due to their inherent electrical conductivity. However, the main disadvantages in using bulk metal sheets in EMI shielding applications are their weight and bulkiness, which can be a design challenge. In contrast, conductive coatings, whilst light and thin, are susceptible to scratches and delamination, rendering them less effective. The usage of conductive composites is becoming more common as they offer lightness of weight, durability and manufacturing flexibility, as well as the protection of the conductive coatings on fillers (if they were used to fabricate conductive composites). Although bulk metal sheets and conductive coatings are still appropriate for certain EMI shielding purposes, the advantages offered by conductive composites are making them a more common form of material for EMI shielding applications [7].

The approach chosen in this thesis is to explore the possibility of using natural fibres obtained from plants to fabricate an EMI shielding composite. Natural fibres from plants can be classified into two groups: vegetable fibres and cellulose fibres. Vegetable fibres typically consist of bast fibres, leaf fibres, seed fibres and they generally contain lignin. Common examples of vegetable fibres are; cotton, hemp, jute, flax, ramie, sisal, bagasse and banana. Cellulose fibres, such as those extracted from wood chips, originate from tree sources. Cellulose fibres are extracted through the Kraft pulping process which removes lignin. Both vegetable and cellulose fibres can be incorporated into a polymer to improve the mechanical properties of the composite materials. The main disadvantage of vegetable fibres is the uncertainty of their quality and supply; this is because commonly used vegetable fibres such as Hemp and Sisal are agricultural fibres which are harvested on a seasonal basis. However, the production of cellulose fibres via the Kraft pulping process produces a cheaper and more consistent quality of fibres in plentiful supply. Therefore, cellulose fibres are materials of interest for this study [8].
One of the cheapest forms of cellulose fibre is obtained from Kraft Pinus Radiata. This fibre is much lighter than metal fibres. Previous research has shown that composites prepared from cellulose fibres and polypropylene fibres demonstrate an improvement in mechanical strength compared to pure polypropylene [9]. Unfortunately, cellulose fibres in their natural form are not electrically conductive, and thus do not offer EMI shielding capability [10]. In order to use a cellulose/polypropylene fibre composite for EMI shielding, it is necessary to deposit an electrically conductive coating onto the cellulose fibres before they are processed into a composite.

To make certain that every cellulose fibre contributes consistently to the overall EMI shielding; this project aims to uniformly deposit an electrically conductive coating onto individual cellulose fibres. This can be achieved more easily in an aqueous environment where cellulose fibres are suspended individually instead of being strongly bonded to each other via hydrogen bonding in its dry state. There are various methods of depositing conductive coating onto a substrate, such as; vacuum metallization, ion plating, electroplating, electroless plating, zinc arc spraying and conductive paints [11-13]. However, due to cellulose fibres varying in shape and size, as well as the preferred aqueous process, electroless plating was selected to uniformly deposit a continuous and adherent conductive coating onto individual cellulose fibres.

Electroless plating is a chemical technique in which a metal coating is deposited onto a substrate. For a non-conductive substrate, such as cellulose fibre, the surface of the substrate is activated with chemicals or metal particles prior to the plating process. The main advantages of electroless plating is that it is one of a few techniques applicable to non-conductive substrate and it can also generally deposit a more uniform coating when compared to other techniques [14, 15].

Silver, copper and nickel are common metals that can be deposited electrolessly. Silver is the most expensive, making it less attractive [16, 17]. Copper is the cheapest but can readily oxidise during composite processing, which would reduce the composite’s EMI shielding ability [18]. Nickel was chosen for this study as it possesses superior resistance to corrosion and oxidation, as well as exhibiting lower skin depth compared to silver and copper. Lower skin depth means less material is necessary to obtain the same level of EMI shielding effectiveness, making nickel the most cost-effective metal for electroless deposition [7, 16, 17].
Little work has been done on electroless coating of cellulose fibres. Zabetakis [19] reported electroless copper plating of cellulose fibres. This method involved activating the surface of cellulose fibres with palladium followed by freeze-drying. These palladium-activated cellulose fibres were then immersed into an electroless copper plating solution. These steps are both complex and costly, making the method unattractive for this project. Other than this, the most relevant information currently available is the electroless nickel plating of wood veneer. Li et al [20] have reported that they have successfully developed a new, simple and cheap process to deposit nickel onto wood veneer. In this case, sodium borohydride was used to activate the surface of the wood veneer, which is much cheaper than using precious metals like palladium. Both wood veneer and cellulose fibres contain hydroxyl groups that can bond with sodium borohydride; thus, this activation method was selected for the purposes of this study.

The first stage of the project was designed as a proof-of-concept stage. Here, filter paper (consisting mostly of cellulose fibres) was used to confirm the possibility, as well as to improve the understanding of the electroless nickel plating technique. Once nickel coatings were successfully deposited on filter paper, the second stage was the modification and optimisation of the electroless nickel plating technique to produce a uniform, continuous and adherent coating on individual cellulose fibres. Then, in the third stage, nickel coated cellulose fibres (NCCF) were incorporated into polypropylene to create an electrically conductive composite suitable for EMI shielding. The aim was also to determine the level of NCCF loading necessary to attain the percolation threshold. Additionally, in order to establish a comparable baseline for NCCF composite and also to study the influence of fibre microstructure on percolation, a composite based on commercially available SSF was fabricated. Various material properties such as EMI SE, surface resistivity, volume resistivity and flexural strength were measured to assess the performance of NCCF and SSF composites.

**Project Aim**

The aim of this research is twofold:

1. to develop a novel composite material based on nickel coated cellulose fibres that can offer a cost effective and light-weighted solution for EMI shielding; and
2. to understand the microstructure–property relationship for composites based on electrically conductive fillers and non-conductive resin matrix; in particular, the
correlation between 3-D distribution and connection of fibres in a composite and its percolation threshold.

Research scope and directions will be further outlined in chapter 5.
Chapter 2

EMI, Shielding Theory, Material and Design

Electromechanical equipment, such as a washing machine, generally emits low-frequency waves (kHz range). At the other end of the spectrum, electronic devices such as computers and mobile phones emit electromagnetic waves at much higher frequencies (MHz – GHz range) [21]. The most common type of EMI occurs in the radio frequency (RF) range of the electromagnetic spectrum, 10 kHz – 100 GHz. This energy can be radiated by computer circuits, radio transmitters, fluorescent lamps, electric motors, overhead power lines, lightning and many other sources [22]. As electronic devices become more integrated and miniaturised, they become more susceptible to EMI. Hence, EMI shielding has become increasingly important. Figure 2.1 illustrates the electromagnetic spectrum [1].

Figure 2.1: Electromagnetic spectrum showing common shielding range. Reprinted with permission from [1]
2.1 Electromagnetic Interference Theory

For EMI to occur, three essential components are required, as shown in Figure 2.2.

![Figure 2.2: Three essential components for EMI: Emitter, Coupling Path, Susceptor. Reprinted with permission from [1]](image)

These three components are: (1) the source of electromagnetic energy; (2) the receptor of electromagnetic energy and (3) the path for propagation. EMI can be reduced by decreasing the emission from the source, improving the immunity of the receptor, or altering the path of propagation of electromagnetic waves. The first two EMI reduction options can be achieved by shielding the source or the receptor with suitable material. Regarding the latter option, it should be noted that electromagnetic emission can propagate via conduction or radiation. Electromagnetic propagation via conduction requires power lines or signal lines for transmission. This requirement means that conducted interference can be managed by adding filters to the power or signal lines. However, electromagnetic propagation via radiation can reach the receptor by travelling through air (or space). For this reason, radiated interference is much more difficult to mitigate. Thus, EMI due to radiated electromagnetic waves is of greater concern [1].

An electromagnetic wave consists of an electric field (E-field) and a magnetic field (H-field) propagating perpendicular to each other. The wave impedance (\(Z_w\), in ohms) can be defined as the ratio of electric to magnetic fields (E/H). An electromagnetic wave can be categorised in two regions.

1. **Near-field region:** This region occupies the space within \(\lambda/2\pi\) radius from the source. The electromagnetic wave in this region exhibits a spherical wave front and its wave impedance will be characterised by the source. The characteristic impedance of air, \(Z_0\), is approximately \(377 \ \Omega\) [23]. Small wave impedance (H-field dominant, lower than the characteristic impedance of air) would signify that the source is operating at low voltage and high current.
Alternatively, large impedance (E-field dominant, higher than the characteristic impedance of air) would indicate that the source is operating at high voltage and low current.

(2) Far-field region: As distance from the source increases, both H-field and E-field start to attenuate until the electromagnetic wave demonstrates a planar wave front. This region occupies the space outside the $\lambda/2\pi$ radius from the source. The wave impedance is characterised by the property of the medium through which the field is propagating. If the medium is air, then the wave impedance is comparable to the characteristic impedance of air. Figure 2.2 illustrates both the near-field and far-field regions.

It is generally accepted that shielding EMI in a far-field region is more difficult than in a near-field region [24]. Consider an electromagnetic wave travelling in a near-field region. If the wave impedance is E-field dominant ($Z_w > 377 \, \Omega$, refer to Figure 2.3) then a larger amount of electromagnetic energy would be reflected due to greater impedance mismatch. If the wave impedance is H-field dominant ($Z_w < 377 \, \Omega$) and also exhibits a frequency > 100 kHz (modern electronic devices generally operate at frequency > 1 MHz) then the induced eddy currents would cancel out the magnetic field [25].

![Figure 2.3: The wave impedance measures the relative strength of electric and magnetic fields. It is a function of source structure. Reprinted with permission from RFCafe.com [26]](image_url)

### 2.2 Electromagnetic Interference Shielding Theory

Shielding materials with a broad range of electrical conductivity, magnetic permeability and geometries have been used. Ideally, enclosures need to fully envelop the electrical system of interest to minimise leakage of electromagnetic energy. However, for practicality and ease of manufacture, a shielding enclosure usually contains apertures or openings which allow for
easy access and sufficient ventilation [27]. Furthermore, the application of the shielding system level ranges from integrated circuits (IC) to printed circuit boards (PCB) to shielding rooms and even to shielding buildings. Nevertheless, shielding principles will remain unchanged regardless of the size of the enclosure. The shielding principle can be split into two categories: (1) electric field shielding and (2) magnetic field shielding [28].

Electric field shielding is based on the principle of Faraday’s cage. In 1821, Michael Faraday introduced the concept that an electrically conductive enclosure would display a zero electric field. When a conductive enclosure is placed inside an electric field, an electric current is induced within the conducting material such that it opposes and cancels out the electric field which induces it. As a result, the volume inside the enclosure exhibits a zero electric field, as shown in Figure 2.4 [25, 29]

![Figure 2.4: Illustration of Faraday's cage, showing the distribution of electrical changes on conducting enclosure under applied electric field. Redrawn based on original by [29]](image)

In the case of magnetic field shielding, Faraday’s cage is not applicable. Magnetic fields can only be shielded with soft magnetic materials with high permeability ($\mu >> 1$). Materials with high permeability will provide a low reluctance pathway, a more favoured path for a magnetic field to travel on. Therefore, a magnetic field will tend to remain on the surface of the material which will reduce the intensity of the magnetic field present within the enclosure, as illustrated in Figure 2.5 [25].
Unlike electric field shielding, where a zero electric field is present inside a conductive enclosure, magnetic field shielding can only reduce the intensity of the magnetic field inside a high-permeability enclosure. For this reason, shielding a magnetic field is far more difficult than shielding an electric field. However, as the frequency of the electromagnetic radiation increases, magnetic field shielding through the application of conducting material becomes possible. In this situation, the presence of an alternating magnetic field inside a conducting material will induce eddy currents, which generate a secondary magnetic field that opposes the incident magnetic field. As a result, the intensity of the magnetic field present inside the enclosure is reduced, as shown in Figure 2.6. Materials with good conductivity can be used to shield both electric and magnetic fields at high frequencies (frequency > 100 kHz; otherwise, a material with high permeability should be used for magnetic field shielding) [25].
The Federal Communications Commission (FCC) was given the authority to control civilian radio, communications and interference in USA. Electronic devices such as digital computing devices, garage door openers, radio-controlled toys, cordless telephones and other intentional low-power transmitters must comply with FCC regulations. Both Class A equipment (intended for commercial and industrial use) and Class B equipment (intended for residential use) are covered by FCC regulations, with the rules being stricter for Class B equipment. This regulation covers all devices which have timing (clock) pulses higher than 10 kHz. With technology advancing rapidly, equipment having clock frequencies higher than 100 MHz is common. Since the upper frequency of modern electronic devices is approximately ten times the clock frequency, electromagnetic compatibility (EMC) regulations will cover emissions well into the gigahertz range [27]. Furthermore, it is vital to shield EMI in the range of 30 MHz to 1.5 GHz since it can interfere with broadcast communications [31].

2.3 Commercial EMI Shielding Materials

Metals have been used in many applications, such as in electrical equipment and high speed machinery; this is due to their excellent thermal and electrical conductivity. These properties allow metals to dissipate both static and heat build-up within the equipment, which protects them from unnecessary damage. Similarly, a metal enclosure around an EMI emitter or receiver can prevent EMI from damaging the equipment [32].

Various types of metal have been used to create an enclosure for EMI shielding. These include; brass, copper, aluminium, magnesium, silver, nickel, stainless steel and a high permeability alloy composed of 14% iron, 5% copper, 1.5% chromium and 79.5% nickel. These metals have proved to be effective at shielding EMI but they also demonstrate several disadvantages. Silver has the highest conductivity but it is expensive. Copper, the next best, is susceptible to corrosion. Although aluminium and magnesium both exhibit low density, they also possess low conductivity. Therefore, a significant amount of material is required to obtain satisfactory EMI shielding properties, which makes the material more expensive. Furthermore, aluminium is also susceptible to oxidation. Stainless steel and nickel both exhibit good electrical conductivity and corrosion resistance but suffer severe weight penalties as they exhibit high specific gravity [4].
Conventional polymers have relatively low density compared to metals (1.20 g/cm$^3$ for polycarbonate compared to 8.96 g/cm$^3$ for copper). Therefore, the application of plastic for EMI shielding would solve the weight penalty issues caused by metals. However, electromagnetic waves generally pass through conventional polymers without being significantly reflected or absorbed, because these plastics generally exhibit comparable impedance to air, as well as low absorption coefficients. Thus, plastics need to be electrically conductive to facilitate improved shielding of electromagnetic waves. A common solution is to apply a thin and uniform metal coating to the plastic to make conventional plastics electrically conductive (also known as metal-coated plastic). Different coating techniques include [11-13]:

- Ion plating
- Vacuum metallization
- Zinc flame spraying
- Cathode sputtering
- Conductive paints
- Electroless plating/Electroplating

Conductive paints, electroplating and electroless plating are the three most common techniques that are used commercially. Nevertheless, there are several disadvantages to metal-coated plastics. Because this coating technique can only be done after moulding, the process requires special equipment, as well as additional surface preparation, which incurs additional cost [16]. Additional disadvantages for metal-coated plastics include thermal expansion variation between metallic coating and plastic, delamination, corrosion and recycling difficulties [11, 33].

Another type of commercially-available EMI shielding materials are composites made from conventional polymers filled with conductive fillers such as stainless steel fibres (SSF) or nickel-coated graphite fibres (NCGF). Use of these would help to minimise several issues such as delamination and corrosion (which are present in metal-coated plastic) as well as weight penalties (which are present in the usage of bulk metals). Despite the many advantages that conductive composites possess, they are still quite expensive to fabricate [34]. Furthermore, Tan et al [35] have shown that the addition of SSF into a polymer decreases the mechanical properties of the composite. For certain applications, where mechanical
performance is also important, glass fibres are also added to improve the mechanical properties [36] but these are rather heavy and hard to process in conjunction with other fillers.

## 2.4 Electromagnetic Interference Shielding Effectiveness of Materials

Shielding effectiveness (SE) in decibels (dB) is a measure of the reduction of electromagnetic energy at a specific frequency achieved by a shield, such as a coating, which is defined as [23]:

\[
SE = 10 \log \frac{P_0}{P_1} = 20 \log \frac{E_0}{E_1} = 20 \log \frac{H_0}{H_1}
\]  

(2.1)

Where \(P_0, E_0\) and \(H_0\) are the power, the electric and the magnetic field intensities incident on the shield and \(P_1, E_1\) and \(H_1\) are the transmitted power, electric and magnetic field through the shield.

When an electromagnetic wave impinges on shielding material, it is partially reflected, partially absorbed and partially transmitted. This is illustrated in Figure 2.7 [1].

![Figure 2.7: Representation of shielding phenomena for electromagnetic waves passing through a homogeneous barrier. Reprinted with permission from [1]](image)

SE (in dB) can also be defined as [1]:

\[
SE = R + A + B
\]  

(2.2)
Where $R$ is the intensity loss caused by reflection, $A$ and $B$ are those by absorption and multiple reflections respectively.

**Shielding via reflection**

The reflection of EMI is related to the impedance mismatch between the wave impedance and the electrical impedance of the shielding material, as mentioned earlier. Reflection loss can be defined as [3, 37-39]:

$$R = 20 \log(Z_1/4Z_s)$$

(2.3)

Where $R$ is the reflection loss in decibels, $Z_s$ is the impedance of the shielding material and $Z_1$ is the impedance of the electromagnetic wave propagating domain.

The impedance, $Z$, is defined as the ratio of electric ($E$) to magnetic field ($H$).

$$Z = \frac{|E|}{|H|} = \sqrt{\frac{j\omega \mu}{\sigma + j\omega \mu}}$$

(2.4)

For electromagnetic plane waves in space or vacuum $\sigma = 0$ (or approximate for air) therefore:

$$Z_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} = 377 \Omega$$

(2.5)

For conductive materials, $\sigma \gg \omega \varepsilon$, therefore:

$$Z_s = \sqrt{\frac{j\omega \mu}{\sigma}} = \sqrt{\frac{2\pi f \mu}{\sigma}}$$

(2.6)

Substituting equations (2.5) and (2.6) into equation (2.3), reflection loss can be expressed as:

$$R = 39.5 + 10 \log(\sigma/2f\mu\pi)$$

(2.7)

Where $\sigma$ is the electrical conductivity and $\mu$ is the magnetic permeability of the shielding material. According to equation (2.7), reflection loss increases as the ratio of $\sigma/\mu$ increases. Additionally, reflection loss decreases with increasing frequency.

**Shielding via absorption**

Unreflected electromagnetic energy would be either partially or totally absorbed by the shielding material. The amount of electromagnetic energy absorbed relates to the absorption coefficient and the thickness of the shielding material. This can be defined as [38, 40]:
Where $A$ is the absorption or penetration loss expressed in decibels, $t$ is the thickness of the shielding material and $\alpha$ is the absorption coefficient. The latter can also be expressed in terms of skin depth, which is defined as [23, 24]:

$$\delta = \frac{1}{\alpha} = \frac{1}{\sqrt{\mu \pi f \sigma}} \quad (2.9)$$

Skin depth, $\delta$ is defined as the distance from the surface of the shielding material at which the electric or magnetic field intensities attenuate to 37% of the original intensities, as shown in Figure 2.6. With $f$ being the frequency in MHz; $\mu$ the relative permeability (1 for copper); $\sigma$ the conductivity relative to copper in the International Annealed Copper Standard (IACS), combining equation (2.8) and (2.9), the amount of energy absorbed by a shield can be simplified to:

$$A = 20 \left(\frac{t}{\delta}\right) \log (e) = 8.69 \left(\frac{t}{\delta}\right) = 131 \ t \sqrt{\frac{f \sigma}{\mu}} \quad (2.10)$$

According to equation (2.10), the absorption loss increases as the thickness and the product $\sigma \mu$ increases. Additionally, absorption loss increases with increasing frequency. A shield with a thickness of one skin depth would exhibit an absorption loss of 8.69 dB.

**Shielding via multiple reflection**

Multiple reflections, $B$ can be positive or negative depending on whether the re-reflected term (refer to Figure 2.6) causes constructive or destructive interference. This term becomes negligible when the shield exhibits a thickness of one skin depth. $B$ can be expressed as [41]:

$$B(dB) = 20 \log \left| 1 - \frac{(K-1)^2}{(K+1)^2} \left(10^{-\frac{A}{10}}(e^{-i2\pi f})\right) \right| \quad (2.11)$$

Where $A$ is the absorption loss ($dB$); $K = Z_s/Z_H = 1.3(\mu/\mu_0)^{1/2}$; $Z_s$ is the shield impedance; and $Z_H$ is the impedance of the incident magnetic field. When $Z_H \ll Z_S$, multiple reflection factors for magnetic fields in a shield with a thickness, $t$, and skin depth, $\delta$, can be simplified as:

$$B = 20 \log(1 - e^{-2t/\delta}) \quad (2.12)$$

Therefore, designing a shield based on absorption properties of the materials as well as using a minimum thickness of one skin depth (greater than 8.7 dB) would allow the multiple
reflections factor (B) to be insignificant to shielding effectiveness calculations. As a result, equation (2.2) can be reduced to:

\[
SE = R + A
\]

(2.13)

2.5 Required Material Properties

Shielding mechanism of electrical conductors

For materials which exhibit excellent electrical conductivity, such as copper, nickel, aluminium, silver and gold, reflection is the primary shielding mechanism [42]. Reflection of the electromagnetic wave is achievable through the impedance mismatch between the impedance of electromagnetic wave and the electrical impedance of shielding material. Electrical impedance of materials is similar to the resistance of a material in an electrical circuit. The only difference is that impedance is applicable for alternating current, whereas resistance is applicable for direct current. Similar to resistance, the impedance of materials decreases as electrical conductivity increases. Therefore, excellent electrical conductors will demonstrate low electrical impedance (in the vicinity of milliohms to a few ohms) [3, 37-39].

Consider an electromagnetic wave propagating in far-field region in air, the wave impedance would be approximately 377 Ω. By comparing this value to an electrical impedance of a few milliohms for these conductors, the large difference between impedance would cause most of the electromagnetic energy to be reflected from the surface of the conductor. Unreflected electromagnetic energy would be absorbed by the conductor and dissipate as heat; this process is also known as joule heating [3, 37-39]. Therefore, for material with excellent electrical conductivity, reflection is the primary shielding mechanism.

Shielding mechanism of electrical insulators

For materials which possess poor electric conductivity, such as paper, plastic, Teflon, glass, ceramic and dry wood, absorption is the primary shielding mechanism. Since electrical impedance is inversely proportional to conductivity, dielectric materials would exhibit high electrical impedance (a value which is close to that of air, since air is a dielectric). This indicates that only a small amount of electromagnetic energy would be reflected; the rest would be transmitted into the material [42].

Normally, transmitted electromagnetic energy would pass through a dielectric without being significantly attenuated. This is because dielectric materials usually demonstrate a low
absorption coefficient [42]. Further, any electromagnetic energy absorbed by dielectric materials will be dissipated as heat, as is similar in the case of metals; the process is known as dielectric heating. In an alternating electric field, polar molecules present in dielectric materials would rotate continuously to align themselves in the direction of the applied field. This movement results in collisions between molecules which generates heat. Dielectric materials without polar molecules are transparent to EMI [43, 44].

Since dielectric materials are not effective EMI shielding materials, conductive fillers such as metals can be added to a dielectric material to improve its electrical conductivity, making them more effective at shielding EMI. The primary shielding mechanism of these composites is absorption because they cannot attain the same value of conductivity as that of metals. This is the preferred shielding mechanism as EMI is absorbed by the shielding material and dissipated as heat so they are not being redirected back into the environment where people and/or other electronic devices could be affected. Figure 2.8 illustrates the application ranges of different material based on their surface resistivity.

![Figure 2.8: “Surface Resistivity,” RTP Company technical brochure 2009-01-14, Surface Resistivity illustration provided as a courtesy by RTP Company [45]](image)

**Designing a shielding material**

The shielding capability of a material based on reflection and absorption can be described in terms of electrical conductivity and relative permeability. Table 2.1 illustrates these values as well as the electrical conductivity relative to copper and the relative permeability of selected materials.
Table 2.1: Electrical conductivity relative to copper and relative permeability of selected materials. Modified from [37]

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity Relative to Copper</th>
<th>Relative Permeability</th>
<th>$\sigma\mu$ (Absorption)</th>
<th>$\sigma/\mu$ (Reflection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>1.05</td>
<td>1</td>
<td>1.05</td>
<td>1</td>
</tr>
<tr>
<td>Copper</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Gold</td>
<td>0.7</td>
<td>1</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.61</td>
<td>1</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>Brass</td>
<td>0.26</td>
<td>1</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Bronze</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Tin</td>
<td>0.15</td>
<td>1</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Lead</td>
<td>0.08</td>
<td>1</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.2</td>
<td>100</td>
<td>20</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Stainless Steel (430)</td>
<td>0.02</td>
<td>500</td>
<td>10</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Mumetal (at 1kHz)</td>
<td>0.03</td>
<td>20000</td>
<td>600</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Superpermalloy (at 1 kHz)</td>
<td>0.03</td>
<td>100000</td>
<td>3000</td>
<td>$3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Both conductivity and permeability are intrinsic properties of a material, whilst thickness is an extrinsic property. Hence, for the purpose of increasing the absorption loss, it is usually easier to increase the thickness of the shielding material than its conductivity or permeability. However, a thicker material is also more expensive or could be too bulky. Therefore, a good absorbent material for shielding purposes should have high conductivity, high permeability, and sufficient thickness to achieve the required number of skin depths at the lowest frequency of concern (five skin depths correspond to 99% absorption). According to equation (2.10), skin depth decreases with increasing conductivity, permeability and frequency [23]. Table 2.2 shows the skin depth of some common materials.

Table 2.2: Skin depth of common materials calculated at 30 MHz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency (MHz)</th>
<th>Conductivity (S/m)</th>
<th>Relative Permeability</th>
<th>Skin Depth (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>30</td>
<td>$5.8 \times 10^7$</td>
<td>1</td>
<td>3.82</td>
</tr>
<tr>
<td>Silver</td>
<td>30</td>
<td>$6.3 \times 10^7$</td>
<td>1</td>
<td>3.66</td>
</tr>
<tr>
<td>Nickel</td>
<td>30</td>
<td>$1.15 \times 10^7$</td>
<td>100</td>
<td>0.86</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>30</td>
<td>$9.8 \times 10^7$</td>
<td>500</td>
<td>1.31</td>
</tr>
<tr>
<td>Electrical Steel</td>
<td>30</td>
<td>$2.12 \times 10^6$</td>
<td>4000</td>
<td>0.32</td>
</tr>
<tr>
<td>Permalloy</td>
<td>30</td>
<td>$1.69 \times 10^7$</td>
<td>50000</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Small skin depth is highly favourable due to the fact that a smaller amount of material would be required to provide sufficient absorption. (As mentioned earlier, five skin depths for 99% absorption.) Equation (2.10) suggests that materials with high magnetic permeability like
electrical steel, permalloy and mumetal would exhibit very small skin depth. However, these values of permeability are generally given as direct current (DC) permeability. The material’s permeability decreases as frequency increases. At 100 kHz, the permeability of mumetal is similar to that of cold-rolled steel, although the DC permeability of mumetal is 13 times that of cold-rolled steel. Therefore, high permeability materials are more useful for magnetic field shielding when the frequency <10 kHz [46]. Based on Table 2.1 and Table 2.2, stainless steel and nickel are the most suitable materials for EMI shielding due to their high absorption properties ($\sigma \mu$ value) and small skin depth.

### 2.6 Polymers for EMI Shielding

Intrinsically conductive polymers (ICPs) refer to conventional polymers which exhibit electrical, magnetic and optical properties similar to metals. However, ICPs can also demonstrate mechanical properties, processability and density comparable to conventional polymers [47]. Polyacetylene (PA) was the first ICP to be synthesised by Shirakawa in 1977 [48]. Since then, polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH) and poly(p-phenylene-vinylene) (PPV) have been successfully synthesised [49]. In addition to the fact that ICPs exhibit low specific gravity, the electrical conductivity of ICPs can be tuned based on the synthesis pathway. The major disadvantage associated with ICPs is the insolubility of common organic solvents. This makes processing of ICPs problematic. Therefore, extensive research has been done to improve the solubility of ICP via the process known as doping [50]. Many potential applications for ICPs include electrochromic display [51], corrosion protection [52], electrostatic discharge (ESD) [5] and EMI shielding. In general, for conducting plastics, a volume resistivity of 1 $\Omega$.cm, which corresponds to a shielding effectiveness of 35 dB, is considered to be the minimum performance, as shown in Figure 2.9. When volume resistivity exceeds 100 $\Omega$.cm, the materials will cease to function as effective EMI shielding materials. Nonetheless, these materials can still be used in the application of electrostatic discharge (as seen in Figure 2.8: the static dissipative region is where the electrical conductivity requirement of a material is not as high as the EMI shielding region) [5, 11]. For EMI shielding applications, PANI and PPY have been comprehensively studied [53].
One of the first methods used to create an EMI shielding material based on PANI was grafting conductive PANI onto glass fabric, glass wool and nylon cloth to improve the mechanical strength and flexibility of PANI, which is otherwise unprocessable. There are several advantages of using these conductive flexible surfaces instead of metal-filled polymer. Firstly, PANI surfaces have better corrosion resistance and there is no problem with uneven mixing or filler/polymer incompatibility, which is problematic for a metal-filled polymer. Secondly, PANI-grafted surfaces demonstrate no degradation under any level of acidic fume, or high levels of humidity. Table 2.3 demonstrates the shielding effectiveness of PANI-grafted glass fibres [54-56].

**Table 2.3:** EMI shielding effectiveness Studies on PANI – PTSA/CMC and PAn– CSA/CMC Reinforced conducting E-Glass Fabric. Reprinted with permission from [16]

<table>
<thead>
<tr>
<th>Sample (EMI SE observed in dB)</th>
<th>Conductivity (S/cm)</th>
<th>Frequency in MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>PAn–PTSA/CMC reinforced</td>
<td>0.2</td>
<td>22</td>
</tr>
<tr>
<td>conductive E-glass fabric (t = 0.15 mm)</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>PAn–PTSA/CMC reinforced</td>
<td>0.8</td>
<td>39</td>
</tr>
<tr>
<td>conductive E-glass fabric (t = 3 mm)</td>
<td>0.04</td>
<td>18</td>
</tr>
<tr>
<td>PAn–CSA/CMC reinforced</td>
<td>0.1</td>
<td>22</td>
</tr>
<tr>
<td>conductive E-glass fabric (t = 1.4 mm)</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>PAn–CSA/CMC reinforced</td>
<td>0.4</td>
<td>23</td>
</tr>
<tr>
<td>conductive E-glass fabric (t = 3 mm)</td>
<td>0.3</td>
<td>20</td>
</tr>
</tbody>
</table>

$t = $ thickness.

Another method of creating an EMI shielding material is to form a PANI composite. Table 2.4 illustrates shielding effectiveness values for various types of filler materials dispersed in different polymer matrices [52, 57-61].
Although shielding effectiveness values are reasonable for EMI shielding applications (> 35 dB), commercialization of these composites is not viable due to poor processing properties. Moreover, PANI loading is still considerably high (20 - 25 wt%) for practical applications [53].

Similar to PANI, PPY-grafted fabrics and PPY composites have been investigated. Table 2.5 illustrates EMI shielding effectiveness values of PPY-grafted fabric [62].

Table 2.5: EMI shielding effectiveness of various PPY/fabric complexes at 1 GHz. Reprinted with permission from [16]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shielding Effectiveness SE (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY-AQSA/PET</td>
<td>~22</td>
</tr>
<tr>
<td>Ag/PE/Ag</td>
<td>~55</td>
</tr>
<tr>
<td>Ag/PPY-AQSA/Ag Pd/PE/Ag</td>
<td>~80</td>
</tr>
</tbody>
</table>

It can be seen from Table 2.5 that the usage of silver and palladium significantly improves the shielding effectiveness of PPY-grafted fabric. However, the usage of precious metals increases the cost of shielding materials, therefore limiting their field of applications. A shielding effectiveness of 80 dB is suitable for military purposes.

Alternatively, for PPY composites, results have shown that a weight fraction of 25% PPY is needed to obtain a shielding effectiveness value of 30 dB. (This value is similar to those of PANI composites.) Table 2.6 illustrated EMI shielding effectiveness values of PPY composites [62-66].
Table 2.6: EMI shielding effectiveness results of PPY composites. Reprinted with permission from [16]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Frequency range</th>
<th>Shielding effectiveness (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy or poly (3,4-ethylene dioxythiophene) PEDOT fabric complexes</td>
<td>1.5 GHz</td>
<td>36</td>
</tr>
<tr>
<td>PPy based intrinsically hot melt adhesives</td>
<td>300 MHz</td>
<td>30</td>
</tr>
<tr>
<td>PPy/p-toluenesulfonate complexes</td>
<td>300 MHz–2 GHz</td>
<td>&gt;40</td>
</tr>
<tr>
<td>PPy impregnated conducting polymer composites</td>
<td>1–2 GHz</td>
<td>26</td>
</tr>
<tr>
<td>PPy impregnated microporous polyethylene tars</td>
<td>10 KHz–1GHz</td>
<td>40–50</td>
</tr>
</tbody>
</table>

Therefore, it can be concluded that, both PANI and PPY are not suitable for EMI shielding application because a considerably high filler loading (25 wt%) is required. Additionally, poor processing properties pose a significant barrier to commercialisation.

### 2.7 Common Fillers for Composites

Electrical conductivity is essential for EMI shielding as both the reflection and absorption of electromagnetic radiation are directly proportional to electrical conductivity (Equations 2.7 and 2.10 respectively). Moreover, as the EMI shielding range of interest is between 300 MHz – 1.5 GHz (higher than 100 kHz), materials with good electrical conductivity can shield both electrical and magnetic fields (as shown in Figures 2.4 and 2.6). However, it is important to note that absorption is the preferred mechanism for EMI shielding. This is because absorbed EMI is dissipated as heat [3, 37-39] and is not reflected back into the environment where it could affect people as well as other electronic devices. Therefore, compounding electrically conductive fillers with conventional polymers is the system of interest as it produces conductive composites which favour EMI shielding by absorption. This is because the impedance of electrically conductive composites is much closer (since they have lower electrical conductivity than pure metal) to the impedance of electromagnetic radiation propagating in air (377 Ω, far-field shielding is considered as it is harder to shield than near-field EMI). This means that there is less impedance mismatch and therefore, less reflected EMI. There are many potential filler materials available, most of which are based on carbon and/or metals.
Carbon

Many forms of carbon material are available as filler material, these include; carbon black, carbon fibres, vapour-grown carbon nanofibres, multi-walled carbon nanotubes and single walled carbon nanotubes [67].

Carbon black was one of the first materials to be used as a filler for conventional polymers. It is also the cheapest form of carbon material ($2/lb) [68]. Carbon black also possesses the lowest conductivity compared to other forms of carbon. For this reason, the low conductivity of a carbon black-filled composite makes it inadequate for EMI shielding purposes. Thus, it is only applicable in the field of ESD [69]. Additionally, sloughing is a major concern with regard to the application of Carbon black powders as it can damage packaged electronics as well as the environment [53, 70].

In order to resolve these problems, other forms of carbon, such as those already listed, were investigated. In 2007, the prices of vapour-grown carbon nanofibres, multi-walled carbon nanotubes, and 90% pure single-walled carbon nanotubes were $125/lb, $350/lb and $30,000/lb [71] respectively, compared to $15/lb for pitch carbon fibre and less than $2/lb for carbon-black powder [68, 71]. Properties of these materials are illustrated in Table 2.7.

<table>
<thead>
<tr>
<th>Property</th>
<th>Vapour Grown Nanofibres</th>
<th>Single-Walled Carbon Nanotube</th>
<th>Multi-Walled Carbon Nanotube</th>
<th>Carbon Fibres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>50-200</td>
<td>0.6-1.8</td>
<td>5-50</td>
<td>7300</td>
</tr>
<tr>
<td>Length (μm)</td>
<td>50-100</td>
<td>-</td>
<td>-</td>
<td>3200</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>250-2000</td>
<td>100-10000</td>
<td>100-10000</td>
<td>440</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2</td>
<td>-1.3</td>
<td>-1.75</td>
<td>1.74</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>1950</td>
<td>3000-6000</td>
<td>3000-6000</td>
<td>-</td>
</tr>
<tr>
<td>Electrical resistivity (Ω/m K)</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-3}$-$1 \times 10^{-4}$</td>
<td>$2 \times 10^{-3}$-$1 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Tensile Strength (GPa)</td>
<td>2.92</td>
<td>50-500</td>
<td>10-60</td>
<td>3.8</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>240</td>
<td>1500</td>
<td>1000</td>
<td>227</td>
</tr>
<tr>
<td>Reference</td>
<td>[72]</td>
<td>[73] [74] [75] [76]</td>
<td>[73] [77] [75] [76]</td>
<td>[78]</td>
</tr>
</tbody>
</table>

Several trends can be observed from Table 2.7. Generally, as the cost of a material increases, desirable properties for EMI shielding, such as electrical conductivity and aspect ratio,
increase as well. However, due to the expensive nature of these products, achieving a lowest possible percolation threshold while still maintaining a minimum level of shielding effectiveness is essential to facilitate commercial feasibility. A significant amount of research has been done to investigate the problem [67].

Lin and Chung [79] investigated the shielding effectiveness of carbon fibre/polyethersulfone composite. They reported a shielding effectiveness value of 44 dB when the filler concentration was 20 wt%. Yang examined the shielding effectiveness of grown carbon nanofibres/polystyrene composite. Yang reported a shielding effectiveness value of 36 dB when filler concentration was 20 wt%. Yang also reported that, for 7 wt% multi-walled carbon nanotubes-filled polystyrene, a shielding effectiveness value of 26 dB was obtained [80]. Li et al studied the shielding effectiveness of single-walled carbon nanotubes/epoxy composite. They reported a shielding effectiveness value of 20 dB when filler concentration was 15 wt% [81]. In most cases, adequate shielding effectiveness was obtained. However, commercialisation of carbon-based composites is not possible unless the percolation threshold can be further reduced in order to improve mechanical properties.

Metals

Metals (both the particle and fibrous forms) are also common fillers for EMI shielding. These include aluminium, copper, silver, nickel and stainless steel. The advantage of using aluminium is due to its low specific gravity. Copper offers the highest intrinsic electrical conductivity. However, both metals are subject to surface oxidation under normal environmental conditions. Osawa and Kobayashi [18] conducted an experiment to investigate the relationship between shielding effectiveness and the oxidation characteristic of polyethylene filled with different metal fibres, such as aluminium, copper, steel and brass. These composites were heated in an electric oven at 80 °C in air and shielding effectiveness was measured. The researchers reported that there is a slight reduction in shielding effectiveness for carbon, brass and steel systems. In contrast, composites containing copper and aluminium demonstrated a significant reduction in shielding effectiveness. When heated in a vacuum oven, also at 80 °C, those composites demonstrated a smaller decrease in electrical conductivity. It was concluded that oxygen and water had a significant effect on the reduction in electrical conductivity, which ultimately leads to a reduction in shielding effectiveness.
Dixon and Masi [82] also reported that aluminium oxidised rapidly during the moulding process. The formation of an insulating oxide layer degrades both electrical and mechanical properties of the composite. It was reported that, for these composites, electrical conductivity and tensile strength was reduced by three orders of magnitude in addition to a 30% reduction of tensile strength compared to un-oxidised aluminium fibres.

However, despite having poor oxidation resistance, a polymer composite filled with aluminium flakes was able to attain the minimum EMI shielding standard. Wehrenberg [34] reported that, in order to achieve a shielding effectiveness of 40 dB using different fillers, the cost increases in the following sequence: aluminium flake, stainless steel fibre, carbon fibre, nickel-coated graphite. The increase in cost is, aluminium flake at approximately $1/lb compared to $40/lb for nickel-coated graphite. For aluminium flake, a 40 wt% loading is necessary for a shielding performance of 40 dB. High filler loading reduces flexural strength of the composite.

Precious metal powders such as silver, gold and platinum have been used as fillers for EMI shielding purposes. However, the field of applications for composites filled with precious metals is strictly limited due to the high cost of the metals [16, 17].

Nickel-coated graphite fibre is a commercially-available EMI shielding filler which possesses the reinforcing properties of graphite fibre, as well as the electrical conductivity of both nickel coating and graphite fibres. For commercial products, typically 6-15 wt% loading is required [7] to acquire a shielding effectiveness of 35 – 40 dB. However, fibres with a higher aspect ratio (100-300) can reduce the amount of filler required to the range of 5-10 wt%. Technically, any electroplatable metals can be coated onto graphite fibre, but nickel is highly favoured due to its excellent corrosion resistance, electrical and thermal conductivity, in addition to being relatively cheap. Although nickel-coated graphite is more expensive than stainless steel, nickel-coated graphite composites have been commercialised, mainly due to the fact that a thin nickel coating (in the vicinity of a few microns or less) can be obtained through electro-deposition. Since such a small thickness cannot be obtained with stainless steel fibres, nickel-coated graphite becomes more applicable than stainless steel at higher frequency (GHz range) where skin depth is less than one micron. Table 2.8 illustrates the shielding effectiveness of nickel-coated graphite composite [17, 83-87].
Stainless steel fibres (SSF) are also commercially-available EMI shielding filler. SSF exhibit an exceptional property of being able to ‘bend rather than break’ under shear stress. For this reason, SSF maintains its high aspect ratio inside the composite. For commercial products, 6-12 wt% loading is typically required [7] to acquire a shielding effectiveness of 35 – 40 dB. Nonetheless, problems can occur during the processing of a stainless steel composite due to the highly abrasive nature of stainless steel, which affects the moulds and screws of the machine. This problem does not usually occur for copper and aluminium. Despite its disadvantage, low loading of SSF provides several advantages, such as good colourability and good mechanical properties, as well as being more cost-effective than other filler materials; thus making SSF composite commercially feasible. Table 2.9 illustrates the shielding effectiveness of SSF composite based on different polymers [17, 88, 89].

Table 2.9: Stainless steel fibre filled thermoplastic for resin type-7% stainless steel fibre. Modified from [90]

<table>
<thead>
<tr>
<th>Property</th>
<th>ABS</th>
<th>PA 6.6</th>
<th>PC</th>
<th>PPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shielding effectiveness (at 950 MHz)</td>
<td>42</td>
<td>40</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>Volume resistivity (W cm)</td>
<td>0.4</td>
<td>0.9</td>
<td>1.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2.8: EMI shielding effectiveness value of nickel-coated carbon fibre composite. Reprinted with permission from [16]
Chapter 3

Factors Affecting the Properties of EMI Shielding Composites

In order to be able to optimise their properties, it is very important to understand how various factors affect the properties of EMI shielding composites. Composite filled with conductive fillers becomes electrically conductive once certain amounts of filler have been added. This is also known as the percolation threshold. The percolation threshold of the composite can be affected by its processing technique, quantum mechanical tunnelling and thermal expansion; these, in turn affect the cost of fabricating the composite as well as the mechanical properties of the composite.

3.1 Percolation Theory and Modelling

Percolation theory was first introduced by Broadbent and Hammersley [91] in 1957. They used a statistical and geometrical approach to solve the problem of fluid flow through a static random medium. They initially focused on determining the percolation threshold for two and three dimensional geometries by considering two types of percolation:

1) Site percolation - sites in lattice are either filled or empty,
2) Bond percolation - all the sites in a lattice are occupied, but are either connected or not.
Table 3.1 illustrates the calculated values of the percolation threshold for different lattices [92].

**Table 3.1: Probability of cluster formation in two and three dimensional lattices. Permission to reprint obtained from the author. Modified from [93]**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Lattice</th>
<th>Site Percolation Threshold</th>
<th>Bond Percolation Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Honeycomb</td>
<td>0.6962</td>
<td>0.65271</td>
</tr>
<tr>
<td>2</td>
<td>Square</td>
<td>0.59275</td>
<td>0.50000</td>
</tr>
<tr>
<td>2</td>
<td>Triangular</td>
<td>0.50000</td>
<td>0.34729</td>
</tr>
<tr>
<td>3</td>
<td>Simple Cubic</td>
<td>0.3117</td>
<td>0.2492</td>
</tr>
<tr>
<td>3</td>
<td>Body-Centered Cubic</td>
<td>0.2450</td>
<td>0.1785</td>
</tr>
<tr>
<td>3</td>
<td>Face-Centered Cubic</td>
<td>0.1980</td>
<td>0.1190</td>
</tr>
</tbody>
</table>

The concept of percolation has been applied to many diverse applications such as [94, 95]:

1) Quarks in nuclear matter,
2) Spread of disease in a population,
3) Variable range hopping in amorphous semiconductors flow through a porous medium,
4) Behaviour in mixtures of conductive and non-conductive components.

For mixtures of conductive and non-conductive components, the point at which the material changes from an insulator to a conductor is called the percolation threshold. This can be described using the following equation:

$$\sigma_c = \sigma_0(\varphi_f - \varphi_{crit})^t$$  \hspace{1cm} (3.1)

where \(\sigma_c = \) composite conductivity (S/cm), \(\sigma_0 = \) conductivity of conductive reinforcement (S/cm), \(\varphi_f = \) volume fraction of reinforcement, \(\varphi_{crit} = \) percolation threshold and \(t\) is the critical exponent.

This equation is only valid when \(\varphi_f > \varphi_{crit}\). The lattice dimension determines the value of \(t\) (critical exponent).
Table 3.2 summarises the calculated values of the critical exponent ($t$) in both two and three dimensions for model systems of conductive spherical particles in an insulating matrix.

**Table 3.2: Calculated values of critical exponent in two and three dimensions. Permission to reprint obtained from the author. Modified from [93]**

<table>
<thead>
<tr>
<th>Reference</th>
<th>$t$ (2-D)</th>
<th>$t$ (3-D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katsura et al. [96]</td>
<td>1.1</td>
<td>1.725</td>
</tr>
<tr>
<td>Stauffer [92]</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Kirkpatrick [95]</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Redner and Stanley [97]</td>
<td>-</td>
<td>1.75</td>
</tr>
<tr>
<td>Straley [98]</td>
<td>1.1</td>
<td>1.70</td>
</tr>
<tr>
<td>De Gennes [99]</td>
<td>-</td>
<td>1.833</td>
</tr>
<tr>
<td>Lobb &amp; Frank [100]</td>
<td>1.35</td>
<td>-</td>
</tr>
<tr>
<td>Ueda &amp; Taya [101]</td>
<td>1.35</td>
<td>-</td>
</tr>
<tr>
<td>Adler et al. [102]</td>
<td>-</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The researchers used equation 3.1 to fit the experiment data to determine the percolation threshold and critical exponent for the purpose of comparison to model prediction in Table 3.3. This illustrates the percolation threshold and critical exponent for different types of composite system. For composites filled with particles, such as those reinforced with silver particles, carbon black, and YBa$_2$Cu$_3$O$_7$, the critical exponent has a value between 1.5 to 2.0, which is in agreement with the calculated values for three-dimensional systems. For composite filled with fibres, the critical exponent is higher because the aspect ratios of fibres are higher than those of particles. Carbon fibre has the highest value of critical exponent of 3.1 due to its high aspect ratio. The stainless steel fibres have the second-highest critical exponent of 2.4.

Generally, percolation theory describes how a number of particles or fibres can be interconnected when they are either randomly or regularly distributed within a matrix. A cluster is formed when particles or fibres are connected in a given space within a matrix. When these clusters span the entire matrix, the composite will have reached the percolation threshold. In a system consisting of conductive particles dispersed in an insulating matrix, there are three distinct regions [103-105].
Table 3.3: Experimental values of percolation theory variables. Permission to reprint obtained from the author. Modified from [93]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reinforcement</th>
<th>Resin</th>
<th>Critical concentration (%)</th>
<th>Critical exponent, t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katsura et al. [96]</td>
<td>Stainless steel fibres</td>
<td>PP</td>
<td>3.2</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP/maleated</td>
<td>5.93</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP wax</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deutscher &amp; Rappaport [106]</td>
<td>Aluminium particles</td>
<td>Germanium</td>
<td>23</td>
<td>1.7</td>
</tr>
<tr>
<td>Carmona et al. [107]</td>
<td>Carbon black</td>
<td>Epoxy</td>
<td>16.5</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Carbon Fibres</td>
<td>Epoxy</td>
<td>4.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Balberg &amp; Bozowski [108]</td>
<td>Carbon black</td>
<td>PVC</td>
<td>9.2*</td>
<td>2.00</td>
</tr>
<tr>
<td>Paulose et al. [109]</td>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>Ba$_2$YSbO$_6$</td>
<td>30</td>
<td>1.80</td>
</tr>
<tr>
<td>Sun et al. [110]</td>
<td>Stainless steel fibres</td>
<td>LDPE</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Thomas et al. [111]</td>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>YBa$<em>2$HfO$</em>{5.5}$</td>
<td>23</td>
<td>1.7</td>
</tr>
</tbody>
</table>

PP = Polypropylene, PYC = Polyvinyl chloride, PET = Polyester, PC = Polycarbonate, LDPE = Low density polyethylene. Critical concentrations are expressed as volume percent unless denoted by * where it is in weight percent.

Region 1 – low filler concentration: At low filler concentration, there is not enough physical connection between conducting particles to make the composite electrically conductive. As a result, a composite in this region can act as an insulator.

Region 2 – percolation threshold: When the concentration of conductive fillers reaches a point where there is sufficient physical connection between conductive particles throughout the entire system, the composite will demonstrate a sudden reduction in resistivity. This point is known as the percolation threshold, where composites become electrically conductive.

Region 3 – high filler concentration: Further increase in filler concentration beyond the percolation threshold does not significantly decrease the resistivity of the composite [103-105].

These three regions are illustrated in Figure 3.1.
It is important to minimise the mass of filler required to reach the percolation threshold for two reasons: cost and mechanical properties. As filler content increases, the composite would become more expensive, heavier and exhibit reduced flexural strength. Furthermore, research has shown that reducing the percolation threshold increases the maximum electrical conductivity of the composite Taipalus [60], Tsotra [61], Sohi et al. [62], Iosif [65] Carter [40] and Clingerman [47].

There are three factors which influence the percolation threshold of a composite. These factors are filler aspect ratio, filler orientation and filler distribution [88].

In this study, it is desirable to minimise filler loading for cost reduction and improved mechanical properties. Filler aspect ratio, or length-to-width ratio, is considered to be the most important factor in reducing the percolation threshold. Fillers with a high aspect ratio have a better chance of connecting with other fillers. Therefore, the percolation threshold decreases with increasing filler aspect ratio. The relationship between the fibre aspect ratio and the filler content required to attain the percolation threshold is illustrated in Figure 3.2.

Figure 3.1: Schematic sketch of the resistivity of a composite as a function of filler concentration for isotropic particles (full line) and carbon black (dashed line) concentration. Reprinted with permission from [112]
Jana [114] demonstrated the effect of aspect ratio on EMI shielding effectiveness. For carbon fibre-filled polychloroprene composites, it was shown that an increase in fibre aspect ratio from 25 to 100 corresponded to an increase in EMI shielding effectiveness from 10 to 50 dB at an interference signal of 8 GHz for composite samples with a thickness of 3.5 mm and a filler loading of 10 wt%. Additionally, it was also determined that by increasing fibre aspect ratio, shielding effectiveness due to reflection decreased but shielding effectiveness due to absorption significantly increased. Hence, the overall shielding effectiveness of the composite increases as the aspect ratio increases.

Filler orientation can also influence the percolation threshold of the composite. It is important that fillers are oriented in such a way that maximises number of contact points since percolation relies on physical contact. Kortschot and Woodham [115] reported that a composite with random distributed filler demonstrated a lower percolation threshold, as well as a higher EMI SE, compared to a composite containing aligned filler.

Filler dispersion is very important for a metal-filled composite because a poorly dispersed composite allows electromagnetic waves to pass through without being significantly attenuated. As a result, the shielding effectiveness of the composite is drastically reduced. Several techniques were used to achieve good filler dispersion, such as using a dispersion agent or applying sonication. This was demonstrated by Ward [60] for example, who showed
that the loading could be reduced by a factor of four when a dispersion agent was added to a
stainless steel composite while maintaining the same level of EMI SE [88].

Fibre waviness is another factor which affects the percolation threshold of the composite. Xoan et al. [116] reported that the percolation threshold increases as the waviness ratio increases. Waviness ratio is defined as the ratio between the wave amplitude (a) and the effective length (Leff), as shown in Figure 3.3. This means that the waviness ratio increases as fibres become more curved. Xoan also reported that, when the aspect ratio is low, increasing waviness ratios have a more significant effect on the percolation threshold. As the aspect ratio becomes higher, increasing waviness ratios have less impact on the percolation threshold.

![Figure 3.3: Geometry of curved fibre. Reprinted from [116] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.](image)

Monte Carlo simulation is a modelling technique which can be used to calculate the amount of filler require to achieve the percolation threshold [101, 115, 117-120]. The modelling logic is outlined below:

1) A grid of either two or three dimensions is defined and sites are randomly distributed on the grid by a random number generator.
2) The system then places fillers (circle and spheres for particulate fillers or line segments for fibrous filler) with a given length and orientation at a portion of the sites.
3) The system is checked for connectivity between the particles. If two particles contact each other then they are designated as a cluster. If a cluster spans the sample, the system is said to percolate. Otherwise, additional particles are added to the grid sites and connectivity is checked again.
4) This procedure continues until a cluster is formed which spans the grid. The area or volume fraction of fibres is then calculated and reported as the percolation threshold.
Pike and Seager [117] applied the Monte Carlo simulation to obtain the percolation threshold for the randomly oriented circles and squares in a two dimensional matrix. Kortschol and Woodhams [115] applied the Pike and Seager model to a two-dimensional network of rectangular particles. Table 3.4 illustrates the model predictions for percolation threshold of a two-dimensional system. For circles, increasing the surface area reduces the percolation threshold, whereas, changing the size does not have a significant impact. The percolation threshold is lower for rectangles than for circles. The higher the aspect ratio, the lower the percolation threshold. Furthermore, randomly oriented rectangles exhibit a lower percolation threshold than oriented rectangle units. This is because inducing alignment reduces the probability of fibre-fibre contact, which increases the threshold. The percolation threshold is highest when the fibres are aligned in the direction of flow.

Balberg and Binenbaum [118] extended the work of Pike and Seager to the case of conductive sticks. They used the Monte Carlo simulation to determine the minimum length of the conductive sticks (with same diameter) required to achieve the percolation threshold in both longitudinal and transverse directions.

Table 3.4: Predictions from two dimensional Monte Carlo simulation (values are reported as critical area fraction). Permission to reprint obtained from the author. Modified from [93]

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Orientation</th>
<th>Pike &amp; Seager [117]</th>
<th>Kortshot &amp; Woodhams [115]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform-size circles</td>
<td>-</td>
<td>0.680</td>
<td>0.682</td>
</tr>
<tr>
<td>Variable-size circles</td>
<td>-</td>
<td>0.682</td>
<td>0.681</td>
</tr>
<tr>
<td>Uniform-size squares</td>
<td>-</td>
<td>0.668</td>
<td>-</td>
</tr>
<tr>
<td>Rectangles (L/D = 5)</td>
<td>-(\pi/2 &lt; \theta &lt; \pi/2) (Random)</td>
<td>-</td>
<td>0.459</td>
</tr>
<tr>
<td>Rectangles (L/D = 10)</td>
<td>-(\pi/2 &lt; \theta &lt; \pi/2) (Random)</td>
<td>-</td>
<td>0.333</td>
</tr>
<tr>
<td>Rectangles (L/D = 20)</td>
<td>-(\pi/2 &lt; \theta &lt; \pi/2) (Random)</td>
<td>-</td>
<td>0.211</td>
</tr>
<tr>
<td>Rectangles (L/D = 20)</td>
<td>-(\pi/8 &lt; \theta &lt; \pi/8)</td>
<td>-</td>
<td>0.276</td>
</tr>
<tr>
<td>Rectangles (L/D = 20)</td>
<td>-(\pi/32 &lt; \theta &lt; \pi/32)</td>
<td>-</td>
<td>0.417</td>
</tr>
<tr>
<td>Rectangles (L/D = 20)</td>
<td>(\theta = 0) (Aligned)</td>
<td>-</td>
<td>0.487</td>
</tr>
</tbody>
</table>

Samples with randomly oriented conductive sticks exhibited a lower percolation threshold than samples with preferred orientation. Furthermore, for both the longitudinal and transverse direction, the percolation threshold of randomly oriented samples was identical. However, for
aligned samples, the percolation threshold was slightly different. This difference in the percolation threshold between transverse and longitudinal direction was shown to decrease as the length of the fibres increased. Additionally, the larger the size of the lattice, the more reliable were the results.

Balberg et al.[121] and Taya and Ueda [101] extended the previous two-dimensional Monte Carlo work to three-dimensions. This is because the three dimensional system of conducting particles is more appropriate when it comes to predicting the behaviour of real composites. In both studies, the fibres can penetrate each other because they are deemed to have soft cores. However, this simulation will not be able to predict the behaviour of the actual composite because fibres cannot be penetrated.

Wang and Ogale [120] proposed a more realistic model where a filler component is made up of an impenetrable core surrounded by a soft shell. The presence of soft shell enables the potential for quantum mechanical tunnelling between the two fibres which are almost in contact with each other. Two particles were considered connected if the distance between their centres was greater than the hard core diameter but less than the diameter of the core and the shell together. The percolation threshold of composite containing spheres was determined with a Monte Carlo simulation. Initially, the percolation threshold in a finite-sized system was calculated. Then, the results were extrapolated using finite size scaling to obtain the percolation threshold in infinite system. The primary variable in scaling was the number of inclusions because its dependence was dimensional invariant. The equation 3.2 below illustrates the relationship:

\[ |P_{av} - P_c| = N^{-0.375} \]  

(3.2)

where \( P_{av} \) = percolation threshold in a finite sized system, \( P_c \) = percolation threshold in an infinitely large system, \( N \) = average number of fibres in a finite sized system. The number of fibres present is proportional to the size of the system. The value of \( (N) \) can be related to the length of a box side (L) for cubic system. In this case, the scaling exponent becomes 0.89. Stauffer [92] has reported that the scaling exponent should be 0.9 for spheres. There is good agreement between the two values which validates the use finite-size scaling theory. The original work for spheres was extended to fibres in cubic [122]
and non-cubic [123] boxes. Both researches reported that the scale law given by equation 2.14 had still been obeyed.

The researchers have been comparing the percolation threshold obtained via experiment results to the prediction from Monte Carlo simulation. Table 3.5 illustrates that there is a good agreement between prediction and experimental values. Holm and Cima [119] reported that there is a slight variation in the predicted percolation threshold compared with the experimental percolation. This is due to the use of the Monte Carlo simulation which allows for fibre-fibre penetration. Wang and Ogale [120] used a more realistic model for prediction, impenetrable core with soft shell, which gave more accurate predictions regardless of the shell thickness. The model prediction is most accurate for nickel powders with small diameter (mono-disperse size distribution). However, when the diameter of nickel is too high, the particles exhibit poly- disperse size distribution. As a result, there is a variation in the predicted percolation threshold compared to experimental data.

Table 3.5: Predicted and experimental value of percolation threshold for various systems. Permission to reprint obtained from the author. Modified from [93]

<table>
<thead>
<tr>
<th>Author</th>
<th>Composite</th>
<th>Experimental threshold (vol %)</th>
<th>Predicted threshold (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holm &amp; Cima</td>
<td>Silicon carbide Whiskers/alumina</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>Wang &amp; Ogale</td>
<td>Nickel powder/polyethylene</td>
<td>10 (d=2.9 µm)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23 (d=8.9 µm)</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43 (d=68.0 µm)</td>
<td>48</td>
</tr>
</tbody>
</table>

Excluded volume is another simulation technique which can be used to determine the percolation threshold of an electrically conductive composite. For the excluded volume simulation:

1) The fibres are allowed to penetrate each other,
2) The material is assumed to be statistically homogeneous,
3) The probability of intersection between cylinders is determined.

Munson-McGee [124] studied the effects of fibre orientation and length in a three-dimensional network with an excluded volume theory. Figure 2.13 illustrates the percolation predictions from the Monte Carlo [122] and excluded volume [124] models. It can be seen that three states for fibre orientation have been investigated, these were:
1) Planar random - fibres are randomly oriented in the x-y plane,
2) 3-D random - fibres are randomly oriented in all three planes,
3) Aligned - fibres are aligned parallel to the flow direction.

According to Figure 3.4, for both the Monte Carlo and the excluded volume simulation, the percolation threshold was lowest in the case of 3-D randomly oriented fibres. For both the Monte Carlo and excluded volume theories, the percolation thresholds of the aligned samples were higher than those with random fibres arrangement. Furthermore, the percolation threshold for aligned sample is independent of the aspect ratio of the fibres. There is also a variation in the prediction of percolation threshold between the Monte Carlo and excluded volume simulation. This is especially true for samples containing randomly oriented fibres.

![Figure 3.4: Comparison of critical concentration (volume fraction) predictions from Monte Carlo and excluded volume models. Reprinted with permission from the author of [93]](image)

Yong et al. [125] investigated the effects of fibre waviness on the percolation threshold using the Monte Carlo simulation. Yong reported that the percolation threshold of the composite increases as the fibres becomes more curved. Furthermore, as fibres become more curved, the number of contact points required for the percolation threshold increases. This means that the number of fibres required to attain the percolation threshold also increases.
3.2 Quantum Tunnelling and Thermal Expansion

It is necessary to understand the effect of filler loading and temperature on electrical conductivity before fabricating electrically conductive composites. Three mechanisms have been proposed: percolation, quantum mechanical tunnelling and thermal expansion [6]. Of these proposed mechanisms, percolation is the most important mechanism which has been mentioned earlier in section 3.1. The following sub-section will briefly describe the effect of quantum mechanical tunnelling and thermal expansion.

Quantum mechanical tunnelling

Quantum mechanical tunnelling is a concept used to describe an electron transporting process on a microscopic scale. In a system consisting of conducting particles dispersed in an insulating matrix, there are three regions (as mentioned previously under the percolation concept). In Region 1, there is not enough physical connection between the conducting fillers throughout the composite. As a result, the composite behaves as an insulator. However, when the distance between two conducting particles is less than 100 angstroms, electrons can tunnel, quantum mechanically, between conducting particles. Therefore, it is possible to create an electrically conductive network, via tunnelling, within a composite even though global physical connections between conducting particles are not present. Carbon black-filled polymer composite is one of the most common examples. When quantum mechanical tunnelling throughout the composite is possible, the composite will become electrically conductive, as is similar to a composite at percolation threshold [6, 126]. Quantum mechanical tunnelling is illustrated in Figure 3.5. The spheres’ hard cores represent the particles and the halo around them represents the range over which the tunnelling is significant. The tunnelling nearest-neighbour connections are marked by bold segments while the connections to more distant neighbours are marked by thin segments. The bias is applied in that case between a conducting tip and the ground counter electrode. For composites where tunneling exists, the composites will percolate at a lower fibre loading compared to a composite which percolates only via physical contact between fillers. However, percolation involving tunneling may also result in lower electrical conductivity due to the presence of a non-conductive matrix between conductive fillers and the polymer matrix. It is possible to improve electrical conductivity by replacing the insulating polymer matrix at the CNT-CNT junction with conductive components such as conductive polymers [127].
Thermal expansion

The coefficient of thermal expansion (CTE) for polymers is significantly higher than that of metals (CTE of polyethylene is $200 \times 10^{-6}$ m/m.k compared to $13 \times 10^{-6}$ m/m.k for nickel). Therefore, as the temperature of the metal-filled composite increases, the distance between each individual filler particles will also change. Generally, as the temperature of the metal-filled composite increases, both polymer host and metal fillers will expand based on their CTE. As polymers have a higher CTE, they will expand faster than metal fillers. As a result, the distance between conducting particles will also increase. If the composite is initially conductive, there will be an abrupt increase in resistivity when the temperature reaches a certain point, as shown in Figure 3.6 [6].

It can be seen from Figure 3.6 that the resistivity of a metal-filled composite either increases or decreases following the sudden increase in resistivity. The latter case usually happens
when delamination between polymer host and metal fillers occurs. This will lower the thermal expansion of the composite which will lessen the increase in resistivity [6].

3.3 Compression Moulding and Injection Moulding – Their Effect on Percolation Threshold and EMI Shielding Effectiveness

Compression moulding and injection moulding are the two most common polymers/composite fabrication techniques used to make commercial products. In compression moulding, polymer pellets or composite pre-forms are inserted between the moulds. Then, with the application of heat and pressure, the materials are pressed into shape with minimal mechanical mixing.

In injection moulding, there is more mechanical mixing involved. Firstly, polymer or composite pellets are fed through a hopper. The materials enter the cylinder barrel containing a rotating screw where the materials are heated. Then the screw motor drive pushes the melted material into the mould to form a shape, as shown in Figure 3.7.

![Figure 3.7: Schematic of injection moulding. Reprinted with permission from [128]](image)

There are several advantages of compression-moulded composites over injection-moulded composites. Firstly, fibre orientation within a composite will be random as long as the fibres were randomly distributed to begin with, since there is minimal mechanical mixing [115]. This is illustrated in Figure 3.8 where SSF are randomly distributed within the compression-moulded SSF composite [129].
Furthermore, an injection-moulded composite will have a skin-core microstructure. With respect of fibre orientation, this means fibres are aligned in the flow direction on the surface of the composite with two-dimensional randomly distributed fibres at the core of the composite [93]. It can be seen from Figures 3.9 (A) and (C), that there is some SSF orientation on the surface of the injection-moulded SSF composite (blue line). Furthermore, according to Figure 3.9 (B) and (D), SSF appeared to be randomly distributed at the centre of SSF composites, similar to the compression-moulded SSF composite.
Randomly distributed fibres exhibit a lower percolation threshold than aligned fibres due to more fibre contact; this is further reinforced in Figures 3.10 and 3.11 [115]. As shown earlier, Figure 3.4 illustrates that the percolation threshold of composites containing aligned fibres does not change with the aspect ratio (length to width or length to diameter ratio) of fillers, making them inferior to composites containing randomly distributed fibres where the percolation threshold can be decreased when fibres with higher aspect ratio are used. This is because a higher percolation threshold makes the composite more expensive to produce as more filler is needed.

Fibres will generally retain their aspect ratio in a compression-moulded composite. This is because there is very little mechanical mixing during compression moulding [113].
comparison, there are more mechanical mixing and shear forces during the injection moulding process, which reduces the aspect ratio of fibres. Additionally, if polymer and fibres were both compounded prior to injection moulding then the aspect ratio of fibres would be further reduced. This is most likely to be the reason that randomly oriented fibres have better EMI shielding properties than aligned fibres, as shown in Figure 3.11 [115].

![Figure 3.11: Shielding effectiveness versus flake loading for composites containing and randomly oriented flakes. Reprinted with permission from [115]](image)

Compression-moulded composites require less material for the fabrication process as there is no purging cycle, unlike injection moulding which requires extra feed material. Additionally, if compounding is require before injection moulding, more feed material is required in order to maintain good consistency in the compounded material. For situations where precious raw materials are involved, this could make compression moulding a cheaper process for composite fabrication. However, injection moulding becomes more cost-effective than compression moulding with a high production volume, where cost per material is significantly reduced due to higher production rate. An additional advantage for the injection moulding process is that it could be fully automated.

Therefore, to produce a cost-effective composite with excellent EMI shielding capability, compression moulding is the preferred method for fabrication. However, although the relationship between percolation and the effects of composite processing techniques are clear, there is little research that relates percolation to the microstructure of the composite. This is because composite microstructures taken with SEM or a light microscope are in 2-D, while percolation occurs in 3-D. Therefore, to establish a relationship between percolation and microstructure, 3-D images of the composite are investigated and analysed in this research.
Chapter 4

Electroless Nickel Deposition

The electroless deposition of nickel is the process which reduces nickel ions to nickel metal on the surface of the substrate. After the initial deposition of nickel onto the surface of the substrate, the deposited nickel acts as a catalyst for further reduction of the nickel. There are many industrial applications for which electroless nickel coating is applicable. This is due to the excellent mechanical, physical, electrical, corrosion and wear-resistance properties of electroless nickel coating. This chapter highlights the parameters which affect the electroless nickel deposition process and the way in which nickel can be deposited onto wood substrate. It is important to understand the factors which affect the electroless deposition process to assist in the fabrication and optimisation of nickel coating on cellulose fibres.

4.1 Electroless Nickel Deposition

There has been an increase in the usage of electroless nickel-phosphorus coating in the past twenty years. This is due to the many outstanding properties of electroless nickel coating, such as its exceptional corrosion and wear resistance, uniform coating thickness, great mechanical properties, high quality surface finish characteristics and excellent adhesion properties. These properties are useful in many industries such as chemical, automotive, aerospace, electronics, mining, oil and gas. The electroless nickel coating process is a redox reaction where nickel ions are reduced onto the surface of the material as a result of the oxidation of the reducing agent. The initial deposition of nickel onto the surface of the substrate further catalyses the electroless deposition of nickel. The coating will be an alloy of
nickel and phosphorus if the reducing agent used in the electroless plating process is sodium hypophosphite [130].

There are numerous parameters affecting the electroless nickel deposition process. Riedel [131] suggested the deposition rate as being a function of the effective parameters of the electroless nickel deposition method, as described as follows:

\[ D = F(T, \text{pH}, C_{\text{Ni}^{2+}}, \text{Red}, C_{\text{Red}}, \text{O/V}, n_1, \ldots) \]  \hspace{1cm} (4.1)

Where: \( D \) = Deposition rate

\( T \) = Temperature

\( \text{pH} \) = solution pH

\( C_{\text{Ni}^{2+}} \) = Concentration of nickel in the solution

\( \text{Red} \) = Type of the reducing agent

\( C_{\text{Red}} \) = Concentration of reducing agent

\( \text{O/V} \) (Bath load) = Ratio of the surface of the working piece to the volume of solution in the tank

\( n_1 \) = Agitation factor

Temperature is the most important parameter affecting the deposition rate of electroless nickel plating. Since the electroless deposition of nickel mainly involves endothermic reactions, increasing temperature will also increase the deposition rate [132]. Generally, an alkaline bath operates at low temperature (could be as low as 40 °C), making it suitable for coating plastic substrate. However, an acid bath generally operates at higher temperatures (around 80 – 90 °C).

Many electroless nickel deposition processes are sensitive to pH changes. Increasing the pH of the plating solution increases the deposition rate of nickel but reduces the reduction rate of phosphorus. This means that the phosphorus content of nickel coating decreases as its pH increases [132].

Reidel [133] suggested that increasing the pH of the plating solution would have the following effect:
1) Increasing the deposition rate in an almost linear manner

2) Modification of the hypophosphite reaction from catalytic to homogeneous. A consequence of this can be the spontaneous decomposition of the solution with nickel deposition

3) Lowering the solubility of the nickel phosphate. Deposition of this unwanted component may initiate decomposition and often leads to rough deposits

4) Reducing the phosphorus content of the deposit.

Alternatively, Reidel [133] also suggested that decreasing the pH of the plating solution has following effect:

1) Prevention of the deposition of basic salts and hydroxides
2) Lowering the reducing power of the hypophosphite
3) More effective buffering action of species in the bath
4) At a pH below 4 the deposition occurs at a retarded rate.

The concentration nickel ions in the plating solution as well as the ratio of nickel ions to hypophosphite ions affect the electroless deposition of nickel. Riedel [131] suggested that:

1. The concentration of hypophosphite should lie between 0.15 and 0.35 mol/l
2. The optimum ratio of nickel ions to hypophosphite ions should be maintained between 0.25 and 0.6, preferably between 0.3 to 0.45.

As the following reaction shows, each mole of Ni ions consumes 3 moles of hypophosphite.

\[
3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni \quad (4.1)
\]

Therefore theoretically, the ideal ratio of nickel ions to hypophosphite ion would be 0.33, which is close to the measured value of 0.3 to 0.45.

The ratio of surface of the substrate to the volume of the plating solution in the container is known as bath loading. Commercial baths are operated in a bath loading range of 0.1 to 1.0 \( \frac{dm^2}{l} \) depending on the bath solution [133].

Electroless nickel plating solution has a finite life. The age of the plating solution is defined as the number of times the entire nickel ion content (g/l) is consumed and replenished. Electroless plating solution is generally discarded when the amount of nickel ions replenished reaches 30 to 80 g/l. This usually happens when nickel ions have been replenished
somewhere between 5 and 13 times. Generally, the phosphorus content increases as the number of replenishments increase [134].

Riedel [133] and Duncan [135] reported that the age of the plating solution affected the electroless nickel deposition, as well as other properties, such as internal stress, ductility, corrosion resistance and fatigue resistance. Riedel reported that there was a minor change in the properties of the electroless nickel deposit (including phosphorus content). The corrosion resistance reduced significantly after the fifth replenishment. Therefore, for commercial electroless nickel plating, the plating solution is replaced after the fifth replenishment [134].

Table 4.1 summarises the effect of various plating parameters on the nickel deposition rate and phosphorus content. The parameters which affect the phosphorus content of nickel coating also affect the electrical conductivity which, in turn affects the EMI shielding capability of the nickel coating. Therefore, phosphorus content is one of the important parameters for optimisation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Nickel deposition rate</th>
<th>Phosphorus content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Increases with temperature</td>
<td>-</td>
</tr>
<tr>
<td>pH (4 to 6)</td>
<td>Increases with pH</td>
<td>Decreases with pH</td>
</tr>
<tr>
<td>Ratio of nickel to hypophosphite</td>
<td>Maximum when the ratio is approximately 0.5</td>
<td>Decreases if ratio is too high</td>
</tr>
<tr>
<td>Bath loading</td>
<td>Decreases with bath loading</td>
<td>-</td>
</tr>
<tr>
<td>Number of nickel replenishments</td>
<td>Decreases with number of replenishments</td>
<td>Increases with number of replenishments</td>
</tr>
</tbody>
</table>

The phosphorus content is also linked to the crystallinity of the nickel coating. At low phosphorus content (1 – 5 wt%), nickel is crystalline. When phosphorus level is between 6 – 9 wt%, nickel is semi-crystalline. At high phosphorus level (10 – 13 wt%), nickel will be amorphous. This means that reducing the phosphorus content within the nickel coating will
not only increase the electrical conductivity of the coating (as shown in Figure 4.1) but will also improve the crystallinity of the nickel. There is a possibility of a correlation between the crystallinity and the electrical conductivity of the coating. This means that if there is a technique which could be used to improve the crystallinity of the nickel coating, then it possible that the electrical conductivity of the nickel coating would also improve.

![Figure 4.1: Correlation between electrical resistivity and phosphorus content of nickel coating on steel substrate. Reprinted with permission, courtesy of Nickel Institute [136]](image)

There are two methods for reducing the phosphorus content within the nickel coating: 1) post-plating heat treatment, and 2) changing the pH of the plating solution. Baudrand [137] performed heat treatment on nickel coated steel with phosphorus content of 10 and 10.5 wt%. Baudrand found that, to achieve approximately 30% reduction of electrical resistivity, the heat treatment time used for nickel coating with phosphorus content of 10 and 10.5 wt% was about 50 and 200 hours respectively. (Heat treatment temperatures were not disclosed). The reduction in electrical resistivity is due to the migration of phosphorus and the formation of nickel phosphides, which are more electrically conductive than phosphorus [130]. However, 50 hours is too long and expensive for the post-plating heat treatment of NCCF. Therefore, the experiment will focus on changing the pH of the plating solution to reduce the phosphorus content within the nickel coating.

4.2 Electroless Nickel Plating of Wood

Wood is a natural renewable biomass material with many useful properties, such as a high strength to weight ratio, an ability to control humidity in addition to its capabilities in heat
and sound insulation. Since wood is also an electrical insulator, its applications in the fields of electromagnetic shielding and electrostatic discharge are limited.

In order to impart electrical conductivity into wood, research has been done using an electroless plating technique to deposit metal coating, such as copper, silver or nickel, onto wood substrate, mainly wood veneer.

The traditional method of palladium activation involves dipping a non-active substrate into a solution containing PdCl₂ (activation) and SnCl₂ (sensitization). Pd colloid, surrounded by Sn²⁺ ions, is deposited on the surface of the substrate which catalyzes the nickel deposition [138, 139]. However, due to environmental concerns about tin, a new Sn-free palladium activation process has been developed where Pd²⁺ is directly absorbed onto the surface of the substrate. Prior to Pd²⁺ adsorption, the substrate is pre-treated with organosilane to improve adhesion between the palladium and the substrate [20, 140-142]. Subsequently, the substrate is treated with reducing agents such as sodium borohydride or sodium hypophosphite to reduce Pd²⁺ ions to Pd⁰. Since palladium activation is the most expensive process, it is considered as the last option for this study.

Silver activated surfaces can be achieved in a similar manner to Sn-free palladium activation. Firstly, the substrate is pre-treated with organosilane to improve adhesion between silver particles and the substrate. Subsequently, the pre-treated substrate is dipped into silver nitrate solution to initiate silver seeding onto the surface. The silver-activated substrate is then immersed in a nickel bath, where the silver catalyzes the nickel deposition [143]. This method is cheaper than palladium activation.

Nickel activation is also known as the palladium-free activation. In this process, the substrate is pre-treated with sodium borohydride which allows BH₄⁻ ion to be adsorbed onto the surface. After that, the pre-treated substrate is immersed in a nickel plating solution. Since borohydride ions provide a stronger reducing agent than hypophosphite ions (which are present in a nickel-plating solution) the reaction between Ni²⁺ ions and BH₄⁻ ions occurs first; this reduces nickel colloid onto the substrate. The nickel colloid acts as a catalyst which catalyzes further nickel deposition [20]. Due to the fact that precious metals are not involved in the electroless plating process, palladium-free activation is considered to be the cheapest process. Therefore, this study focuses on obtaining nickel coating via the palladium-free process.
Studies of the deposition of nickel on wood veneer suggest that sodium borohydride (NaBH₄) initiates the nickel deposition process. Sodium borohydride is a strong agent which hydrolyses easily. However, hydrolysis reaction does not occur in the presence of an alkaline solution. In earlier research, wood veneer was pre-treated by immersion into an alkaline solution containing sodium borohydride at room temperature. Hydroxyl groups in cellulose will form hydrogen bonds with the borohydride ions BH₄⁻, allowing its strong adsorption onto the substrate. Subsequently, the pre-treated wood veneer was immersed in a nickel-plating solution to initiate the plating reaction. Since BH₄⁻ is a stronger reducing agent than H₂PO₂⁻, the reaction between Ni²⁺ and BH₄⁻ will occur first, initiating nickel deposition onto the wood veneer, according to the following equation:

\[
2\text{Ni}^{2+} + \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{Ni}^{0} + 2\text{H}_2 \uparrow + \text{BO}_2^- + 4\text{H}^+ \quad (4.2)
\]

Equation 4.2 illustrates the electroless deposition of Ni⁰ cluster which activates the surface of wood veneer. The present of Ni⁰ cluster will catalyse subsequent electroless deposition of nickel onto wood veneer, according to the following two equations:

\[
2\text{H}_2\text{PO}_2^- + 4\text{OH}^- + \text{Ni}^{2+} \rightarrow 2\text{HPO}_3^{2-} + 2\text{H}_2\text{O} + \text{Ni} \downarrow + \text{H}_2 \uparrow \quad (4.3)
\]

\[
3\text{H}_2\text{PO}_2^- \rightarrow \text{H}_2\text{PO}_3^- + 2\text{H}_2\text{O} + 2\text{OH}^- + 2\text{P} \downarrow \quad (4.4)
\]

After activating the surface of the wood with nickel clusters, H₂PO₂⁻ and Ni²⁺ ions are adsorbed onto the clusters which react to form a continuous coating of nickel and phosphorus [20]. Several researchers have reported EMI shielding effectiveness values of 60 dB in the frequency range of 30 MHz – 1.5 GHz for electroless nickel plating on wood veneer [144-146]. However, there are no reports on the shielding effectiveness of composites containing NCCF.
Chapter 5

Research Scope and Directions

EMI shielding theory suggests that a material with electrical conductivity can shield both electric and magnetic fields at frequencies greater than 100 kHz [25]. This study focuses on the common EMI shielding range from 300 MHz – 1.5 GHz, as this is where EMI interferes with radio communication. Since this frequency range is quite high in the electromagnetic spectrum, materials with excellent electrical conductivity are of interest as they can shield both electric and magnetic fields. Furthermore, far-field shielding is investigated, as previous research suggests this is harder to shield than near-field EMI. Far-field shielding is also the way in which EMI shielding materials are tested and ranked according to ASTM D4935 – 99.

Of the two mechanisms for shielding EMI (reflection and absorption), it is important to note that the preferred form of shielding EMI is absorption. In this form, electromagnetic radiations are absorbed by the EMI shielding material and dissipated as heat. In contrast, shielding by reflection simply redirects electromagnetic radiation back to the environment where it could affect both people and other electronic devices. To maximise shielding by absorption, the impedance of EMI shielding material should be as close as possible to the impedance of air (377Ω), as impedance mismatch favours shielding by reflection. This implies that materials with excellent electrical conductivity, such as bulk metals, may not be as favourable as conductive composites, which exhibit impedance ratios closer to air than do bulk metals. This makes conducting composites materials of interest in this study.

Conventionally, a conductive composite is composed of a non-conductive polymer filled with conductive fillers. In order for the composite to be electrically conductive, enough fillers
need to be added until the percolation threshold has been reached. Previous research studies [113] have indicated that fillers with a high aspect ratio demonstrate lower the percolation threshold. This suggests that the usage of fibre is more desirable than the use of particles. Additionally, skin depth calculations have indicated that, due to their small skin depth, stainless steel and nickel are the two most favourable metals for EMI shielding applications (refer to Table 2.2). This conclusion has been confirmed by two commercial EMI shielding product ranges based on stainless steel fibres and nickel coated graphite fibres [7]. The slight variations between using nickel coated graphite fibres rather than solid nickel fibre were due to the fact that a thinner nickel coating is more beneficial at gigahertz frequency (due to smaller skin depth). For this reason, nickel becomes a material of interest for this study.

One of the cheapest fibre substrates available are cellulose fibres. However, since they are form non-conductive substrate, applying a conductive coating on such fibres is essential for EMI shielding purposes. Although the only information available in literature concerns the electroless deposition of nickel onto a wood veneer, it is highly likely that this technique will also be applicable to cellulose fibres; this is because they each contain the hydroxyl group in their structure. Therefore, the nickel activation technique will be used to deposit nickel onto cellulose fibres as it is an inexpensive and simple method and because there are no precious metals involved in the surface activation step. The primary focus of this study is to investigate the possibility of producing a nickel coated cellulose fibre (NCCF) composite for commercial EMI shielding application. For this purpose, an important factor to consider is phosphorus content, as it relates to the electrical conductivity of the coating which affects the EMI shielding capability. The lower the phosphorus content, the higher the electrically conductivity which means higher EMI shielding effectiveness. Furthermore, it is also important to deposit a uniform, continuous and adherent nickel coating on cellulose fibres. The kinetics of nickel deposition onto cellulose fibre has very small influence on improving the EMI shielding capability of NCCF. Additionally, it is difficult to model the kinetics of nickel deposition due to a large mass of cellulose fibres with different dimensions, as well as the formation of nickel lumps. As long as the deposition rate of nickel onto cellulose fibres is not sufficiently slow as to be impractical, then the kinetics of the nickel deposition are considered to be acceptable. For these reasons, the kinetics of nickel deposition will not be investigated in this study.
The aim of this research is to develop a potentially cheaper alternative composite material based on polymer and NCCF for the purpose of shielding EMI. Therefore, the ultimate goal is to achieve a commercial EMI shielding standard of 30 – 40 dB, while minimising the cost of production. Prior research [113, 115] has indicated that these NCCF should be incorporated into a polymer via a compression-moulding technique. This is because, firstly, the compression moulding process uses less raw material than in injection moulding; thus enabling the composite to be less expensive to produce. Secondly, there are very few shear forces in compression moulding when compared to injection moulding, which allows the fibres to retain their aspect ratio. This means that composite that has been fabricated via compression moulding generally exhibits a lower percolation threshold due to the higher aspect ratio. A lower percolation threshold means less materials are required; thus making the composite cheaper to fabricate. Lastly, fibre orientation also affects both the percolation threshold and EMI shield effectiveness. Composites produced via compression moulding generally exhibit randomly oriented fibres, whereas, injection moulded composites have some alignment in fibre orientation. Composites with randomly oriented fibres have a lower percolation threshold than those with aligned fibres. Furthermore, randomly oriented fibre composites also have better EMI shield performance than do aligned fibres composites. Earlier researches have concluded that, for the purpose of producing cheaper composites with better EMI shielding capability, compression moulding is the preferred method of composite fabrication.

Porras et al. investigated the effect of compression moulding parameters, such as; chemical treatment concentration, chemical treatment time, compression moulding temperature, compression moulding pressure, compression moulding time and fibre weight ratio for the mechanical property of composites made from PLA and Manicaria Saccifera palm. It was concluded that the optimal processing parameters are: low chemical treatment concentration, high chemical treatment time, high compression moulding temperature, high compression moulding pressure, high compression moulding time, and medium fibre-weight ratio. [147]. Jean et al. investigated the effect of injection moulding parameters such as screw speed, injection time, back pressure, injection pressure and injection speed on the mechanical property of composite made of PP and flax fibres via injection moulding. It was concluded that the optimal processing parameters are: low temperature profile, high screw speed, low barrel temperature, low mould temperature, high injection temperature, low back pressure,
high injection pressure and high injection speed [148]. As mentioned earlier, to achieve the aim of this thesis, optimal mechanical properties are not initially required. However, it is recommended that, when NCCF composite with commercial EMI shielding effectiveness has been successfully fabricated, then the mechanical properties of NCCF should be optimised.

In this research, the mechanical properties of the composites are not extensively investigated, as they are not the main aim of this research. For the purpose of fabricating and optimising EMI shielding composites, the mechanical properties of the composite need only to be comparable to existing systems, although not necessarily superior. However, it is acknowledged that there has been extensive research [147-155] on the effect of various factors which influence the mechanical properties of natural fibre reinforced composite. These factors include; composite processing parameters (compression and injection moulding), interfacial adhesion and the moisture content of natural fibres.

Moisture content is another important factor which affects the mechanical properties of natural fibre composite. It is essential to dry the fibres before processing them into composite because any moisture on the fibre surfaces can act as a de-bonding agent at the fibre-matrix interface. Furthermore, any water evaporated during composite processing can leave voids inside the matrix (as composite processing temperature is general greater than 100 C). These will result in a reduction of the mechanical properties of the composite. It has been reported in the literature that the mechanical properties of natural fibre composite decreases as the moisture content of natural fibres increases [151-153]. Furthermore, it has been reported that the presence of water molecules can increase the maximum strain of the composite materials by acting as a plasticizer. Once again, the optimisation of the mechanical property of the composites is not the primary focus of this study. In terms of moisture content, the composite pre-form only needs to be dried enough so that the fibres can be fabricated into a composite without obvious signs of porosity and swelling. The mechanical property may be important in the later stages of commercialisation.

The relationship between percolation and the microstructure of a conductive composite is poorly understood. The relationship between the percolation threshold and the 2-D microstructures obtained from SEM or light microscope images has been reported in literature. However, it is known that percolation is in 3-D, thus the images which relate to percolation should also be in 3-D; currently, there is no information available on this. This thesis will attempt to investigate the relationship between percolation and the 3-D
microstructure of the composite. Furthermore, as natural fibres are flexible compared with stainless steel fibres and nickel coated graphite fibres, the effective aspect ratio would be lower than the actual aspect ratio. This means the percolation threshold would be higher.

This research has been carried out in three stages. Stage one is the proof of concept stage which focuses on testing the possibility of depositing nickel onto filter paper. Stage two focuses on the development and optimisation of a methodology for depositing a nickel coating onto cellulose fibres. In stage three, composites containing NCCF are produced and characterised. Additionally, composites based on stainless steel fibres (SSF) have also been fabricated for comparison.

Each stage consists of an experimental section, in addition to the results and discussions relevant to each stage of the thesis.
Chapter 6

Developing Nickel Coating on Natural Fibres

The first stage was a proof-of-concept stage; this was to understand and check whether the method of electroless nickel plating on wood veneer could also be applicable for cellulose fibres. In Stage one of this study filter paper was used to represent cellulose fibres as filter paper is commonly available and is also primarily composed of cellulose fibres.

Once a uniform, continuous, adherent and electrically-conductive nickel coating was successfully deposited onto filter paper, the next step was to develop a methodology to nickel coat cellulose fibres. Stage two was a step up from coating the surface of a small section of filter paper to fully coating nickel onto individual cellulose fibres to ensure that they could shield EMI. The guidelines established in the previous stage were used to assist the optimisation and modification of the electroless nickel plating process.

Stage three was to process nickel coated cellulose fibres into an electrically conductive composite for EMI shielding.
6.1 Stage One: Nickel Coating on Filter Paper – Experimental Procedures

Whatman filter paper, Grade 1 (Sigma Aldrich) was used as the substrate for electroless nickel plating. The electroless bath consisted of nickel sulphate hexahydrate (NiSO$_4$.6H$_2$O, Analytical Reagent grade, supplied by ECP Labchem), sodium hypophosphite monohydrate (NaH$_2$PO$_2$.H$_2$O, 99.9% purity, supplied by Ajax Finechem), trisodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$.2H$_2$O, Analytical Reagent grade, supplied by ECP Labchem) and boric acid (H$_3$BO$_3$, Analytical Reagent grade, supplied by ECP Labchem). The pre-treatment solution consisted of sodium hydroxide (Analytical Reagent grade, supplied by Ajax Finechem) and sodium borohydride (Analytical Reagent grade, supplied by ECP Labchem).

Filter paper was pre-treated with sodium borohydride prior to electroless plating. The pre-treated solution contained 3 g/L of sodium borohydride dissolved into an aqueous solution containing 5 g/L of sodium hydroxide. The composition of the nickel plating solution, for electroless plating of filter paper, is given in Table 6.1.

Table 6.1: Composition of nickel plating solution (for filter paper)

<table>
<thead>
<tr>
<th>Bath Component</th>
<th>Content (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO$_4$.6H$_2$O</td>
<td>6</td>
</tr>
<tr>
<td>NaH$_2$PO$_2$.H$_2$O</td>
<td>6</td>
</tr>
<tr>
<td>Na$_3$C$_6$H$_5$O$_7$.2H$_2$O</td>
<td>6</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>6</td>
</tr>
</tbody>
</table>

In Table 6.1, nickel sulphate is the ion source, sodium hypophosphite is the reducing agent, sodium citrate is the complexing agent and boric acid is the buffering agent. The pH of the electroless bath was adjusted using a sodium hydroxide solution. Each sample was coated for 2.5, 5, 10 and 20 minutes at temperatures between 72 – 84 °C. It was then removed from the plating solution, washed with distilled water and air-dried.

Characterisation Technique

SEM and EDS were used to assess the success of electroless nickel deposition, as well as the quality of the coating. SEM equipped with a back-scatter detector provided contrast images between materials with different atomic mass; heavier elements appear brighter on the SEM
image. Since cellulose fibres are much lighter than nickel, the use of this technique illustrated a clear distinction between the two materials, allowing deductions as to whether a coating had been successfully and uniformly deposited onto cellulose fibres. Nickel coated filter paper was placed onto a carbon tape on a stub; this was followed by coating with platinum particles to enhance imaging before examination under the SEM. EDS was used to semi-quantitatively determine the elemental composition of the coating. This technique was used to confirm that nickel had been deposited onto cellulose fibres. XRD was used to assess the crystallinity of the nickel coating and to qualitatively determine the degree of crystallinity. A two-point surface resistivity measurement was used to test whether nickel coated filter paper is electrically conductive. Variables affecting the deposition of nickel, such as temperature, plating time and concentration of electroless plating solution, were investigated in order to establish guidelines for the next stage of the project.

The Scanning Electron Microscopy ("SEM") used in this research is FEI Quanta 200 F (field emission gun). The Energy Dispersive Spectroscopy ("EDS") detector is SiLi (Lithium drifted) with a super ultra-thin window. The accelerating voltage used for the EDS analysis was 20 kV.

For the SEM/EDS analysis, a small section was cut from the NCFP and was mounted onto a stub by placing the section of NCFP onto a conductive carbon tape. NCFP samples were coated with a thin, amorphous layer of platinum via sputtering to minimise the charging effect on the sample; this ensured high quality SEM images. The accelerating voltage was 5 kV, spot size was 2 and a backscattered electron detector was used.

The X-Ray Diffraction ("XRD") used in this research is a Bruker D2 Phaser. The X-Ray source is a copper tube.

For XRD analysis, the NCFP was mounted onto the stage by placing it on top of plasticine wax inside the mount. The plasticine wax was shaped in such a way that the surface of the NCFP aligned with the surface of the mount to minimise error in the XRD analysis. The scanning angles ranged from 10 to 90 degrees and the scanning speed was 5 degrees per minute.

Surface resistivity measurements were performed on Nickel Coated Filter paper, measured according to the equation 5.1 presented by [20]:

\[ R_s = \frac{R}{(L \times D)} \]  

(6.1)
Where $R_s$ is the surface resistivity ($\Omega/cm^2$), $R$ is the electrical resistance ($\Omega$), $L$ is the distance between the two electrodes and $D$ is the diameter of the electrodes (cm).

### 6.2 Stage One: Nickel Coating on Filter Paper – Results and Discussions

Figure 6.1a is an SEM image of uncoated filter paper at 8000x magnification where cellulose fibres can be clearly seen. In terms of elemental compositions from the EDS, Figure 6.1b shows that, for uncoated filter paper (primarily composed of cellulose as per description of Whatman Filter Paper Grade 1), only carbon, oxygen and platinum peaks are present. Whilst carbon and oxygen correspond clearly to cellulose, the minimal peak of platinum is caused by the thin coating put on non-conductive samples to avoid the charging effect in SEM. The presence of cellulose fibres in filter paper is reinforced by the EDS spectra of cellulose fibres (Figure 6.2) which illustrates that cellulose fibres are primarily composed of carbon and oxygen.

![Figure 6.1: a) SEM image and b) EDS spectra of uncoated filter paper](image-url)
After treatment times of 2.5 and 20 minutes at 84 °C (Figures 6.3 and 6.4 respectively) it can be seen that nickel particles have been successfully deposited onto filter paper. The nickel particles appear to bond to the filter paper. As the plating time increases, the coating becomes more uniform, compacted and continuous, with increased particle size.
As the filter paper was coated for 2.5 minutes (Figure 6.3b), nickel and phosphorus peaks were detected in addition to the weaker peaks of carbon and oxygen. The reduction in the intensity of the carbon and oxygen peaks agreed with the SEM image of cellulose partially covered by nickel coating. It is expected that when the nickel coating grows more uniformly and thicker on the substrate, the signals from cellulose (carbon and oxygen peaks) will be less detectable by EDS. When the plating time increases from 5 to 20 minutes (Figure 6.4b), the carbon and oxygen peaks disappear, corresponding to a more uniform and thicker nickel coating. The uniformity of the nickel coating is an essential parameter for establishing electrical conductivity within the nickel coating that is required for shielding electromagnetic radiation.

ImageJ was used to semi-quantitatively characterise the coverage of nickel on filter paper. A threshold was selected to distinguish between uncoated filter paper and nickel coated filter paper. The percentage coverage of nickel was calculated to approximate the optimal plating time. As expected, the nickel coverage increased with coating time. Furthermore, filter papers coated for 20 minutes had the optimal nickel coverage of 99.4% while those coated for 10 minutes had coverage of 94.1%. As the difference in coverage is approximately 5%, it is useful to investigate the plating times of 15 and 20 minutes for the electroless plating of nickel on cellulose fibres. If there is not much difference between the two plating times, in terms of the coverage of the nickel on NCCF, then it would be more cost-effective to use the 15 minute coating time. The results are summarised in Table 6.2, as follows:
Table 6.2: ImageJ analysis of the coverage of nickel on filter paper

<table>
<thead>
<tr>
<th>Coating time (minutes)</th>
<th>Filter paper pixel</th>
<th>Nickel pixel</th>
<th>Coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>174311</td>
<td>43127</td>
<td>41.7</td>
</tr>
<tr>
<td>5</td>
<td>43127</td>
<td>255783</td>
<td>85.6</td>
</tr>
<tr>
<td>7.5</td>
<td>19554</td>
<td>280919</td>
<td>93.5</td>
</tr>
<tr>
<td>10</td>
<td>17777</td>
<td>281975</td>
<td>94.1</td>
</tr>
<tr>
<td>20</td>
<td>1579</td>
<td>297752</td>
<td>99.4</td>
</tr>
</tbody>
</table>

X-ray diffraction confirmed the presence of nickel (see Figure 6.5, XRD scan of coated and uncoated filter paper). The peak at 2θ = 44.5° corresponds to the major peak for nickel (111) and the breadth of the peak indicates that it is poorly crystalline nickel. The relative intensity of the nickel peak increases with plating time compared to those of other peaks. There is a significant increase in the intensity of the nickel peak between filter papers which have been electrolessly plated for 20 and 60 minutes. The observation of the SEM/EDS results suggests that the nickel coating becomes thicker as the plating time increases. The thickness of the nickel coating is another important parameter to consider because thicker conductive materials carry greater skin depth and thus are better than thinner materials at shielding electromagnetic radiation. However, a longer plating time also means higher production costs, which contradicts the aim of the thesis. At this stage, the focus will be on electroless nickel plating for up to 20 minutes; the reason for this is that a uniform coating has already been achieved within this plating time.
Another observation from the XRD of the sample with sixty minutes plating time, is the broadening of the nickel peak. This observation suggests that increasing the plating time does not improve the crystallinity of the nickel coating as there are no reductions in the breadth of the nickel peak. The sixty minutes plating time was done only to check for any improvement in the crystallinity of nickel coating. Image analysis was not conducted on filter paper plated for sixty minutes because there is already a good coverage of nickel for filter paper coated for twenty minutes. Increasing plating time would only increase cost.

A similar conclusion about the dependence of coating quality on plating time is reached by observing cellulose characteristic peaks in the diffractograms. The peaks at $2\theta = 14.5, 16.5$ and $22.5^\circ$ characterise cellulose in filter paper. As the plating time increases, the coating becomes thicker and more uniform; additionally, the cellulose peaks decrease in intensity. The peak at $2\theta = 26^\circ$ is identified as a result of the double-sided tape used to mount filter paper on the sample holder.

The electrical resistivity of nickel coated filter paper was measured and plotted against plating duration. Figure 6.6 shows that the surface resistivity of nickel coated filter paper decreases with increases in time and the temperature of the electroless deposition. At higher deposition temperatures, resistivity decreased more rapidly. This is attributed to the fact that higher temperatures increase nickel deposition rates [156]. Therefore, for the same plating duration, more nickel was deposited onto filter paper at the higher temperature. As more

Figure 6.5: XRD graph of coated and uncoated filter paper
nickel particles are deposited, there are also more ‘least resistant paths’ for electrons to traverse. As a result, filter paper plated at 84 °C has a slightly lower average value of surface resistivity than that plated at 72 °C. These two temperatures were chosen based on the experience of preparing nickel coated filter paper. It was found that the minimum temperature for plating reaction to occur was 72 °C. However, 84 °C was chosen simply because several experiments have indicated that there is too much evaporation from the plating solution at higher temperatures. Another feature shown in Figure 6.6 is the dramatic reduction in the average value of surface resistivity for filter paper plated at 72 and 84 °C for 15 minutes. It is also important to note that the surface resistivity of filter paper plated at 84 °C for 15 minutes is similar to the surface resistivity of filter paper plated at 72 °C for 20 minutes. The lowest average value of surface resistivity obtained from the experiment was 22.3 ohm/cm², when compared to literature value of 0.15 ohm/cm², for nickel coated wood veneer [20]. Although the values are slightly lower than those for coated wood, filter paper is nevertheless electrically conductive.

![Figure 6.6: Surface resistivity of nickel coated filter paper at plating temperatures of 72 and 84 °C](image)

Electrical conductivity is achieved when the amount of nickel particles deposited onto filter paper reaches a critical point where the particles effectively connect to each other to form a network of electrically conductive pathway. The critical point is achieved by increasing the amount of nickel particles deposited, their positioning and quality in terms of individual crystallinity and purity.
Summary

The results of the experiments indicate that a continuous and electrically conductive nickel coating was successfully and uniformly, deposited onto filter paper via an electroless nickel plating technique. As filter paper is primarily composed of cellulose, it should be possible to deposit nickel onto individual cellulose fibres using the same electroless nickel plating technique.

The thickness and coverage of electroless nickel coating increase with increased temperature and plating time. The best condition which produced the most uniform coating with the highest electrical conductivity was plating for 20 minutes at 84 °C. Surface resistivity measurements have shown that two more plating conditions (84 °C for 15 minutes and 72 °C for 20 minutes) exhibited only a slightly higher surface resistivity than the best condition (84 °C for 20 minutes). These two conditions were further investigated alongside the best condition to assist in the determination of optimal plating conditions for depositing nickel onto individual cellulose fibres.

6.3 Stage Two: Nickel Coating on Cellulose Fibres – Experimental Procedures

Bleached Kraft pulp from radiata pine was used as substrate for electroless nickel plating (supplied by Scion). Before electroless plating could be carried out, it was necessary to break down sheets of pressed Kraft pulp into a suspension of cellulose fibres. This process involved soaking pieces of pulp in deionised water (approximately 1% fibre suspension) for 24 hours, followed by mechanical agitation for 30 minutes. The pulp suspension was then filtered through the Buchner funnel into a pad of cellulose fibres which was dried in an oven at 110°C. The oven-dried pulp was the starting material for electroless nickel plating.

A sample of 0.2g of oven-dried pulp was stirred in 20ml of distilled water until a fully-dispersed suspension was achieved. The cellulose suspension was filtered through the Buchner funnel and the pulp was re-dispersed in the pre-treatment solution for 10 minutes. After that, the pre-treated cellulose fibre suspension was once again filtered through the Buchner funnel and then immersed into the electroless plating solution at 72°C for 15 minutes (electroless plating at 84°C was also done but there were too many nickel clusters so
the optimisation of plating conditions at plating temperature of 72°C was done first). The nickel plated cellulose fibres could either be filtered through a funnel, washed with distilled water then air-dried (‘No Refresh Sample’) or filtered through a funnel followed by the re-immersion of the plated pulp in a new electroless plating solution at the same temperature for the same amount of time (‘Refresh Once’ sample). For this experiment, there were no more than two refreshes. Table 6.3 gives the composition of the plating solution for the electroless nickel plating of cellulose fibres.

Table 6.3: Composition of nickel plating solution (for cellulose fibres)

<table>
<thead>
<tr>
<th>Bath Component</th>
<th>Content (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>12</td>
</tr>
<tr>
<td>NaH₂PO₄·H₂O</td>
<td>12</td>
</tr>
<tr>
<td>Na₂C₂O₄·H₂O₂·2H₂O</td>
<td>12</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>12</td>
</tr>
</tbody>
</table>

**Characterisation Technique**

For SEM/EDS analysis, a small sample of NCCF was mounted onto a stub by lightly sprinkling NCCF onto a conductive carbon tape. NCCF samples were also coated with platinum. The accelerating voltage was 20 kV, spot size was 3, pressure was 0.5 Torr and the backscattered electron detector was used.

For XRD analysis, NCCF was mounted onto the stage by placing a substantial amount of NCCF inside the mount. Due to the fluffy nature of NCCF, clear adhesive tape was placed on top of the surface of the mount to prevent NCCF rising above the surface. This was done to minimise error in the XRD analysis. The scanning angles ranged from 10 to 90 degrees and the scanning speed was 5 degrees per minute.

**6.4 Stage Two: Nickel Coating on Cellulose Fibres – Results and Discussion**

In contrast to the process for the nickel coating of filter paper, the electroless nickel plating of cellulose fibres required more work to optimise the coating conditions. Figure 6.7 shows the outcome of an experiment using the following electroless plating conditions: 72 °C, 15 minutes plating time, using a one-off plating solution with a concentration of nickel of 12
g/L. (The amount of nickel available for the electroless deposition was 1.3 g). The image shows that most of the cellulose fibres had not been coated with nickel. In comparison, the electroless deposition of nickel on filter paper where the concentration of nickel required to achieve a uniform coating was only 6 g/L. (The amount of nickel available for electroless deposition was 0.325 g). These differing outcomes are attributed to the much higher total surface area of the individual cellulose fibres compared to that of filter paper. Furthermore, the mass of filter paper used for electroless plating was only 0.03 g compared with 1.0 g for cellulose fibres. This means that the ratio of mass of nickel available for deposition to mass of filter paper was 10.8, whereas, the ratio of mass of nickel available for deposition to mass of cellulose fibres was only 1.3. It is difficult to make corrections to the amount of cellulose available for nickel deposition for cellulose fibres as compared to filter paper. This is because there is a variability in terms of the aspect ratio of cellulose fibres. There is also a greater surface area available for nickel deposition for cellulose fibres.

Variables associated with the amount of nickel available for deposition, such as the concentration of nickel sulfate and the number of refreshes for the electroless plating solution, were investigated together with the plating conditions usually considered: time, temperature and amount of pre-treatment solution. The concept of ‘refreshes’ is introduced taking into account the limited volume of the operating vessel, as well as the advantages of a multi-stage process versus a single stage process. Instead of increasing the volume of the plating vessel to accommodate the increased volume required for cellulose fibres, the vessel is emptied multiple times and replenished with fresh plating solution.
Table 6.4 shows the sequences of the optimisation process of electroless plating parameters to uniformly deposit nickel onto cellulose fibres with good coverage. The effects of each parameter were investigated in turn and a convergence on optimal conditions was attempted. Similar to nickel coated filter paper, ImageJ was used to semi-quantitatively characterise the coverage of nickel on cellulose fibres. A threshold was selected to distinguish between uncoated cellulose fibres and nickel coated cellulose fibres and the percentage of nickel coverage was estimated.

**Trial 1 – plating time**

The first variable investigated (Table 6.4, Trial 1) was the plating time. The dependence of coating coverage on plating time has been included in earlier research [20] and observed in earlier experiments in this study. Li [20] also reported that the electroless deposition of nickel resulted in hydrogen gas evolution. Initial experimental observation was that the electroless plating solution stopped ‘fizzing’ after about 20 minutes, suggesting that the electroless plating process had finished. It is worth noting that the fizzing did not stop at 20 minutes in the Stage One experiments on filter paper. This further supports the hypothesis of depleting nickel available for plating. The ‘fizzing’ indicator is also useful as a signal for the refreshing of the plating solution.

Various plating times of 5, 10, 15 and 20 minutes were investigated and nickel coated cellulose fibres were studied under the SEM. It is difficult to conclude which plating time gave the best nickel coating on cellulose fibres because, for all cases, very small areas of cellulose fibres had been deposited with nickel and the coatings were not uniform (Figure 6.8). Poor coverage was obtained, despite the similar ratio of available nickel over cellulose masses; the plating times of 15 and 20 minutes, were similar. Again, this suggests that there was not enough nickel to fully cover all the surface area of individual cellulose fibres. As previously discussed in the results for nickel coated filter paper, both 15 and 20 minutes plating time was further investigated along with other plating parameters to determine the most optimal plating conditions for cellulose fibres.
Table 6.4: Table of trials to determine the optimal electroless plating conditions to uniformly deposite nickel onto cellulose fibres with good coverage

<table>
<thead>
<tr>
<th>Trial</th>
<th>Mass of cellulose/volume of Pre-Treatment Solution (g/L)</th>
<th>Concentration of Nickel Sulphate (g/L)</th>
<th>T (°C)</th>
<th>Time (mins)</th>
<th>Number of Refreshes</th>
<th>Comments (nickel coverage %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>5.0</td>
<td>0</td>
<td>Poorly coated (17.7)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>10.0</td>
<td>0</td>
<td>Poorly coated (7.8)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Poorly coated (17.4)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>20.0</td>
<td>0</td>
<td>Poorly coated (14.8)</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>1</td>
<td>No Ni clusters, poorly coated (8.6)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>2</td>
<td>Ni clusters formed, poorly coated (6.4)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>3</td>
<td>Bigger Ni clusters, poorly coated (10.0)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>4</td>
<td>Biggest Ni clusters, poorly coated (19.7)</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Ni clusters formed, poorly coated (9.0)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>18.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Ni clusters formed, uniform coating on a cellulose fibres, poor coverage (12.5)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>24.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Similar observations as using 18.0 g/L (14.4)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Similar observations as using 18.0 g/L (11.4)</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>10.0</td>
<td>1</td>
<td>Ni Cluster formed, poorly coated (8.6)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>72.0</td>
<td>15.0</td>
<td>1</td>
<td>No Cluster formed, poorly coated (8.6)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>84.0</td>
<td>10.0</td>
<td>1</td>
<td>Ni Clusters formed, poorly coated (8.8)</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>More fibres are uniformly coated with Ni, moderate coverage (49.8)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Not reproducible (49.8)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>A lot of Ni clusters formed (43.1)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>18.0</td>
<td>72.0</td>
<td>15.0</td>
<td>0</td>
<td>Ni clusters formed, some uniformity in the coating (25.4)</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>1</td>
<td>Uniform coating, good coverage (97.0)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>1</td>
<td>Reproducible (97.0) [Phosphorus content = 8.4 wt%]</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>2</td>
<td>Uniform coating, good coverage (97.6)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.0</td>
<td>72.0</td>
<td>15.0</td>
<td>2</td>
<td>Reproducible (97.6)</td>
</tr>
</tbody>
</table>
Figure 6.8: SEM images of nickel coated cellulose fibres (Plating time: 5(a), 10(b), 15(c), 20(d), plating temperature = 72 °C)

Trial 2 – number of refreshes

The poor continuity suggested that the ratio of ‘nickel available for deposition’ to ‘cellulose fibres’ was too low. Several methods were used to increase this ratio. The first two methods were to increase the number of refreshes and to increase the concentration of nickel in the electroless bath. The third method was to reduce the amount of substrate to be electrolessly plated. The first factor investigated was the number of refreshes. Up to four refreshes were investigated in Trial 2 (Table 6.4). SEM images (Figures 6.9a, b, c and d) suggested that, regardless of the number of refreshes, nickel was not uniformly deposited onto cellulose fibres and there were discrete nickel clusters forming in the cases of two, three and four refreshed times. Furthermore, the size of the discrete nickel clusters increased as the number of refreshes increased and were also becoming lumpier (Figures 6.9b, c and d, circled in red). The lumpiness was the result of the electroless deposition which was occurring more in the solution than it was on the fibres so that the nickel did not bond to the fibre surface. This is undesirable because most of the nickel clusters would fall off the fibres during composite processing due to the mechanical mixing between polymer matrix and nickel coated fibres. The discreteness could also hinder the formation of a unified conduction network. As a result,
the material would have no EMI shielding capability. For this reason, as well as cost minimization, the number of refreshes was limited to two. It is also important to note that there were almost no discrete clusters present in the refresh-once sample (Figure 6.9a). Therefore, refresh-once is currently the optimal number of refreshes. Both conditions (refresh once and twice) were investigated further.

![Images of nickel coated cellulose fibres](image)

Figure 6.9: SEM images of nickel coated cellulose fibres (Refresh: 1(a), 2(b), 3(c) and 4(d), 15 minutes plating time, plating temperature = 72 °C)

**Trial 3 – Concentration of nickel**

The effect of nickel concentration was investigated by increasing the concentration up to 12, 18, 24, and 30 g/L, and the trials are listed in Table 6.4, Trial 3. The SEM images (Figures 6.10a, b, c and d) show that, for all nickel concentrations, discrete nickel clusters were formed and most of the cellulose fibres were not coated with nickel. Further studies of the SEM images suggest that some individual fibres had been uniformly coated when nickel
concentration was at 18, 24 and 30 g/L (Figures 6.10b, c and d, circled in red). However, as most cellulose fibres had not been uniformly coated with nickel, these concentrations (including 12 g/L) will be further investigated with other plating parameters to determine the optimal plating conditions for cellulose fibres.

Figure 6.10: SEM images of nickel coated cellulose fibres (12% (a), 18% (b), 24% (c) and 30% (d), 15 minutes plating time, plating temperature = 72 °C)

**Trial 4 – Temperature**

Jenvanitpanjakul [156] reported that the amount of nickel deposition increases with temperature. Previous observations from coating nickel on filter paper have proved that the electroless plating reaction does not occur until the temperature of the plating solution reaches 72 °C. The upper limit of 84 °C was chosen since the electrical resistivity of nickel coated filter paper was lower when plated at 84 °C, compared to 72 °C. Table 6.4, Trial 4
shows that both temperatures were investigated with 10 minutes plating time and refreshed once. The SEM images (Figures 6.11a and b) of the resulting nickel coated cellulose fibres revealed that coating coverage was poor and discrete nickel clusters also formed. Where the substrate was refreshed once and plated at 72 °C for 15 minutes, it can be seen from Figure 6.11c that, even though nickel coverage was also poor, there were no discrete nickel clusters. This observation suggests that the plating time and temperature of 15 minutes and 72°C should be further investigated with other plating parameters to determine the optimal plating conditions for cellulose fibres.

Figure 6.11: SEM images of nickel coated cellulose fibres a) refresh once, 10 minutes, 72 °C, b) refresh once, 10 minutes, 84 °C and c) refresh once, 15 minutes, 72 °C)
Trial 5 – amount of nickel available for deposition

The next variable investigated (Table 6.4, Trial 5) was over the ratio of ‘nickel available for deposition’ to ‘cellulose fibres’. Since very few cellulose fibres were coated with nickel when 1.0 g of cellulose fibres were used, a much lower value of 0.2 g was chosen for investigation. This variable was fixed whilst nickel concentration, temperature and number of refreshes were varied. SEM images suggested that plating 0.2 g of cellulose fibres (treated with 20 ml of pre-treatment solution) at 72 °C with nickel concentration of 12.0 g/L produced the most desirable coating characteristics, with most cellulose fibres coated uniformly with nickel (Figure 6.12a). When cellulose fibres (treated with 100 ml of pre-treatment solution) were plated with nickel concentration of 12.0 g/L (Figure 6.12b), although the coating was uniform, nickel clusters also formed. A reproducibility check was carried out on this condition (pre-treatment solution = 20 ml, 15 minutes, 72 °C and 12.0 g/L). Unfortunately, a uniform nickel coating was not reproducible so the effect of increasing nickel concentration to 18.0 g/L was investigated (Figure 6.12c). The result indicated that the coating was primarily made of nickel clusters. Therefore, it was concluded that the nickel concentration, plating temperature and the volume of pre-treatment solution should be kept constant at 12.0 g/L, 72 °C and 20 ml, respectively.
Figure 6.12: SEM images of nickel coated cellulose fibres a) pre-treatment solution = 20 ml, 12% nickel, 15 minutes, 72°C, b) pre-treatment solution = 100 ml, 12% nickel, 15 minutes, 72°C and c) pre-treatment solution = 20 ml, 18% nickel, 15 minutes, 72°C)

Trial 6 – optimisation

The last set of experiments (Table 6.4, Trial 6) incorporated ‘numbers of refresh’. The SEM images of nickel coated cellulose fibres produced from the refreshed once (Figure 6.13) and refreshed twice (Figure 6.14) trials have shown that the nickel coating was uniform with high coverage as well as reproducible. Since there was no clear distinction between each plating condition and both plating conditions demonstrated similar nickel coverage (97% for refresh once and 97.6% for refresh twice), refreshed once was concluded to be the optimal plating condition for producing nickel coated cellulose fibres as it is more cost-effective.

Figure 6.13: SEM images of nickel coated cellulose fibres (pre-treatment solution = 20 ml, 12% nickel, 15 minutes, 72°C, refresh once)
It was concluded that, to uniformly deposit nickel onto cellulose fibres with good coverage, these plating conditions are optimal (Table 6.4, Trial 6).

This condition produces approximately 3 g of nickel coated cellulose fibres per run. The phosphorus content in the coating is approximately 8.4 wt% based on the EDS analysis. This suggests that the nickel content is approximately 91.6 wt%. Therefore, it can be concluded that the amount of nickel deposited is approximately 2.56 g.

As a composite fabrication requires many fibres (up to 50 g per composite panel), a scaling-up process was carried out to produce nickel coated cellulose fibres efficiently. The above conditions were slightly modified, this time produced approximately 14 g of nickel coated cellulose fibres per run. Using the same calculation as previously, the amount of nickel deposited was approximately 9.16 g.

The scaling of volume was decided based on the largest beaker available in the laboratory as well as taking into account the practicality of man-handling large amounts of plating solution at an elevated temperature. The volume of the plating solution and the nickel concentration were both increased to accommodate the increase in the amount of cellulose fibres required to be uniformly deposited with the nickel. Several trials were conducted and it was concluded that the optimal mass of cellulose fibres was 4.0 g. Figure 6.15 illustrates nickel coated cellulose fibres fabricated using the scaled-up conditions.
Figure 6.15: SEM images of nickel coated cellulose produced with scaled up conditions

**Original Nickel Coated Cellulose Fibres (Original NCCF)**

Cellulose fibre which has been coated with nickel using the scaled-up conditions will hereby be referred to as Original NCCF. In respect to the conditions reported in Table 6.4, Trial 6, the ratio of mass of cellulose to the volume of pre-treatment solution was kept constant at 10 g/L, nickel concentration was increased from 12 g/L to 30 g/L (since this was the highest concentration investigated as per Table 6.4), plating temperature was kept constant at 72 °C, plating time was kept constant at 15 minutes, number of refreshes was kept constant at 1, volume of plating solution was increased from 500 ml to 2000 ml, and mass of cellulose fibres was increased from 0.2 g to 4 g. The ‘original’ methodology and conditions were used to prepare the composites. Further optimisation was carried out later to reduce the phosphorus content.

In terms of the elemental composition of the coating, results similar to those for nickel coated filter paper were obtained. The elemental composition of the cellulose fibres was similar to that in Figure 6.1b (uncoated filter paper): only carbon and oxygen peaks were present, which corresponds to cellulose. The EDS spectra of NCCF also suggested that the coating was composed of nickel and phosphorus. The intensity of the carbon and oxygen peaks was low, implying that the coating was uniform, similar to Figures 6.3b and 6.4b (nickel coated filter paper).
The XRD graph of coated and uncoated cellulose fibres is shown in Figure 6.16. The peak at $2\theta = 21.5^\circ$ corresponded to the plastic wrap which was used to hold cellulose pulp onto the sample holder and the peak at $2\theta = 29^\circ$ corresponded to the contamination on the sample holder. The broad peak at $2\theta = 44^\circ$ was identified as poorly crystalline nickel. This nickel layer was thick enough to reduce the background signals from the cellulose fibres and the sample holder.

The electrical conductivity of individual cellulose fibres successfully coated with nickel was not measured individually, as this does not truly represent the electrical conductivity of the interconnected bulk. For practical purposes, measurement was also difficult because of the very small size of the individual fibres. However, there are other methods which can be used to assist in the estimation of the electrical conductivity of nickel coated cellulose fibres.

Parkinson [136] reported that there is a linear correlation between the phosphorus content and the electrical resistivity of nickel coating, as shown earlier in Figure 4.1. Although this correlation is for the electroless deposition of nickel on steel substrate, it is expected that this correlation should also be applicable to electroless nickel deposition onto cellulose fibres, but the exact value of the electrical resistivity will not be the same. This is because, although similar chemicals were used in the electroless plating solution, cellulose fibre is an electrically non-conductive substrate (unlike steel, which is electrically conductive).
The current phosphorus content of the Original NCCF was approximately 8.4 wt%. Therefore, reducing the phosphorus content was expected to increase the electrical conductivity of the coating, which also meant increasing the EMI shielding capability of the Original NCCF.

For the electroless nickel deposition on steel substrate [132], the phosphorus content decreases as the pH of plating solution increases. However, it is also important to note, that the possibility of the electroless plating solution breaking down to form nickel hydroxide increases as the plating solution becomes more alkaline.

Therefore, the maximum pH investigated in this thesis is 7. In comparison, the starting pH of the electroless plating solution used to fabricate the Original NCCF was around 4. For the purpose of improving the electrical conductivity (and EMI shielding capability) of the Original NCCF, several options (including increasing the pH of the plating solution) were investigated. Table 6.5 summarises the optimisation parameters for uniformly depositing nickel onto cellulose fibres with good coverage and improved EMI shielding capability. Unless stated otherwise, all other plating parameters remain the same as those used to produce the Original NCCF.

Reidel [157] suggested that, for the electroless deposition of nickel onto steel, to obtain an optimal deposition rate, the concentration of hypophosphite should be between 0.15 and 0.35 mol/L. Gawrilw [158] suggested that 10kg of sodium hypophosphite is required to deposit 2kg of nickel for an average efficiency of 37%. This means that the ratio of nickel to sodium hypophosphite should be at least 1:5. According to Equation (4.2) under Section 4.2, the pH of the plating solution decreases at the start of the electroless deposition process due to the formation of H+ ion. As a result, the phosphorus content within the coating is expected to increase. Therefore, for the optimisation of plating parameters in this thesis, it is necessary to maintain the pH of the plating solution at about 6 – 7 to minimise the amount of phosphorus deposited along with nickel. A sodium hydroxide solution with a concentration of 1M was added during the deposition process to maintain the pH of the plating solution.

The seventh and eighth (Table 6.5, Trials 7 and 8) trials investigated the effect of the following parameters on the phosphorus content within the nickel coating. These are; the starting pH, maintaining pH with the addition of sodium hydroxide solution and adjusting the concentration of hypophosphite and nickel to observe Reidel’s and Gawrilw’s guidelines.
The seventh trial (Table 6.5, Trial 7) investigated the effect of increasing the starting pH and maintaining pH on the phosphorus content within the nickel coating. The original levels of nickel and hypophosphite concentration of 30g/L were used. For the eighth trial (Table 6.5, Trial 8), Reidel’s and Gawrilw’s guidelines were investigated. The starting concentration of sodium hypophosphite was 0.214 mol/L (22.7 g/L) and the concentration of nickel sulfate was reduced to 8.2 g/L to maintain the ratio of nickel to hypophosphite at 1:7.5 (to make certain that there was enough hypophosphite to reduce nickel) while the starting pH varied between 6 and 7. The results are summarised and discussed below.

The Original NCCF (starting pH = 4) contained 8.4 wt% of phosphorus. When the starting pH was increased from 4 to 7 (Table 6.5, Trial 7, first run), the phosphorus content decreased from 8.4 to 5.8 wt% (-2.6 wt%). The coating was uniform and the coverage was good.

When pH was maintained around 7 during the plating process (Table 6.5, Trial 7, second run) the phosphorus content decreased from 5.8 to 4.7 wt% (-1.1 wt%). As with the previous run, the coating was uniform and the coverage was good.

When Riedel and Gawrilw’s guidelines were used at pH 7 (Table 6.5, Trial 8, first run) the phosphorus content decreased from 8.4 to 2.3 wt% (-6.1 wt%). However, the coating was not uniform and the coverage was poor.

When Riedel and Gawrilw’s guidelines were used at pH 6 (Table 6.5, Trial 8, second run) the phosphorus content increased from 2.3 to 4.0 wt% (+1.7). Similar to the first run, the coating was not uniform and the coverage was poor.

It is clear from these results that increasing the starting pH of the plating solution decreases the phosphorus content within the nickel coating whether or not Riedel and Gawrilw’s guidelines were used. Although the results suggest that using the Riedel and Gawrilw’s guidelines had more impact on the reduction of phosphorus content (Number 4 compared with Number 2), the coating was not uniform and coverage was poor. As previously encountered during the fabrication of the Original NCCF, when nickel coverage on cellulose fibres was poor, suggests that there was not enough nickel available for deposition. Therefore, the concentration of nickel was increased to the original value of 30g/L. In order to keep the ratio of nickel to hypophosphite at 1:7.5, the concentration of hypophosphite was increased to 83g/L (Table 6.5, Trial 9). These conditions deliberately violated Reidel’s guideline in order to determine whether the Reidel or the Gawrilw guideline is the more important one.
The results (Table 6.5, Trial 9) show that the plating reaction was vigorous and pH could not be maintained at pH 7 when sodium hydroxide solution was added. However, the coating was uniform and the coverage was good. Most importantly, the biggest reduction of phosphorus content observed was -6.7 wt%, from 8.4 to 1.7 wt%. This means that this condition produced NCCF with the highest value of electrical conductivity. Additionally, this condition produced a uniform and reproducible nickel coating, with a slight increase in phosphorus content to 2.8 wt%. The result also suggests that Reidel’s guideline does not have a significant effect on depositing a uniform coating on cellulose fibres, or reducing the phosphorus content within the coating. It can be concluded that Gawrilw's guideline is more important, as it has a significant effect on the reduction of phosphorus content within the coating (Number 4 compared with Number 2). In summary, the conditions in Table 6.5, Trial 9, were the most favourable conditions producing nickel coated cellulose fibres with an average phosphorus content of approximately 3 wt%.

**Optimised Nickel Coated Cellulose Fibres (Optimised NCCF)**

Cellulose fibre which has been coated with nickel using the following optimal conditions will hereon be referred to as Optimised NCCF. In respect to the conditions used to prepare Original NCCF, the ratio of mass of cellulose to the volume of pre-treatment solution was kept constant at 10 g/L, the nickel concentration was kept constant to 30 g/L, the sodium hypophosphite concentration was increased from 30 g/L to 83 g/L, the plating temperature was kept constant at 72 °C, the plating time was kept constant at 15 minutes, the number of refreshes was kept constant at 1, the volume of plating solution was decreased from 2000 ml to 500 ml, and the mass of cellulose fibres was decreased from 4 g to 0.2 g, the starting pH of the plating solution was increased from 4 to 7, the volume of sodium hydroxide added during electroless plating was increased to from 0 to 500 ml and the concentration of sodium hydroxide solution was 40 g/L.
Table 6.5: Table of trials to determine the optimal electroless plating conditions to uniformly deposit nickel onto cellulose fibres with good coverage and improved EMI shielding capability

<table>
<thead>
<tr>
<th>Trial</th>
<th>Plating Solution (ml)</th>
<th>Concentration of Nickel sulphate (g/L)</th>
<th>Concentration of Sodium Hypophosphite (g/L)</th>
<th>Starting pH</th>
<th>Volume of Sodium Hydroxide added during plating (mL)</th>
<th>Average Phosphorus Content (wt%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>500</td>
<td>30</td>
<td>30</td>
<td>4</td>
<td>0</td>
<td>8.4</td>
<td>Original NCCF</td>
</tr>
<tr>
<td>7</td>
<td>500</td>
<td>30</td>
<td>30</td>
<td>7</td>
<td>0</td>
<td>5.8</td>
<td>Uniform coating, good coverage</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>30</td>
<td>30</td>
<td>7</td>
<td>500 at 1M</td>
<td>4.7</td>
<td>Uniform coating, good coverage</td>
</tr>
<tr>
<td>8</td>
<td>500</td>
<td>8.2</td>
<td>22.7</td>
<td>7</td>
<td>0</td>
<td>2.3</td>
<td>Coating is not uniform, poor coverage</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.2</td>
<td>22.7</td>
<td>6</td>
<td>0</td>
<td>4.0</td>
<td>Coating is not uniform, poor coverage</td>
</tr>
<tr>
<td>9</td>
<td>500</td>
<td>30</td>
<td>83</td>
<td>7</td>
<td>500 at 1M</td>
<td>1.7</td>
<td>Vigorous reaction, pH could not be maintained at 7. However, coating was uniform, good coverage. Coating is uniform, good coverage, phosphorus content varied</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>30</td>
<td>83</td>
<td>7</td>
<td>500 at 1M</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2000</td>
<td>30</td>
<td>83</td>
<td>7</td>
<td>250 at 7M</td>
<td>-</td>
<td>Poorly coated, scaling up unsuccessful.</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>30</td>
<td>83</td>
<td>7</td>
<td>250 at 7M</td>
<td>-</td>
<td>Poorly coated, scaling up unsuccessful.</td>
</tr>
</tbody>
</table>
Scaling up the production of Optimised NCCF

Similar to the scaling up production of the Original NCCF, for the purpose of composite production, an attempt to scale up the production of Optimised NCCF was also conducted. Ideally, based on the previous success (Table 6.5, Trial 9), the volume of sodium hydroxide solution added during the plating reaction, should be the same as the volume of the plating solution, such that, 2000 ml of plating solution will require 2000 ml of 1M sodium hydroxide solution. This condition is very difficult for laboratory-scale experiments because the addition of a large amount of sodium hydroxide solution at room temperature may reduce the temperature of the bath below the temperature required for the plating reaction. Additionally, preheating sodium hydroxide solution was not an option due to technical difficulties. Therefore, instead of adding 2000 ml of 1M sodium hydroxide solution, only 250 ml of sodium hydroxide solution was used but in a higher concentration (7M). This value was chosen as a trial value, as well as for the purpose of maintaining the amount of hydroxide ions present in 250 ml at 7M, so that it is similar to the values present in 2000 ml at 1M sodium hydroxide solution. Unfortunately, the scale-up was unsuccessful, as the cellulose fibres were poorly coated with nickel. As mentioned in the comments section for Table 6.5 (trial 9, first run), vigorous reactions occurred when plating conditions which produced uniform coating on cellulose fibres with lower phosphorus content were used. For this reason, as well as that mentioned above, there were too many complications when the plating reaction was done at high volume (>2L). Another major complication was that the hydrogen evolution during the initial electroless plating reaction was so high that it pushed cellulose fibres along with the plating solution outside the beaker. Additionally, a large amount of hydrogen evolution could potentially become quite dangerous in an enclosed space. Therefore, it is necessary to ensure that there is a system to remove the hydrogen gas. Furthermore, since there is a tendency for cellulose fibres to float on top of the plating solution, it is essential to ensure that there is sufficient mixing to maximise contact between cellulose fibres and the plating solution. It was concluded that any further scaling-up of the process would require a major redesign of the electroless plating apparatus, as well as a significant amount of trial and error. As scaling-up is not the primary focus of this thesis, further attention was directed towards the fabrication of nickel coated cellulose fibre composite.
Summary

The coating of uniform nickel was optimised for cellulose fibres. The effects of temperature, concentration, time, volume of pre-treatment solution, mass of cellulose fibres, initial pH of plating solution, the maintaining of pH throughout the plating process and the ratio of mass of cellulose fibres to the volume of pre-treatment solution were investigated to determine the optimal conditions. Two types of nickel coated cellulose have been fabricated, both with uniform and fully covering coatings, but with differing amounts of phosphorus content. The Optimised NCCF had a lower phosphorus content (3 wt%) than the Original NCCF (8.4 wt%). It was later proven that the Optimised NCCF possesses higher electrical conductivity than the Original NCCF, and thus has higher EMI shielding capability.

Within the scope of this study, the production rate of Optimised NCCF (3 grams per run) is much lower than Original NCCF (14 grams per run). It may be possible to scale-up the production of Optimised NCCF by redesigning the experimental setup, as demonstrated in the case of Original NCCF. However, the merits of both types in EMI shielding are the objectives of the next stages of the research. Both the Original NCCF and the Optimised NCCF will be fabricated into composites and their material properties (including EMI shielding effectiveness) will be extensively characterised.

During the process of optimising phosphorus content, the applicability of the longstanding Reidel and Gawrilw guidelines (for ease of reference, listed in the following paragraph) were tested for cellulose fibres. Cellulose fibres are non-conductive substrate so an activation step is required, this may affect the electroless deposition chemistry. Furthermore, cellulose fibres are porous so there is potentially more area to deposit nickel.

Reidel suggested that the concentration of hypophosphite should be between 0.15 and 0.35 mol/L, Gawrilw reported that 10 kg of sodium hypophosphite is required to deposit 2 kg of nickel for an average efficiency of 37 %.

When both Reidel and Gawrilw’s guidelines were adhered to, the phosphorus content of the nickel coating was significantly reduced, but the coverage of nickel coating on cellulose fibres was poor. However, when Reidel’s guideline was disregarded and only Gawrilw’s guideline was followed, the phosphorus content was reduced to the same extent as when both Reidel and Gawrilws’ guidelines were satisfied. The only difference was that nickel was now uniformly deposited on cellulose fibres. It can be concluded that, to achieve a uniform
deposition of nickel on cellulose fibres with lower phosphorus content, only Gawrilw’s guideline needs to be satisfied.
Chapter 7

Developing NCCF and SSF Composites

Stage Three focused on the incorporation of nickel coated cellulose fibres (NCCF) into polypropylene via compression moulding to create an electrically conductive composite for EMI shielding. Compression moulding was chosen as it minimises fibre breakage as well as maintaining random distribution of fibres within the polymer matrix. A standard EMI shielding composite based on commercially available SSF (Stainless Steel Fibres) was also fabricated for a comparison with the NCCF composite.

7.1 NCCF and SSF Composites – Experimental Procedures

Fabrication of NCCF composites

The matrix used to form a composite with NCCF was polypropylene (PP) fibres. PP fibres (Atofina, provided by FiberVision, USA), exhibits dimensions of 23μm in width and 5mm in length. The fibre has a melting point of approximately 165-166 °C and contains an undisclosed compatibiliser. PP fibres were chosen because they are cheap, easy to use and readily available. Furthermore, researchers at Scion have had many experiences preparing and testing cellulose fibre composites based on PP fibres. Compression moulding was used as composite fabrication technique to maintain the aspect ratio and random distribution of the NCCF within the composite. Firstly, 100 g mixture of PP and NCCF was blended in a 10L bucket full of water (10 g/L) for approximately 5 minutes. Then, the blended mixture was poured through a sieve and pressed with a tamper into compression pads. The compression
pads were dried in the oven at 105 °C for approximately 24 hours. Once dried, the pad was pressed at 180°C for 3 minutes inside a mould under a constant 200 kN load. The composite panel was allowed to cool under pressure until the temperature was approximately 100 °C, and then it was removed from the mould. The dimensions of composite panels are approximately 170 x 170 x 3 mm. The compression moulded 40 wt% Original NCCF composites demonstrated a high level of porosity. Figure 6.1 illustrates the level of porosity present in the Original NCCF composites initially prepared.

![Figure 7.1: Porosity of compression moulded Original NCCF composite](image)

The compression moulding time and temperature which was used to fabricate the Original NCCF composite were 180°C and 3 minutes, respectively [159]. Many factors can cause porosity, such as not enough material in the mould, compression pads were not dried enough, or unsuitable compression moulding time and temperature. These factors were investigated and optimised to eliminate porosity, as shown in Table 7.1.

The first and second runs shown in Table 7.1 indicated that a composite with a low loading of Original NCCF (10 wt%) shows no sign of porosity. The problem with porosity is that it only occurred at high loading of Original NCCF, greater than 20 wt%. The result with the 40 wt% Original NCCF loading is shown as a representative sample in Figure 7.1. The porosity was attributed to the smaller moulded volume of materials in the case of Original NCCF compared to uncoated cellulose fibres. With dense nickel coating, Original NCCF is heavier than uncoated cellulose fibres. Thus, there will be a greater number (or more volume) of uncoated cellulose fibres than that of Original NCCF for the same mass.

For example, 100g of 40 wt% uncoated cellulose fibres composite can be broken down into 60g (66.7cm³) of PP and 40g of uncoated cellulose fibres (33.3cm³) so the total volume is 100cm³. In contrast, 100g of 40 wt% of Original NCCF composite can be broken down into 60g (66.7cm³) of PP and 40g of Original NCCF (27cm³), making a total volume of 93.7cm³. The recommended conditions were specifically designed for compression moulding of at least 100cm³ of material. When the volume of material was less than 100cm³, the formation of a porosity-free composite was unsuccessful.
Table 7.1: Table of trials to determine the optimal compression moulding conditions to fabricate a porosity-free Original NCCF composite

<table>
<thead>
<tr>
<th>Run</th>
<th>Mass of Compression Pad (g)</th>
<th>Mass of Original NCCF (wt%)</th>
<th>Mass of PP (wt%)</th>
<th>Pressing Temperature (°C)</th>
<th>Pressing Time (minutes)</th>
<th>Drying Time (hours)</th>
<th>Thickness of Composite (mm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>10</td>
<td>90</td>
<td>180</td>
<td>3</td>
<td>24</td>
<td>3</td>
<td>No porosity</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td><strong>40</strong></td>
<td><strong>60</strong></td>
<td>180</td>
<td>3</td>
<td>24</td>
<td>3</td>
<td>Small leaking, medium level of porosity</td>
</tr>
<tr>
<td>3</td>
<td><strong>120</strong></td>
<td>40</td>
<td>60</td>
<td>180</td>
<td>3</td>
<td>24</td>
<td>3</td>
<td>Leakage occurred during pressing, high level of porosity</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>40</td>
<td>60</td>
<td>180</td>
<td>3</td>
<td>24</td>
<td>2</td>
<td>Leakage occurred during pressing, high level of porosity</td>
</tr>
<tr>
<td>5</td>
<td><strong>120</strong></td>
<td>40</td>
<td>60</td>
<td>180</td>
<td>3</td>
<td>24</td>
<td>2</td>
<td>Leakage occurred during pressing, high level of porosity</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>40</td>
<td>60</td>
<td>180</td>
<td>3</td>
<td><strong>72</strong></td>
<td>3</td>
<td>No differences from 24 hours of drying time</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>40</td>
<td>60</td>
<td><strong>200</strong></td>
<td>5</td>
<td>24</td>
<td>3</td>
<td>Massive leakage occurred during pressing, very high level of porosity</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>40</td>
<td>60</td>
<td>170</td>
<td>5</td>
<td>24</td>
<td>3</td>
<td>No porosity</td>
</tr>
</tbody>
</table>
This problem did not occurred for a composite with 10 wt% of Original NCCF because, based on a 100g panel, the composite can be broken down into 90g of PP (100cm$^3$) and 10g of Original NCCF (6.25cm$^3$), making the total volume of 106.25cm$^3$. As the volume of material was greater than 100cm$^3$, this was sufficient and a composite with no observable porosity was formed. For the third, fourth, and fifth runs, the factors which affect the volume of material presented in the mould were investigated.

The 40 wt% of Original NCCF composites in the third, fourth and fifth runs, shown in Table 7.1, were prepared together. For the third run, the mass of compression pad was increased to 120g: 72g of PP (80cm$^3$) and 48g of Original NCCF (30cm$^3$), making the total volume of 110cm$^3$. This should be more than enough material so it was expected that a better result would be achieved. All other processing parameters were kept the same unless otherwise stated. However, there were leakages from the mould and the composite had more porosity than the 40 wt% Original NCCF composite prepared using the recommended conditions. For composites prepared in the fourth (thickness of spacer was reduced to 2mm) and the fifth runs (thickness of spacer was reduced to 2mm, mass of compression pad was increased to 120g) and similar observations to the third run were made. It was concluded that there are other important factors which affect the formation of Original NCCF composite with no observable porosity.

As the compression pads were formed in water, it was also possible that the pads were not dry enough. Moisture content is an important factor which can cause porosity. If a compression pad with a high level of moisture was compression moulded, high temperature in the mould can cause water to evaporate rapidly, leaving porosity in the composite. The change in conditions for the sixth run in Table 7.1 was increasing the drying time to three days to make certain that the composite had dried sufficiently. There was no observable difference to the composite which was dried for one day. This suggested that drying for one day was enough to remove any excess water which could cause porosity.

It is possible that the compression moulding time and temperature was not optimal for fabricating the Original NCCF composite. The change in condition of the seventh run in Table 7.1 was increasing moulding temperature and time to 200°C and 5 minutes. The results indicated that this condition was the worse as there was massive leaking from the mould. It was concluded that there was too much flow in PP at 200°C so the moulding temperature was reduced to 170°C for the eighth run while keeping moulding time constant at 5 minutes.
Using this condition, a porosity-free Original NCCF composite was successfully fabricated (Figure 7.2). It was necessary to lower the temperature because; firstly, the original NCCF conducts heat better than uncoated cellulose fibres do, this is due to the presence of nickel and secondly, nickel has a much lower heat capacity than cellulose fibres.

For the same weight percent of filler loading, there are more cellulose fibres in the composite containing uncoated cellulose fibres than those containing the Original NCCF. For example, 100g of 40 wt% uncoated cellulose fibres composite contained 40g of cellulose fibre while 100g of 40 wt% of the Original NCCF composite contained 11.4g of cellulose fibre. Since nickel has a much lower heat capacity than cellulose fibre, for the same amount of heat supplied, the temperature of the 40 wt% Original NCCF composite during compression moulding was slightly higher than the 40 wt% uncoated cellulose fibre composite. This could be why the polymer leaked from the mould.

![Figure 7.2: SEM image of cross-section of compression moulded Original NCCF composite. (bright areas indicate nickel coated cellulose fibres)](image)

**Fabrication of SSF composites**

It was initially proposed that SSF composites should be prepared in the same manner as NCCF composites. Since the SSF was supplied in pellet form, it was necessary to process into loose SSF prior to composite fabrication. The process involved dissolving the thermoplastic polyester sizing and coating to obtain SSF, followed by high-speed mechanical agitation which produced loose SSF. These loose SSFs were then fabricated into SSF composites by blending in water with PP fibres, pressed into compression pads, oven-dried
and compression moulded into composite panels (same as in the fabrication of NCCF composites).

Unfortunately, for the SSF composites fabricated via compression moulding, lumps of SSF could be seen on the composites indicating poor dispersion of the SSF within the PP matrix. It was concluded that the technique used to fabricate NCCF composites was not suitable for fabricating SSF composites. Therefore, both SSF and PP were processed from pellet form into composite via injection moulding as recommended by the supplier.

There are two approaches for fabricating composite via injection moulding. The first approach involves dry blending SSF and PP pellets followed by injection moulding. The second approach involves compounding SSF and PP pellets into SSF/PP pellets followed by injection moulding. Both approaches were attempted and it was concluded that the second approach produced composite with better fibre dispersion than the first approach. This is because the compounding stage helps to uniformly disperse the SSFs within the PP matrix.

As fibre dispersion is important for EMI shielding, the second approach was used to fabricate SSF composite for characterisation. Both the compounding and injection moulding steps took place at 220 °C. Furthermore, composite fabrication via compounding plus compression moulding was also investigated. However, the surface finish of the composites was not as good as those fabricated via compounding plus injection moulding.

SSF was supplied by Bekaert (Japan) as 5 mm pellets. Each pellet contained 75 wt% of SSF (8 microns diameter), 10 wt% of thermoplastic polyester sizing and 15 wt% of ionomer coating. SSF is very fluffy so it needs to be bind with the polyester sizing before the palletisation process. Both sizing and coating material help to maintain the shape of the SSF pellets during transportation. Additionally, the coating assists the dispersion of SSF into the base polymer. This grade is suitable when polypropylene is the base polymer and the processing temperature is below 290 °C. Injection moulding was used to prepare the SSF composites since it is the method used for the fabrication of commercial EMI shielding composites. Additionally, PP copolymer pellets (AR564) supplied by Sumitomo Chemical Asia were used as the polymer matrix. These PP pellets do not contain a compatibiliser. Since the polymer matrix and filler are both in pellet form, they were compounded before injection moulding in order to obtain a good dispersion of fibres within the composite as well as minimising fibre orientation. PP and SSF pellets were compounded at 220 °C with a twin crew extruder speed of 50 rpm, with different filler loadings. The compounded materials
were pelletised into 3 mm pellets. Prior to injection moulding, the SSF/PP pellets were dried overnight at 70 °C. The injection moulding was undertaken by a plastic injection moulding company called ES Plastic at 220°C; the injection moulding enabled plaques with approximate dimensions of 300 x 220 x 3 mm to be produced. These plaques were subsequently cut down into 150 x 150 x 3 mm panels before characterisation could be done. These dimensions were selected as they are the preferred dimensions for EMI SE measurement. Similarly, PP panels were also fabricated for control purposes.

A series of composites with varying amounts of NCCF and SSF were fabricated for the purpose of characterizing their EMI SE, surface resistivity, volume resistivity and flexural strength. The EMI SE and surface resistivity measurements were performed on each composite panel (with approximate dimensions of 150 x 150 x 3 mm). The composite panel was then cut into nine strips (with approximate dimensions of 15 x 150 x 3 mm). Volume resistivity and flexural strength measurements were performed on each composite strip. Next, a strip near the centre of the composite panel was cut into four sections (with approximate dimensions of 15 x 30 x 3 mm). The middle sections were chosen for analysis with micro-CT to minimise edge effects. The illustration that follows (Figure 7.3) shows how samples were prepared from the main panel for the various materials characterisations.

Several material properties of NCCF and SSF composites were characterised, including EMI shielding effectiveness (EMI SE), surface resistivity and flexural strength.

Additionally, smaller pieces of a composite sample (approximate dimensions of 5 x 5 x 3 mm) were analysed using the SEM.
Figure 7.3: Illustrations of the characterization process of the NCCF and SSF composites
Characterisation Techniques

EMI SE analysis for NCCF and SSF composites:

EMI SE measurement is a simple test which utilises a signal generator, a coaxial cable and a sample holder. After the test sample is inserted into the sample holder, signals are generated at the required frequency (30 MHz – 1.5 GHz) and sent through the coaxial cable. Figure 7.4 below illustrates the schematics of EMI SE measurement. EMI SE values were calculated by comparing the intensity of the signal transmitted through the test sample, to the incident signal. EMI SE results were used to determine the feasibility of using the test composite for EMI shielding application.

![EMI SE measurement schematic](image)

Figure 7.4: “Coaxial Transmission Line Test,” RTP Company technical presentation 2014-09-05, Spectrum Analyzer/Tracking Generator illustration provided as a courtesy by RTP Company [160]

Electrical Resistivity

Surface resistivity measurements were carried out by placing test samples between a Megohmeter and a guarded ring. The electrode was energised with the desired voltage (500V for non-conductive materials) and the electrode was allowed 60 seconds to be energised before the measurement could be taken. The range on the Megohmeter was adjusted to obtain the most accurate measurement of resistivity. These surface resistivity values were used to determine the percolation threshold of the composite because it was conducted on the composite panel, which is similar to how EMI SE was measured. This allowed direct correlation between surface resistivity and EMI SE.
Volume resistivity measurement was done by placing composite strips sandwiched between the top and bottom terminals of the four-point probe apparatus. The top terminal had two points-of-contact while the bottom terminal had four points-of-contact with the composite. The two outermost contacts (for both terminals) were 100 mm apart and the two innermost contacts were 18 mm apart. An electrical current was supplied to the outer terminals and the voltage drop between the two inner probes was determined. The volume resistivity was calculated using the following equation:

\[ \rho = \frac{V W t}{1.8 I} \]  

(7.1)

Where \( \rho \) is the volume resistivity of the composite (ohm.cm), \( V \) is the voltage between the two inner probes, \( W \) is the width of the sample, \( t \) is the thickness of the sample and \( I \) is the current. Although surface resistivity was used to predict percolation threshold, the values of surface resistivities are average across a region of interest. The volume resistivity results are more accurate as the measurements were conducted over a smaller region. These values were used to assist the determination of percolation threshold.

**Mechanical properties analysis for NCCF and SSF composites**

The three-point bending test was done to determine the flexural strength of the composite. Composite strips with dimensions of approximately 150 x 15 x 3 mm were placed on the three-point bending apparatus which was set up on an Instron machine. The length of the span was 50 mm. Load was applied to the centre of composite strip at a rate of 0.1 mm/s until maximum flexural was observed. This test is commonly used to measure the flexural strength of composites. Results were used to compare the mechanical properties of NCCF composite with SSF composite.

**Sample preparation for the SEM/EDS analysis of NCCF and SSF composites**

A small sample of NCCF composite was prepared using a hand saw. Composite samples were attached to a metal clip before placing into the mould to maintain the stability of the composite as well as to ensure that the composite would not float during the mounting process. NCCF composite samples were mounted onto epoxy resin and the surface of NCCF composite samples were ground and polished in following order: 400 grit SiC paper for 30 - 60 seconds, 800 grit SiC paper for 30 - 60 seconds, 1200 grit SiC paper for 30 - 60 seconds, 6
micron diamond solution for 30 - 60 seconds, 3 micron diamond solution for 30 - 60 seconds, 1 micron diamond solution for 30 - 60 seconds.

The mounted NCCF composite samples were also coated with platinum. The accelerating voltage was 20 kV, the spot size was 4 and a backscatter electron was used.

Stainless Steel Fibres (SSF) composite used for SEM characterisation were prepared and analysed in the same manner.

**Computer tomography and image analysis for NCCF and SSF composites**

Micro CT is a radiographic imaging technique that can produce 3D images of a material's internal structure at a spatial resolution better than 1 micrometer. The technique is non-destructive for many materials so that the samples can be scanned many times in different conditions. The sample preparation is also quite simple. The technique is complementary to higher resolution 2D microscopy and lower resolution 3D ultrasonic imaging [161]. Micro CT originated from Computerized Axial Tomography (CAT or CT) scans for which have been used for medical imaging for 40 years [162, 163]. Although computerised tomography was initially used for medical imaging, the possibility of generating a 3D model of the internal structure led to an adaptation of the technique in the field of material science.

The computer tomography (micro-CT) used in this research was Skyscan 1172 (Bruker MicroCT). Camera specification of 10 megapixels, (4000x2300), 12 bit digital, cooled CDD coupled by fibre optic to scintillator (50 mm field of view). This machine uses x-ray tomography to generate 3D data sets of specimens measuring up to 55 x 55 x 55 mm. Resolutions of 2µm are possible and a wide range of specimens can be examined, from food to teeth. Micro-CT uses x-rays to scan an object, which then produces a series of 2-D images. The thickness of each image slice depends on the resolution setting on the camera used to capture the images.

The NCCF composite was cut into small sizes with approximate dimensions of 15 x 40 x 3 mm. Each sample was scanned along its length which produces approximately 2000 slices of images. The image pixel size is 8.63 µm. The cone beam X-ray source was set to be 49 kV, giving a beam current of 200 µA and 0.5 mm of Al filter was applied. A Hamamatus 10 Mp camera was used.
Stainless Steel Fibre (SSF) composites used for microCT characterisation were prepared and analysed in the same manner.

**Image analysis [164]**

Images obtained from the microCT were combined into stacks and analyzed using image analysis software, ImageJ. The steps are illustrated in Figure 7.5. Firstly, a series of images were combined into stack and converted into 8-bit images. Then, an area inside the composite was selected and cropped. Finally, the function called “3D Object Counter” [165] was used to analyze the connectivity of fibres. The threshold was automatically selected to distinguish between fibre and matrix.

Once this function has been executed, the program will start scanning the first image of the stack. When a white pixel is discovered, the program will mark it with a number and then search for nearby white pixels. If white pixels are found in the immediately adjacent pixels, they are considered to be connected as one cluster. Connection defined in this fashion reflects both the physical contacts, and those deemed to be so, as the result of micro-CT spatial resolution and subsequent thresholding in ImageJ. The program will continue scanning the remaining pixels on the first image, adding them to a connected object or counting them as separate ones. Once the first image has been scanned, the program will start scanning the second image in the stack.

Once all images have been scanned, the program will run through the stack again to determine if there are any white pixels which are connected between the images in the stack. If there are white pixels connected between the images, they are considered as a 3D cluster and are marked as one cluster. At the end of the program, the function will output a text file listing the number of 3D clusters found in the stack.

As previously described in Section 3.1, the percolation threshold describes the connectivity of random or aligned particles (or fibres) which span across the entire matrix. Therefore, the lowest result obtainable from the “3D object counter” would be that there is only one 3D cluster spanning the entire matrix. However, a percolation threshold can be reached at a much higher number of 3D objects because the percolation threshold does not require all 3D objects to be inter-connected. This tool can be used to approximate the continuity within the composites.
7.2 Electrical Resistivity of SSF and NCCF Composites

SSF composites

The surface resistivity of composite panels with different filler loadings was measured. Figure 7.6 illustrates the results of the surface resistivity measurements of the SSF composites. The percolation threshold of the composite is estimated to be approximately 50 – 75 % within the transition region. Therefore, the percolation was estimated at 10 wt%. This is an acceptable threshold; as earlier research has suggested, the percolation threshold of SSF composite should be around 6 – 12 wt% [7].
In terms of volume resistivity, the most interesting result obtained was from the composite containing 8 wt% SSF. In Figure 7.7 these composites were broken down into three regions. Region 1 is deemed to be the electrically non-conductive region. Regions 2 and 3 have moderate and good electrical conductivity, respectively. The principle which was used to justify this selection will be explained later. Since most composite strips were in the electrical non-conductivity region (40 strips out of 54), global conductivity could not be established throughout the entire composite panel fabricated with 8 wt% SSF. As a result, the entire composite panel remained electrically non-conductive. This observation agreed with the trend observed in Figure 7.6, which suggests that the 8 wt% composite panel had not reached the percolation threshold.

For the composites which have reached percolation threshold, (12, 16 and 20 wt%), only the electrically conductive region was observed; the composite containing 16 wt% SSF in Figure 7.8, was chosen for illustration purposes. In contrast, for the composites containing less than 8 wt% SSF (i.e. 4 wt%), only the electrically non-conductive region was present; Figure 7.9 illustrates the volume resistivity profile of the composite containing 4 wt% SSF.

These results suggest that the percolation threshold was nearly reached in the 8% SSF composite.
Figure 7.7: Volume resistivity profile of injection moulded SSF composite at 8 wt% loading

Figure 7.8: Volume resistivity profile of injection moulded SSF composite at 16 wt% loading
Figure 7.9: Volume resistivity profile of injection moulded SSF composite at 4 wt% loading

In relation to their electrical properties, both surface and volume resistivity measurements showed that the composites containing 16 and 20 wt% SSF are electrically conductive. The surface resistivity measurement of SSF composite in Figure 7.6, indicated that the attainment of the percolation threshold has a more significant impact than obtaining higher electrical conductivity. This can be seen in Figure 7.10 which illustrates that, when the surface resistivity of the composites decreased by 5 orders of magnitude (4 to 8 wt%), EMI SE increased by approximately 8 dB. However, when the surface resistivity of the composites decreased by 2 orders of magnitude (8 to 12 wt%) as well as reaching the percolation threshold, EMI SE increased by approximately 15 dB. This suggests that connected fibres are able to shield electromagnetic radiation more effectively than is the case with individually isolated fibres as connected fibres combine to shield electromagnetic radiation. This is because there are fewer leakages of electromagnetic radiation through a connected fibres matrix.

Figure 7.10 also demonstrated that the EMI SE is between 0 and 10 when the surface resistivity is between $10^7$ and $10^{12}$ ohm/cm$^2$. In relation to Figure 7.7, this was approximated to be the non-conductive region (region 1). The moderate electrically conductive region (region 2) was approximated to be between $10^5$ and $10^7$ ohm/cm$^2$ when EMI SE is between 10 and 25 dB. The good electrically conductive region (region 3) was approximated to be
below $10^5$ when the EMI SE is between 25 and 45 dB. The principle of selecting these three regions will be applied to Original NCCF and Optimised NCCF as well.

![EMI SE of SSF composite at different surface resistivity](image)

**Figure 7.10**: EMI SE of SSF composites and their respective surface resistivity

**Original NCCF composites**

There is a great variability in terms of the density of NCCF (1.2 – 3.4 g/cm$^3$). Therefore, the properties of NCCF composites are reported in terms of weight fraction to maintain accuracy. The comparison between NCCF and SSF composite in terms of fibre volume fraction was done using the average density value of 2.3 g/cm$^3$ for NCCF and 7.93 g/cm$^3$ for SSF. Since the density of SSF is approximately 3.4 times the average density of NCCF, this means that the weight fraction of SSF composites should be approximately 3.4 times higher than NCCF composites for the same volume fraction. The percolation threshold of SSF composites is approximately 1.25 volume percent, which is a reasonable approximation to the value in Figure 3.2. This suggests that, if SSF and NCCF exhibits the same aspect ratio, then the percolation threshold of NCCF composites should be approximately 1.25 volume percent as well. However, instead of 10 wt% require for SSF (1.25 volume percent), only about 3.13 wt% of NCCF is required (1.25 volume percent). Since the aspect ratio of NCCF (approximately 42), is much lower than that of SSF (approximately 625), the percolation threshold of NCCF
composites should be higher than 1.25 volume percent. This is reinforced by literature data (Figure 3.2) which suggests that, for fillers with an aspect ratio of 42, percolation threshold occurs at approximately 9 percent by volume. This means that the percolation threshold should be between 11.6 and 27.2 percent by weight.

Similar to SSF composites, the surface resistivity of Original NCCF composites was also measured. Figure 7.11 illustrates the surface resistivity measurement of Original NCCF composites. It can be seen that the percolation threshold of Original NCCF composite is approximately 45 wt% based on the surface resistivity measurement. There are many factors which could contribute to the variation between measured percolation threshold and calculated percolation threshold. These factors are fibre length distribution, fibre flexibility, fibre electrical conductivity and fibre distribution.

As the percolation threshold was approximated from the average aspect ratio of cellulose fibres, the actual percolation threshold may be different. In reality, there are many fines and cellulose fibres with an aspect ratio below 42. The distribution of fibre length due to fines and shorter fibres means that not every NCCF would have an aspect ratio of 42. As a result, the percolation threshold of NCCF composite is higher than expected.

According to literature, the bending and entanglement of fillers can reduces the influence of aspect ratio on percolation threshold [116, 125]. As flexibility promotes bending and entanglement, the effective aspect ratio would be lower than the actual which in turn increases the percolation threshold of NCCF composite.

Since cellulose fibres are electrically non-conductive, it is very important to uniformly and completely deposit nickel onto individual cellulose fibres to ensure that every individual fibre is electrically conductive. Otherwise, even if there is a global connectivity between fibres throughout the matrix, the percolation threshold will not be reached if some of the fibres are not fully coated with nickel. This is because contact between two or more fibres may occur at poorly coated (non-conductive) sites.

The distribution of fibres within the polymer matrix could be another reason that the percolation threshold is higher than expected. If the distribution of fibres is uneven/clustering then more fibres is required to achieve global connectivity. Hence, the percolation threshold could be higher.
The Original NCCF composites demonstrated a similar trend of volume resistivity profile compared to SSF composites. Figure 7.12 illustrates the exhibition of three regions (similar to Figure 7.7), which again suggests that only parts of the composite had reached the percolation threshold and had become electrically conductive. Region 1 is deemed to be the electrically non-conductive region. Regions 2 and 3 have moderate and good electrical conductivity, respectively. Most of the composite panel at 40 wt% of Original NCCF is in the electrically non-conductive region (region 1) and there are several strips which are in the moderate electrically conductive region (region 2). This is slightly different from what was observed for the 8 wt% of the SSF composite panel. However, the fact that some strips are within region suggests that this is the onset of achieving the percolation threshold. It is also important to note that the electrical conductivities of Original NCCF composites are generally lower than those for SSF composites.
For the Original NCCF composites, which reached the percolation threshold (50 and 60 wt%), only the electrically conductive region can be seen; a composite containing 50 wt% of Original NCCF was chosen for illustration purposes, as shown in Figure 7.13. In contrast, for the Original NCCF composites below 45 wt% (10, 20, 30 and 40), all the measured panel is an electrically non-conductive region. Figure 7.14 illustrates the volume resistivity profile of a composite containing 20 wt% Original NCCF. For the percolated Original NCCF and SSF composites, the volume resistivity of the 50 wt% Original NCCF composite and the 12 wt% SSF composite were approximately $10^6$ and $10^2$ ohm.cm, respectively, indicating that the electrical conductivity of the SSF is higher than that of the Original NCCF. This is because the SSF is 100% pure stainless steel (i.e. 100% conductor) whereas the nickel coating deposited on filter paper and cellulose fibres is a compound of nickel (conductor) and phosphorus (insulator) and fibres (insulators). As illustrated earlier, the presence of phosphorus increases the electrical resistivity of the nickel coating.
Figure 7.13: Volume resistivity profile of compression moulded Original NCCF composite at 50 wt% loading

Figure 7.14: Volume resistivity profile of compression moulded Original NCCF composite at 20 wt% loading

**Optimised NCCF composites**

Figure 7.15 illustrates that the percolation threshold of the Optimised NCCF composites had significantly decreased from 45 wt% to 15 wt%. Although the aspect ratio is similar for both cases, other factors such as coating coverage and quality can also affect the percolation
threshold. The reduction in the percolation threshold could be due to the improvement in the conductivity of the coating as a result of the reduction in phosphorus content as well as the formation of coating with better coverage.

![Surface Resistivity of Optimised NCCF Composite](image)

**Figure 7.15: Surface resistivity of the compression moulded Optimised NCCF composite at different loading**

However, volume resistivity measurement (Figure 7.16) illustrates that the composite containing 20 wt% Optimised NCCF was electrically non-conductive, with consistent high resistivity similar to pure PP. This measurement does not support the percolation threshold presumed at 15 wt% Optimised NCCF by surface resistivity measurement (Figure 7.15). Furthermore, the volume resistivity measurement of composite containing 40 wt% seems to suggest that the percolation threshold occurred above 40 wt% loading. Figure 7.17 illustrates that the composite containing 40 wt% Optimised NCCF exhibited both electrically conductive and non-conductive regions, similar to those observed in Figure 7.7 (8 wt% SSF composite) and 7.12 (40 wt % of Original NCCF composite). It can be seen in Figure 7.18 that, for Optimised NCCF composite at 50 wt % loading, all composite strips are in the good electrically conductive region (region 3). It is important to note that, for composites with filler loading above the percolation threshold, the volume resistivity of Optimised NCCF composites is lower than that of the Original NCCF composites but not as low as that of SSF composites.
Figure 7.16: Volume resistivity profile of the compression moulded Optimised NCCF composite at 20 wt% loading

Figure 7.17: Volume resistivity profile of the compression moulded Optimised NCCF composite at 40 wt% loading
Figure 7.19: Volume resistivity profile of the compression moulded Optimised NCCF composite at 50 wt% loading

7.3 EMI SE of SSF and NCCF Composites

SSF composites

The EMI SE of the SSF composites at different loadings are summarised in Figure 7.19. The general trend was that EMI SE increases with SSF loading. This is to be expected because, as SSF loading increases, there are more SSF available to shield electromagnetic radiation. Another important feature of Figure 7.19 is that the largest increase in EMI SE of approximately 15 dB occurred between the composites containing 8 wt% SSF (below percolation threshold) and that with 12 wt % SSF (above percolation threshold). It can be seen that composites containing 16 and 20 wt% SSF have reached the commercial EMI shielding standard of 30 – 40 dB. It is interesting to see that the necessary SSF loading required for commercial standards is higher than the percolation threshold of the SSF composite (10 wt%). This suggests that the SSF were distributed within the polymer matrix in such a way that they could not optimally shield electromagnetic radiation. As a result, more material was required to reach the commercial EMI shielding standard.
Figure 7.19: EMI shielding effectiveness of injection moulded composite panels with different loading of SSF at different frequency

Original NCCF composites

The EMI SE of the Original NCCF composite is shown in Figure 7.20. In general, EMI shielding effectiveness increases with Original NCCF loading. Its highest value, shown in Figure 7.20, is approximately 12dB. This was achieved by the Original NCCF60 at 1.5MHz. A significant improvement was required to reach the shielding effectiveness of 40 dB for commercial applications.

For a composite to be able to shield EMI effectively, it should have sufficient (good) electrical conductivity. However, for a composite to be electrically conductive, sufficient fibres need to be added so that the composite can reach the percolation threshold. According to the surface resistivity measurement of Original NCCF composite (Figure 7.11), the percolation threshold of Original NCCF composite is approximately 45 wt%. Therefore, for composites containing 50 and 60 wt% Original NCCF, the percolation threshold has already been reached. This suggests that the Original NCCF may not have sufficient electrical conductivity to effectively shield EMI. Figure 7.13 illustrates that the majority of the NCCF50 composites were in region 2 (moderate electrical conductivity). This corresponded to a maximum EMI SE for NCCF50 of 9.5 dB at 1.5 MHz. Therefore, the EMI SE of the
Original NCCF50 and the Original NCCF60 could be improved by increasing the electrical conductivity of the composite.

![Figure 7.20: EMI shielding effectiveness of compression moulded composite panels with different loading of Original NCCF at different frequency](image)

**Optimised NCCF composites**

Composites based on optimised nickel coated cellulose fibres (Optimised NCCF) were also fabricated for characterisation. Figure 7.21 illustrates the EMI shielding effectiveness of the Optimised NCCF composites.

Since both 50 and 60 wt% composite demonstrated similar EMI SE, composite containing 50 wt% Optimised NCCF is the optimal material in terms of production cost and material properties. There was an overall improvement in EMI shielding performance of these samples compared to those in Figure 7.20. In particular, the composites containing 50 and 60 wt% of Optimised NCCF demonstrated a significant improvement in EMI SE. A repeat for composite containing 50 wt% Optimised NCCF (referred to as 50SP) was done as another point of comparison to check for reproducibility.

There was an approximate increase in EMI SE from 6 to 15dB, even when there was no significant change in surface resistivity of the Optimised NCCF composite compared to the Original NCCF composite. When there was a reduction of surface resistivity (50SP), EMI SE
increased to 21dB. This level of EMI SE may be suitable as EMI shielding material for desktop and laptop computers because measurements were done for a similar ranges of frequency [166].

Figure 7.21: EMI shielding effectiveness of the compression moulded composite panels with different loading of Optimised NCCF

Relationship between EMI SE, Surface and Volume Resistivities

In order to gain a better understanding, the relationship between surface, volume resistivities and EMI SE were studied. Firstly, for SSF composites, it can be seen in Figure 7.19 that the largest increase in EMI SE values happened between 8 wt% SSF (10dB) and 12 wt% SSF (25dB). Both volume and surface resistivities measurements agree that the percolation threshold is between 8 and 12 wt% (around 10 wt%). For the Original NCCF composites, the largest increase in EMI SE values (as seen in Figure 7.20) occurred between 40 wt% of Original NCCF (8dB) and 50 wt% of Original NCCF (15dB). Both the volume and surface resistivities measurements agree that the percolation threshold is between 40 and 50 wt% (around 45 wt%). However, for the Optimised NCCF composites, the percolation threshold was around 15 wt% based on surface resistivity measurements and approximately 45 wt% based on volume resistivity measurements. In terms of EMI SE of the Optimised NCCF composites (Figure 7.21), the largest increase occurred between 40 wt% Optimised NCCF (10 dB) and 50 wt% Optimised NCCF (to 15dB, or 22dB for 50SP composite). As shown
previously for the SSF and Original NCCF composites, the percolation threshold generally occurred between the two loadings where the increase in EMI SE was greatest, which is between 40 and 50 wt% loading (around 45 wt%) for Optimised NCCF composites. This percolation threshold agrees with the changes observed in the volume resistivity measurements of Optimised NCCF composite. This is because both volume resistivity and EMI SE measurements were conducted through the thickness of the composite, making the correlation more straightforward. In contrast, surface resistivity represents only the surface state and potentially the edge effect of plastic/composite moulding. The edge effect was excluded from the further microstructural investigation described in the next chapter.

As previously mentioned towards the end of Chapter 6.4, the phosphorus content of the Optimised NCCF was approximately 3 wt% compared to 8.4 wt% of the Original NCCF. This means that there is more nickel being deposited onto the Optimised NCCF, which leads to an improvement in electrical conductivity of NCCF.

Furthermore, it can be seen from Figure 7.22 that the volume resistivity of the 50 wt% of Optimised NCCF composite decreased by approximately two to three orders of magnitude compared with the 50 wt% Original NCCF composite. This suggests that the reduction in volume resistivity was the result of the intrinsically higher conductivity of the nickel coating on Optimised NCCF compared to Original NCCF. Consequently, it was demonstrated that a reduction in phosphorus content in electroless nickel coating led to the improvement of EMI SE of composites based on NCCF. The reduction of phosphorus content also means that there are a larger amounts of nickel being deposited on Optimised NCCF compared with Original NCCF. Since there is a larger amount of material available for shielding EMI, the EMI SE increases.
Figure 7.22: Volume resistivity profile of the compression moulded Original and Optimised NCCF composite at 50 wt% loading

**EMI SE comparison with other polymer composite**

The achieved EMI SE were similar to other results reported in (Table 7.2), though potentially at a much lower cost once the mass production of NCCF can be achieved. It is important to note that the cost of each filler reported in Table 7.2, is based on mass production rates, unlike nickel coated cellulose fibres where only laboratory-scale costs could be approximated. Although the Optimised NCCF composites did not reach the EMI SE level required for general commercial applications, they may be suitable for EMI shielding in desktop and laptop computers as the shielding level requirement is between 15 – 20 dB.
### Table 7.2: Summary of composite of conducting fillers and conventional polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Percolation Threshold (wt%)</th>
<th>Frequency</th>
<th>EMI Shielding Effectiveness (dB)</th>
<th>Cost ($/kg filler)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline Coated Nickel Flakes Composite</td>
<td>20 - 25</td>
<td>300 MHz – 1 GHz</td>
<td>20</td>
<td>N/A</td>
<td>[59]</td>
</tr>
<tr>
<td>Carbon Nanofibres Composite</td>
<td>20</td>
<td>8 – 12 GHz</td>
<td>20</td>
<td>276</td>
<td>[80]</td>
</tr>
<tr>
<td>Single-Walled Carbon Nanotube Composite</td>
<td>15</td>
<td>300 MHz – 10 GHz</td>
<td>20</td>
<td>772</td>
<td>[81]</td>
</tr>
<tr>
<td>Multi-Walled Carbon Nanotube Composite</td>
<td>5</td>
<td>8 – 12 GHz</td>
<td>26</td>
<td>66,225</td>
<td>[80]</td>
</tr>
<tr>
<td>Nickel Coated Graphite Fibres Composite</td>
<td>6 – 15</td>
<td>300 MHz – 1.5 GHz</td>
<td>35 – 40</td>
<td>88</td>
<td>[7]</td>
</tr>
<tr>
<td>Stainless Steel Fibres Composite</td>
<td>6 – 12</td>
<td>300 MHz – 1.5 GHz</td>
<td>35 – 40</td>
<td>75</td>
<td>[7]</td>
</tr>
<tr>
<td>Nickel Coated Cellulose Fibres Composite</td>
<td>45</td>
<td>300 MHz – 1.5 GHZ</td>
<td>15 – 24</td>
<td>500 (lab scale)</td>
<td>Current Work</td>
</tr>
</tbody>
</table>

#### 7.4 Mechanical properties of SSF and NCCF Composites

**SSF composites**

The flexural strength of the composites was measured to determine the effect of incorporating fibres into a polymer. Figure 7.23 illustrates the flexural strength of SSF composites. The general trend was that the average value of flexural strength of SSF composite decreases with increasing filler loading. This is due to poor bonding between the polypropylene matrix and SSF which affects pre-existing cracks [35]. Higher SSF loading means a higher number of pre-existing cracks, which leads to lower flexural strength. As the SSF slip against PP under
load, those cracks extended to reduce the strength of the composite. Tan et al. have reported
an SEM images showing SSF fibre pull-out [35]. The load-induced structural evolution in
this case is different from that in normal fibre-reinforced composites, where fibres anchor the
polymer matrix to improve strength.

![Maximum Flexural Strength of SSF composites](image)

**Figure 7.23: Maximum flexural strength of injection moulded SSF composite at different loading**

Tan et al. [35] investigated the effect of interfacial modification on the mechanical properties
of composite based on PP and SSF. The agent used to improve bonding between SSF and PP
was maleic anhydride. They successfully prepared SSF composites by melting mixing
polypropylene with chopped SSF, followed by compression moulding at 200 °C. The flexural
strength of PP with maleic anhydride is 52 MPa. The addition of SSF to PP with maleic
anhydride increased the flexural strength of the SSF composites up to 68 MPa at 40 wt%
loading. This is because the addition of maleic anhydride improved the bonding capability
between the SSF and PP due to the presence of many reactive groups in maleic anhydride,
thus increasing the flexural strength of the composite.
In comparison, the flexural strength of pure PP without maleic anhydride was 39 MPa (similar to the value observed in Figure 7.23). The flexural strength of SSF composites increased to 41 MPa when 8 wt% of SSF was added. This is different to what was observed in Figure 6.22. Tan reported that, above 8 wt% SSF loading, the general trend was that the flexural strength decreased with SSF loading. At 20 wt% SSF loading, the flexural strength of SSF composite decreased to 37 MPa and continued to decrease to 22 MPa at 40 wt% SSF loading. Although the exact flexural strength values of SSF composites prepared in this thesis (using PP pellets without compatibiliser) were not the same as those reported by Tan, the general trend observed above 8 wt% SSF loading is similar.

The Young’s modulus of SSF composites was also measured and the results are illustrated in Figure 7.24. It can be seen that the average value of Young’s modulus increases slightly as SSF loading increases. This is similar to the report by Tan et al, which reported that, the Young’s modulus of pure PP is approximately 1.5 GPa and increases linearly with SSF loading. At 40 wt% SSF loading, the value of Young’s modulus is approximately 2 GPa. However, due to the variation in terms of the Young’s modulus result in this thesis, there is no significant difference in terms of the Young’s modulus of the composite as SSF loading increases. Tan et al. [35] also reported that the increase in the Young’s modulus is more pronounced at higher SSF loading.

![Figure 7.24: Young’s modulus of injection moulded SSF composite at different loading](image-url)
Original NCCF composite

In terms of mechanical properties, Figure 7.25 illustrates that the average values of flexural strength of Original NCCF composites ranges from 39 to 50 MPa. This is higher than the average values of flexural strength for SSF composites which ranges from 34 to 38 MPa. However, there is a large variability in the flexural strength results of the Original NCCF composites. Due to this variability, it is hard to see if there is any trend with loading. Furthermore, it can also be seen that the flexural strength of pure PP is different from Figure 7.23. In Figure 7.23, PP panels were fabricated via injection moulding from PP pellets. As a comparison, in Figure 7.25, PP panels were fabricated via compression moulding from PP fibres. There were porosities within the PP panels fabricated from PP fibres which mean that the flexural strength would be lower than those PP panels fabricated from PP pellets.

![Graph Image](image)

**Figure 7.25: Maximum flexure strength of compression moulded Original NCCF composite at different loading**

Reported values of the average flexural strength of composite based on PP (with compatibiliser) and uncoated cellulose fibres (40 wt% loading) is 83.2 MPa [8]. When PP (without compatibiliser) was used, the average flexural strength is 67.1 MPa [167]. Both these values are consistently higher than the flexural strength of Original NCCF composites.
It can be seen that the electroless deposition of nickel onto cellulose fibres reduces the reinforcing capability of cellulose fibres.

It has been reported in much of the literature [8, 168-174] that there is poor bonding between natural fibres and PP matrix. This is due to the incompatibility between hydrophobic PP and hydrophilic natural fibres. This incompatibility causes a weak interaction between the two components, which results in a weak interface [174]. Regardless of this incompatibility, it is evident that the addition of cellulose fibres to PP reinforces the material, which increases the flexural strength of the composite [8, 175].

One of the most common coupling agents used to improve the bonding between fibres and matrix is maleic anhydride grafted polypropylene (MAPP) [175-178]. The flexural strength of composite based on PP and cellulose fibres is approximately 59 MPa. When MAPP was used, the flexural strength of the composites increased to 75 MPa. [175]. This is because MAPP improves the bonding between filler and matrix by forming an ester bond between the hydroxyl group in cellulose fibres and the anhydride carbonyl group in MAPP [179]. As a result, the flexural strength of natural fibres composites based on MAPP is higher than that of natural fibre composites without maleic anhydride.

The reinforcing capability of fibres depends on the critical aspect ratio. This value is defined as the ratio between the tensile strength of the fibres and the interfacial shear strength [180]. For cellulose fibres in PP (with compatibiliser), the estimated critical aspect ratio is approximately 25. This is the minimum aspect ratio for cellulose fibres to exhibit maximum reinforcing capability in PP matrix [9]. As the aspect ratio of cellulose fibres used in this thesis is around 42, composites based on cellulose fibre have received reinforcement. Therefore, the achievable flexural strength of cellulose fibre composite should be 83.2 MPa, as reported in [8]. If the aspect ratio of cellulose fibre is below the critical value, the reinforcing capability of cellulose fibre decreases. Therefore, the flexural strength of composite containing cellulose fibres with aspect ratio below the critical value is less than 83.2 MPa [9]. The flexural strength of composite based on PP (without compatibiliser) and cellulose fibres is 67.1 MPa [167].

It is expected that the aspect ratio of NCCF and uncoated cellulose fibres should be similar. This suggests that the deposition of nickel onto cellulose fibres may have change the tensile strength of the fibres and/or the interfacial shear strength, which could have increased the
critical aspect ratio beyond the aspect ratio of NCCF. This could be the reason why the flexural strength of NCCF composites is lower than that of cellulose fibre composite.

Based on the mechanism of MAPP described in the literature [179], it is possible that the compatibiliser (present in PP used in this thesis) may function in a similar manner to maleic anhydride. Although the nature of the compatibiliser was not disclosed by the supplier, the improvement in flexural strength, as reported in the literature [8], suggests the possibility that there is a functional group in the compatibiliser which could effectively bond with the hydroxyl group in cellulose fibres.

If the above assumption is true then it is possible that the compatibiliser could not improve the bonding between NCCF and PP matrix. This is because the hydroxyl group could either be mechanically blocked or chemically unavailable due to the electroless deposition of nickel onto cellulose fibres. It is known that the hydroxyl group in cellulose enables hydrogen bonding between individual fibres [173, 174]. As part of the electroless deposition process, individual cellulose fibres were pre-treated with sodium borohydride. The borohydride ions form hydrogen bonding with the hydroxyl group in cellulose fibres [20]. During the electroless deposition process, borohydride ions reduced nickel onto cellulose fibres, thus disrupting the hydrogen bonding between individual fibres. The absence in the ability of NCCFs to naturally physically bond to each other when dried is evidence of the loss of hydrogen bonding.

Alternatively, even if the compatibiliser was able to enhance the bonding between the PP matrix and NCCF, the enhancement between the two materials would not be comparable to the case of uncoated cellulose fibre composite. This is in agreement with the result which indicated that the flexural strength of NCCF composite is less than the flexural strength of uncoated cellulose fibre composites.

Therefore, the improvement in flexural strength of NCCF composites relative to pure PP (as seen from Figure 7.25) suggests that NCCF has reinforcing property. No additional surface treatment was done to enhance the adhesion between NCCF and the PP matrix because optimising the mechanical properties of NCCF composites is not the main aim of this thesis.

The SEM analysis of the fracture surfaces of the Original NCCF are shown in the Figure 7.26. It can be seen that there is no evidence of fibre pull-out from the fracture surfaces of the composite (as shown by the NCCF appearing end on). This suggests that the load has been
successfully transferred to the fibres and that the NCCF is acting as a reinforcing material. Regardless of whether NCCF is appearing end on, or side on, this figure suggests that there is good interfacial bonding between the NCCF and the PP matrix.

However, with regards to NCCF appearing on its length, there is a mixture of failure mechanisms. The first mechanism is the fracture occurring along the NCCF (as a circle in dashed lines) which is the same mode of failure for the NCCF appearing end on. The second mechanism is the fracture between the nickel coating and the cellulose fibres (as a circle in dotted line). This mode of failure, which occurred at the weak point between the nickel coating and the cellulose fibres, reduced the reinforcing capability of NCCF fibres. This is most likely to be another reason for the reduction of the flexural strength when NCCF was used as reinforcing material instead of uncoated cellulose fibre.

![Fracture surface of compression moulded Original NCCF composite at 40 wt% loading](image)

**Figure 7.26: Fracture surface of compression moulded Original NCCF composite at 40 wt% loading**

The fracture surface of 40 wt % uncoated cellulose fibre composite is different from that of NCCF composites. It can be seen in Figure 7.27 that, at same weight percent loading, there are a larger amount of uncoated cellulose fibres present compared to NCCF. This is because the density of uncoated cellulose fibres is lower. Therefore, for the same weight percent loading, there are more uncoated cellulose fibres than for NCCF.
It can be seen in Figure 7.28 that there are several fracture surfaces for uncoated cellulose fibres (dashed circle) which implies that uncoated cellulose has successfully acted as a reinforcing material by transferring the load from the matrix to the fibres. There are traces of fibre pull-out or porosity (filled circle) and also several fibres showing signs of pulling out (dotted circle). These two factors could potentially reduce the reinforcing property of uncoated cellulose fibres as the load cannot be successfully transferred onto the fibres. Therefore, the flexural strength of uncoated cellulose fibres can be further increased by improving the bonding between uncoated cellulose fibres and polymer matrix. The fracture surface of uncoated cellulose fibres composites is similar to the fracture surface of many of the natural fibre composites reported in the literature. For example: cellulose fibres/PP composite [181], hemp fibre/PP composite [182], sisal/PP, flax/PP and banana/PP composite [183], kenaf/epoxy composite [184].
Figure 7.28: Fracture surface of compression moulded uncoated cellulose fibres composite at 40 wt% loading at 800x magnification

The Young’s modulus of the Original NCCF composite was also measured and the results are illustrated in Figure 7.29. The values of the modulus of PP reported in the literature are similar to those being reported in this thesis. The flexural modulus of PP as reported in the literature is approximately 1.0 GPa [181]. Other published literature reported the elastic modulus of PP to be 1.3 GPa [182] and 1.6 GPa [183]. According to Figure 7.29, the general trend is that the average value of Young’s modulus of the composite increases as the Original NCCF loading increases but there is greater variability at a higher loading of the Original NCCF. Furthermore, the average value of Young’s modulus of composite containing 40 wt% of uncoated cellulose fibres was measured to be approximately 4.20 GPa. Therefore, it was once again confirmed that the deposition of nickel onto cellulose fibres reduces the reinforcing capability of NCCF. However, it can still be concluded that the addition of Original NCCF into the PP matrix improves the Young’s modulus of the Original NCCF composites.

In terms of the flexural modulus of cellulose fibres/PP composite reported in the literature [176], the flexural modulus of composites containing PP with 40, 50 and 60 wt% cellulose is approximately 2.5, 2.7 and 3.1 GPa, respectively. As mentioned earlier, the average value of a modulus of 40 wt% uncoated cellulose fibres composite is approximately 4.2 GPa, which is
higher than the 2.5 GPa reported in the literature. The main reason for this discrepancy may be due to the processing technique for the composite. The technique used in the literature involved extrusion, which usually results in a reduction in the average fibre length of the fibre. The reduction in fibre length (and therefore the aspect ratio) decreases the reinforcing capability of cellulose fibre; this is due to the fact that some of cellulose fibres may not have been loaded because they are shorter than the critical fibre length value [185]. Furthermore, composite fabrication via extrusion could potentially cause fibre alignment within the composite which could affect the mechanical properties of the composite as well. The uncoated cellulose fibres composite prepared in this thesis were compression moulded, which helps maintain the length (and therefore the aspect ratio) of the cellulose fibres. This is the reason why composite containing 40 wt% of Original NCCF possessed a higher average value (3.18 GPa) of flexural modulus than 40 wt% of uncoated cellulose fibres reported in the literature (2.5 GPa) even though the deposition of nickel on cellulose reduces the reinforcing capability of cellulose fibres. This gives further emphasis to the importance of maintaining the aspect ratio of fibres during composite processing; it minimises not only the negative impact on the percolation threshold, but also on the mechanical property of the composite.

Figure 7.29: Young’s modulus of compression moulded Original NCCF composite at different loading
Optimised NCCF composite

The average value of flexural strength of the Optimised NCCF composite at 20, 30 and 40 wt% loading is higher than that of the Original NCCF composite at their respective loadings (as seen in Figure 7.30 for the Optimised NCCF composite and Figure 7.25 for the Original NCCF composite). However, in the case of the optimised NCCF composite, there is a clear trend of decreasing flexural strength with increasing loading.

Both the Original NCCF and Optimised NCCF composites showed improved flexural strength relative to pure PP. However, there is less variability in the flexural strengths of the Optimised NCCF composites so a trend of decreasing strength with increasing loading (similar to SSF composites) as can be clearly seen in Figure 7.30. The incorporation of Optimised NCCF into PP still increases the flexural strength of the composite, up to 50 wt% loading. Therefore, it can be concluded that the EMI SE of NCCF composites has been improved without further jeopardizing the flexural strength of NCCF composites.

![Figure 7.30: Maximum flexural strength of compression moulded Optimised NCCF composite at different loading](image-url)
The Young’s modulus of Optimised NCCF composites was also measured and the results are illustrated in Figure 7.31. The general trend is that the average value of the Young’s modulus of the composite increases as the Optimised NCCF loading increases to 40 wt% loading. At higher loadings of Optimised NCCF, the average value of Young’s modulus starts to decrease. Additionally, similar to the Original NCCF composite, there is a large variability in composites at high loading of Optimised NCCF composite. It can be concluded that the addition of Optimised NCCF into the PP matrix also improves the Young’s modulus of the Optimised NCCF composites. The variability after the percolation threshold may be due to the difficulties in evenly dispersing NCCF within the PP matrix at a high filler loading.

![Figure 7.31: Young’s modulus of compression moulded Optimised NCCF composite at different loading](image)

**Comparison of mechanical properties with commercially available EMI shielding composites**

An example of commercially available EMI composites are based on polycarbonate (PC) and stainless steel fibres (SSF) [186]. The flexural strength and modulus of PC is approximately 90 MPa and 2300 MPa respectively [187]. When 5 wt% of SSF is incorporated into PC, the flexural strength reduces to 62 MPa and the modulus increases to 2758 MPa [188]. For EMI shielding composite where the mechanical properties are important, at least 10 wt% of glass is also added. For composite containing 10 wt% glass fibres and 5 wt% SSF, the flexural strength and modulus is 138 MPa and 4137 MPa, respectively [189]. As the composites
fabricated in this thesis are based on PP, direct comparison of flexural strength and modulus may be inappropriate. Therefore, comparison was made based on the percentage increase in mechanical properties. This is based on the assumption that the addition of NCCF to PC would improve the mechanical properties of the composite to the same extent as when NCCF was added to PP.

The addition of glass fibre into commercially available EMI shielding composites resulted in at least a 100% increase in flexural strength and 50% increase in modulus. When NCCF was incorporated into PP, the flexural strength and modulus increased by approximately 80% and 150% respectively. Therefore, if the addition of NCCF into PC increases the mechanical properties to the same extent, there is a possibility of commercialising the composite for EMI shielding purposes (provided that a satisfactory shielding level have been achieved). The required strength will depend on the particular EMI shielding application. The addition of coated fibres improves the mechanical properties over those for non-reinforced PP. However, coating with nickel may have a slightly negative influence on the mechanical properties when compared to uncoated fibres.

7.5 Density of SSF and NCCF Composites

SSF composites

The density of SSF composites is illustrated in Figure 7.32. As expected, the density of SSF composites increases as SSF loading increases. It is also important to note that the variability of SSF composites within the composite panel is quite small. This suggests that the SSF composites were manufactured with high degree of reproducibility. As a result, the effects of density on the other material properties are minimised.
Figure 7.32: Density of injection moulded SSF composite at different loading

**Original NCCF composite**

The density of Original NCCF composites are illustrated in Figure 7.33. As expected, the density of the composites increases as the Original NCCF loading increases. This is due to the fact that there is a greater amount of denser material at high filler loading. In comparison with the SSF composite, there is greater variability in the density of the Original NCCF composite, especially at higher fibre loading. This is most likely the reason that there are certain degrees of variability in terms of the flexural strength and in the Young’s modulus of the Original NCCF composites as well. Furthermore, assuming the composites have negligible porosity, this variability suggests that the distribution of NCCF is not the same throughout the composite panels. The raw measurements indicate that the density reaches its maximum at the centre and decreases to a minimum at both sides of the panel. This would affect the mechanical property of the Original NCCF composite as there are varying amount of NCCF within the composite strips. The optimisation of the manufacturing technique to produce composite with optimum mechanical properties should be further investigated once a composite with commercial EMI shielding capability has been produced.
The densities of the optimised NCCF composites are illustrated in Figure 7.34. There is a greater variability in the density of the optimised NCCF composite, especially at a higher fibre loading, as is similar for the original NCCF composites. This is the most likely reason why there are certain degrees of variability in terms of the flexural strength, and with the Young’s modulus of the optimised NCCF composites as well. Similar to the original NCCF composite, there are varying amounts of NCCF within the optimised NCCF composite as well, which contributes to the variability in the mechanical properties of the composites. Furthermore, the slight reduction in the density of the optimised NCCF composites could be due to porosity. There is a higher chance of porosity forming at higher filler loading because it is more difficult to obtain good fibre dispersion within the polymer matrix as compared to a composite with low filler loading.
Figure 7.34: Density of compression moulded Optimised NCCF composite at different loading

Summary

Composites (with no observable porosity) based on the original nickel coated cellulose fibres, the Original NCCF and the Optimised nickel coated cellulose fibre Optimised NCCF, have been successfully fabricated via compression moulding, and various material properties such as EMI SE, surface resistivity, volume resistivity and flexural strength have been characterised. EMI shielding composites based on commercially available SSF were fabricated via injection moulding and characterised in the same manner as the nickel coated cellulose fibres composite for the purpose of comparison.

The percolation threshold of SSF composite was approximately 10 wt%, within the range of 6 – 12 wt%, as suggested by Hardwick [7]. However, the commercial EMI shielding standard of 40dB was only reached at 20 wt% loading of SSF. This suggests that the injection moulding condition used to fabricate SSF composites was not optimal and further improvements can be achieved. Additionally, SSF composites had a consistent thickness of 3 mm and the EMI SE was measured. If SSF composites were to be made and tested in the optimum conditions, then EMI SE could be higher.
In comparison, neither the Original NCCF nor the Optimised NCCF composites were able to attain the commercial EMI shielding standard of 40dB, even when the percolation threshold was reached at 45 wt%. This loading is much higher than in the case of SSF composite and thus leaves a significant opportunity for further reduction in the costs for nickel coated cellulose fibre composites. The most significant factor which affected the percolation threshold is the aspect ratio of the fibres. If longer fibres can be obtained and nickel can be successfully deposited, the percolation threshold of the composite could be reduced.

The highest values of EMI SE obtained from the Original NCCF and the Optimised NCCF composite were 8dB and 24dB respectively. The 16dB improvement was attributed to the reduction of phosphorus content within the nickel coating, from 8.4 wt% for the Original NCCF to 3 wt% for the Optimised NCCF. It has been further confirmed that reducing phosphorus content within the coating increases the composite’s electrical conductivity, which ultimately increases its EMI SE. Even though the achieved EMI of 24dB is sufficient for application in personal computers, wider commercial applications require a much higher value of 40dB. One possible avenue is to further reduce the phosphorus content in the nickel coating through greater optimisation of the electroless plating parameters. Another possibility is to align the fibres for a better conducting network in conjunction with the investigation into other fibres with the greater aspect ratios mentioned above. Both of these possibilities could not be pursued within the resources and time allowed for this project. However, the understanding of microstructures and the resulting properties in the next chapter will be useful for future endeavours.

The general trend observed for SSF and Optimised NCCF composites is that their flexural strength decreases as filler loading increases. In comparison, for the Original NCCF composites, a general trend between flexural strength and loading of nickel coated cellulose was not observed due to the large variation in the results. However, it was observed that the addition of Original NCCF or Optimised NCCF increases the flexural strength of the composite. If EMI SE and the percolation threshold of nickel coated cellulose fibres composites were comparable to SSF composites, then nickel coated cellulose fibres composites could replace SSF composites in EMI shielding application where mechanical strength is important.

The cost of production of nickel coated cellulose fibres ($500/kg) is a lot higher than for commercially available EMI shielding fillers, such as SSF ($75/kg) and nickel coated
graphite fibres ($88/kg), as it is still laboratory-scale. It is believed that further optimisation can be done to reduce the cost as the optimisation process which was carried out in this thesis was mainly focused on improving the EMI SE of the nickel coated cellulose fibres. Additionally, if mass production can be successfully achieved, production costs will reduce further.

Table 7.3 summarises the measured properties of SSF, Original NCCF and Optimised NCCF composite above the percolation threshold.

Table 7.3: Summary of the average values for EMI SE, electrical resistivities, mechanical properties and density of composites

<table>
<thead>
<tr>
<th>Properties</th>
<th>SSF (12 wt %)</th>
<th>Original NCCF (50 wt %)</th>
<th>Optimised NCCF (50 wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface resistivity</td>
<td>2 x 10⁵ ohm/cm²</td>
<td>2 x 10⁵ ohm/cm²</td>
<td>8 x 10⁵ ohm/cm²</td>
</tr>
<tr>
<td>Volume resistivity</td>
<td>50 ohm/cm</td>
<td>2 x 10⁶ ohm/cm</td>
<td>500 ohm/cm</td>
</tr>
<tr>
<td>EMI shielding effectiveness</td>
<td>26 dB</td>
<td>6 dB</td>
<td>21 dB</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>36.0 MPa</td>
<td>52.8 MPa</td>
<td>49.2 MPa</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>1.38 GPa</td>
<td>3.37 GPa</td>
<td>2.93 GPa</td>
</tr>
<tr>
<td>Density</td>
<td>0.98 g/cm³</td>
<td>1.14 g/cm³</td>
<td>1.18 g/cm³</td>
</tr>
</tbody>
</table>
Chapter 8

Image Analysis, Spatial Analysis and 3-D Microstructure

General imaging techniques such as light microscopy and SEM are capable of producing 2-D images. An image analysis of the SEM images was used to investigate the relationship between the microstructure and percolation threshold of the composite. Aspect ratio, feret ratio, fibre waviness and statistical functions were used to analyse the fibres within the composite. Additionally, since EMI SE and percolation threshold are better explained in three dimensions, the 3-D microstructures of the composites were analyzed with x-ray microtomography (micro-CT). There is a limited amount of literature reviews available on the relationship between the percolation threshold and the 3-D microstructure of the composites. Most literature reviews are based on theoretical models rather than an experimental model. The goal of using Micro-CT and ImageJ to analyse the 3D microstructure of the composite is to assist in the detection of the percolation threshold and to gain further understanding as to why the percolation threshold of the SSF composite is lower than that of the NCCF composite.

8.1 Aspect Ratio, Feret Ratio analysis and approximating fibre waviness

Previous literature [113] has suggested that the aspect ratio of filler affects the percolation threshold of the composites. Higher aspect ratio means lower percolation threshold. Therefore, it is necessary to investigate the aspect ratio of the fibres in the composite. The
aspect ratios of the fibres are automatically computed by dividing the major axis by the minor axis of the particle’s fitted ellipse. The aspect ratio would be high for straight fibre and low for curved fibres.

A Feret ratio is the ratio between maximum ferret diameter (longest distance between two parallel planes in the region of interest) and minimum ferret diameter (shortest distance between two parallel planes in the region of interest). Similarly to aspect ratio, this means that the feret ratio would be high for straight fibres and the feret ratio would decrease as fibre curvature increased. The values of the aspect ratio and feret ratio attempt to characterise the curvature of fibres.

If the fibres are straight then the measured “particles” should exhibit high aspect ratio and high feret ratio. Both aspect ratio and feret ratio decrease as fibres curve more. It is important to characterise the fibre curvature because curvature in the fibres reduces the effective aspect ratio, which in turn means more fibres are required to reach the percolation threshold. It is expected that the SSF should be straight in the microstructure, whereas, NCCF would show a certain degree of curvature due to its flexibility.

The aspect ratio and feret ratio of the NCCF and the SSF distributed within composites were extracted from SEM images using the ImageJ “analyse particle” function. A threshold function was used on each image to separate fibres (region of interest) from the matrix and then ImageJ calculated a range of parameters relating to the fibre dimensions.

It can be seen from Figure 8.1 and 8.2 that the mean aspect ratio and feret ratio of the NCCF and the SSF are very similar. These values range from approximately 1.5 to 2. For NCCF composites, there are four factors attributing to this result: short fibres, clusters, fibres appearing on end or at an angle and curved fibres (see Figure 8.3 an example of NCCF composite at 10 wt % loading). For the SSF composites, there is only one factor attributing to the low values of aspect ratio and feret ratio: fibres appearing on end or at an angle (see Figure 8.4 an example of SSF composite at 4 wt % loading). When analyzing 2D images, the factors above are to be expected and will affect the results. It should be noted that there are additional limitations when analysing 2D images. Firstly, it is almost impossible to determine whether the dots on the SEM image are actually fibres appearing on end or just nickel particles/clusters. Secondly, it is uncertain whether fibres that appear end on would also curve into the page. The main reason that that NCCFs appear to exhibit a larger aspect ratio and feret ratio (according to the values of max aspect ratio and max feret ratio with a standard
deviation approximately between 0.5 – 1.5) is because a lot of the NCCFs captured on images were on their sides (Figure 8.3). In comparison, a many of the SSFs captured on images were on their ends (Figure 8.4).

Due to its many limitations, this quantitative analysis does not explain why SSF composites exhibited a lower percolation threshold than NCCF composites. However, qualitatively, many of the NCCF SEM images illustrate that there are many clusters and curved fibres. Furthermore, dots on the NCCF SEM images are most likely to be fines/particles, because there are disintegrated cellulose fibres (i.e. the starting material for electroless nickel plating) present. Clusters/fines exhibited AR close to one and curved fibres have smaller effective AR compared to straight fibres with the same length. These features are not observed in SSF

---

**Figure 8.1: Aspect ratio and Feret ratio of NCCF composites**

**Figure 8.2: Aspect ratio and Feret ratio of SSF composites**
fibres. Qualitative analysis suggests that there are a mixture of low and high aspect ratio particles within NCCF composites. As a result, NCCF composites would have a higher percolation threshold than that of SSF composites. This is in agreement with results illustrated previously.

Figure 8.3: SEM image of NCCF 10 at 200x magnification

Figure 8.4: SEM image SSF 4 at 200x magnification

The fibre waviness of the NCCFs were approximated using the waviness ratio as described in [116]. These results are illustrated in Figure 8.5. Furthermore, NCCF still exhibits a certain degree of fibre waviness within the composite containing high loading of NCCF (40 wt% NCCF composite). It is difficult to determine the effect of fibre loading on the waviness ratio of NCCF.
Figure 8.5: Waviness ratio of NCCF

Even though some NCCFs are straight, the presence of curved fibres increases the percolation threshold of the composites. For fibres with low aspect ratio, such as NCCFs, this effect is more significant compared to fibres with high aspect ratio. Furthermore, curved fibres require more contact points to reach the percolation threshold; this means that more fibres are required. The waviness ratios of the SSFs were not calculated as they appeared straight in the SEM images.

8.2 Particle distribution analysis

In order to quantitatively analyse the distribution of fibres in the composites some statistical functions have been investigated. This plugin could suggest whether the distribution is random, tending towards clustering (attraction) or tending towards uniformity (repulsion). Examples of these three types of distributions are illustrated in part A of Figure 8.6.

The distribution of particles within the matrix is important because it affects the percolation threshold. If the particle distribution is clustered then the percolation threshold will be higher than expected as more material is required to establish connectivity.

Two statistical functions (F and G) [190] have been investigated and reported in this thesis. The G function is the cumulative distribution function (CDF) of the distance between a typical point in the pattern and its nearest neighbour (orange line). A typical point pattern is a
series of random point overlaying the SEM image. The F function computes the CDF of the
distance between a typical position (blue cross) within the reference structure and its nearest
point in the pattern (orange line). These features are illustrated in parts B and C of Figure 8.6,
respectively.

For the G function, a small distance indicates clustering and a large distance indicates
uniformity. For the F function, small distance indicates uniformity and large distance means
clustering.

![Figure 8.6: Illustration and explanation about the characteristic of the F-function and G-function [190]](image)

Graphs for the F function and a graph for the G function are plotted against distance. There
are three main features on these graphs: a plot of expected function for a random pattern, a
confidence interval and the distribution of the observed pattern.

In reference to Figure 8.7, the red line represents the distribution of the random pattern; the
green lines represent the 95 % confidence interval and the blue line represents the distribution
of the observed pattern. If the observed distribution lies to the right of the confidence interval
then the distribution is tending towards clustering. If the observed distribution lies to the left
of the confidence interval then the distribution is tending towards uniformity. The opposite is
true for the G function (i.e. right of confidence interval – uniformity, left of confidence
interval – clustering).

If the statistical function analysis suggests that the distribution of particles is clustering then
there is the potential to reduce the percolation threshold by modifying the manufacturing
process to promote random distribution of particles. However, if the distribution of particles
is uniform then further Monte Carlo simulation is required to determine whether a random or
uniform distribution would exhibit a lower percolation threshold.
Results and analysis of the graphs for the F-function and G-function for the SEM images of the NCCF and SSF composites are summarised in Table 8.1. The results suggest that the NCCFs were not randomly distributed within the composites. The graph of F-function and G-function suggests that the distributions of particles are leaning towards being clustered. This is shown in Figure 8.8 and 8.9 (graph of F-function and G-function for NCCF 10 illustrates an example).

Therefore, the results obtained from the spatial distribution analysis of the SEM images suggest that SSF composites exhibit random distribution; whereas, the distribution of NCCFs within the composite is not random, with spatial distribution leaning towards clustering. It is expected that the clustering distribution will promote high percolation, as more material would be required to connect the fibre clusters. Therefore, in addition to the presence of fines (inconsistency of aspect ratios) in the NCCF composites, the particle distributions leaning towards clustering, suggests that NCCF composites may have exhibited a higher percolation threshold than expected. This would also means that if the NCCFs could be dispersed within the composite in a random manner, there is the possibility for reducing the percolation threshold of NCCF composites.
### Table 8.1: Analysis of F-function and G-function graph for SEM images

<table>
<thead>
<tr>
<th></th>
<th>F-Function</th>
<th>G-Function</th>
<th>Distribution</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCCF 10</td>
<td>Right</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards random distribution</td>
</tr>
<tr>
<td>NCCF 20</td>
<td>Right</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards random distribution</td>
</tr>
<tr>
<td>NCCF 25</td>
<td>Inside</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards random distribution</td>
</tr>
<tr>
<td>NCCF 30</td>
<td>Right</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards random distribution</td>
</tr>
<tr>
<td>NCCF 40</td>
<td>Right</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards random distribution</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSF 4</td>
<td>Right</td>
<td>Left</td>
<td>not random</td>
<td>leaning towards cluster distribution</td>
</tr>
<tr>
<td>SSF 8</td>
<td>Inside</td>
<td>Inside</td>
<td>random</td>
<td>N/A</td>
</tr>
<tr>
<td>SSF 12</td>
<td>Inside</td>
<td>Inside</td>
<td>random</td>
<td>N/A</td>
</tr>
<tr>
<td>SSF 16</td>
<td>Inside</td>
<td>Inside</td>
<td>random</td>
<td>N/A</td>
</tr>
<tr>
<td>SSF 20</td>
<td>Inside</td>
<td>Inside</td>
<td>random</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Figure 8.8:** F-function for NCCF 10

- **Black** – Random distribution
- **Red** – Experiment data
- **Grey** – 95% confidence interval
The 3D object counter plugin was used to analyse a selected area of an image stack to determine the number of 3D objects present. One 3D objects is a series of connected pixels within and/or between images. It is expected that the number of 3D objects would be higher below the percolation threshold. This is because lower filler loading means there is less chance for particles to connect into 3D objects. When the percolation threshold has been reached, it is expected that there will be a significant reduction in the number of 3D objects due to the formation of the percolating cluster which potentially connects many clusters into one 3D object.

Generally, for both NCCF and SSF composites, it is expected that the number of 3D objects should decrease as filler loading increases even though increasing fibre loading also increases the number of 3D objects. This is because there is also a greater chance that fibres will connect into 3D objects at higher loading. Thus, this will reduce the number of 3D objects detected.

It can be seen in Figure 8.10 that, for SSF composites, the number of 3D objects is much higher than the number of 3D objects for NCCF composites. This is because, in terms of the fibre volume fraction in the composite, SSF composites contain at least a 3.4 times lower amount of fibre loading compared with NCCF composites. Since more fibres means that there is a greater chance that they will connect, therefore a lower number of 3D objects were detected in the NCCF composites. There is a reduction in the number of objects counted as
loading increases. Furthermore, there is no sign of a significant reduction in 3D objects when the percolation threshold was reached for the SSF and the NCCF composites. This is will be discussed later.

Figure 8.10: Number of 3D objects found in SSF, Original and Optimised NCCF composite at various loadings

Figure 8.10 also illustrates that the there is a larger reduction in the number of 3D objects for SSF composites with increasing filler loading when compared with NCCF composites. This is summarised in Table 8.2.

Based on the data in Table 3, it can be approximated that, when the volume fraction of SSF increases by 0.5 and 1 percent, the number of 3D objects will decrease by 80,000 and 121,000 objects, respectively. For Original NCCF composite, there is a reduction of 36,000 and 52,000 objects when the number of NCCF increases by 11.8 and 19.2 percent by volume.

These means that, an increase in 1 volume percent of SSF (121,000 reduction in 3D objects) corresponds to a greater reduction of 3D objects than an increase in 19.2 volume percent NCCF (52,000 reduction in 3D objects). This suggests that SSFs are more effective at forming a connecting network, which could potentially be another reason why the percolation threshold of SSF composite is lower than for NCCF composite.

For Optimised NCCF composite, the amount of nickel deposited onto cellulose is higher than the Original NCCF because the Optimised NCCF exhibited lower phosphorus content. This would mean that the density of Optimised NCCF would be slightly higher than Original NCCF. Therefore, at the same weight percentage of fibre loading, the density of Optimised
NCCF composites would be less than that of the Original NCCF composites. However, SSFs are still able to form a more effective network than Optimised NCCFs.

Table 8.2: summary of 3D objects detected in SSF and NCCF composite at various filler loading

<table>
<thead>
<tr>
<th>Composite</th>
<th>Weight percent</th>
<th>Volume percent</th>
<th>Number of 3D objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSF</td>
<td>4</td>
<td>0.47</td>
<td>180,000</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.98</td>
<td>100,000</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.52</td>
<td>79,000</td>
</tr>
<tr>
<td>Original</td>
<td>20</td>
<td>8.91</td>
<td>100,000</td>
</tr>
<tr>
<td>NCCF</td>
<td>40</td>
<td>20.69</td>
<td>64,000</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>28.13</td>
<td>48,000</td>
</tr>
<tr>
<td>Optimised</td>
<td>20</td>
<td>-</td>
<td>80,000</td>
</tr>
<tr>
<td>NCCF</td>
<td>40</td>
<td>-</td>
<td>75,000</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-</td>
<td>47,000</td>
</tr>
<tr>
<td>Best NCCF</td>
<td>50</td>
<td>-</td>
<td>53,000</td>
</tr>
</tbody>
</table>

From Table 8.2, the numbers of 3D objects within the selected zone for the percolated 50 wt% NCCF composites are approximately 48,000, 47,000 and 56,000 for the composite containing the Original NCCF, Optimised NCCF and best-Optimised NCCF, respectively. As the best-Optimised NCCF was produced in the same manner as the Optimised NCCF; both fibres are expected to possess the same aspect ratio, and correspondingly, percolation threshold. However, the best-Optimised NCCF composite displayed lower volume resistivity compared to the Optimised NCCF (on average: $4.11 \times 10^2 \pm 1 \times 10^2$ and $1.82 \times 10^3 \pm 5.73 \times 10^2$ ohm.cm, respectively) and accordingly had higher EMI shielding capability (22 dB for best-Optimised NCCF and 15 dB for Optimised). Standard errors showed that the range of volume resistivities of best-Optimised NCCF and Optimised NCCF are comparable and, based on Figure 2.9, an approximate reduction of volume resistivity from $10^3$ to $10^2$ ohm.cm resulted only in 4dB improvement in EMI SE. This means that exhibiting a small number of 3D objects does not imply that it is the most ideal microstructure for EMI shielding. The fact
that both Optimised NCCF and best-Optimised NCCF were produced in the same way but exhibited different EMI shielding capabilities suggests that there is another factor apart from the reduction of the intrinsic electrical conductivity of the composite. This is potentially attributed to the dispersion of fibres within the polymer matrix. There are three possible scenarios.

In scenario one, the fibres are well-dispersed without touching each other so the composite will not percolate (40 wt% Original NCCF composite). In scenario two, the fibres are not well-dispersed but distributed in such a way that they are connected. The composite will then percolate but without the optimal fibre orientation (50 wt% Optimised NCCF composite). In scenario three, the fibres are well-dispersed in such a way that they are connected. The composite will then percolate with optimal fibre orientation (50 wt% best-Optimised NCCF composite).

For both NCCF and SSF composite, although a lot of 3D objects were identified, there was only one major cluster. For the composite with loading above the percolation threshold, this major cluster is part of the percolating cluster. As the composites reach the percolation threshold, the amount of voxels found within the cluster increase at a slower rate.

For NCCF composites, as loading increases, there is a higher chance that particles will connect and join another cluster which reduces the number of individual particles identified via the 3D object counter. Therefore the total number of 3D objects will decrease. Since there is a higher chance that a 3D object will join cluster at higher loading, there is also a higher chance for the particle to join the major cluster. Therefore, number of voxels identified in the largest cluster also increases, as seen in Figure 8.11.

For SSF composites, the trend is similar to that for NCCF composites. The only difference is that the number of 3D objects in SSF composites is much higher than in NCCF composites. Since there are a lot of individual particles identified via the 3D object counter, there are fewer particles in the major cluster.
Figure 8.11: Number of voxel found in the major cluster in SSF, Original and Optimised NCCF composite at various loadings

Figure 8.12 illustrates that the microstructure of SSF composites demonstrates a more web-like microstructure than do NCCF composites (NCCFs showed an agglomerated-like microstructure). This feature can also be seen in the animation of SSF and NCCF progressing through the stacks. The difference is attributed to the SSF having a higher aspect ratio than the NCCF. The web-like microstructure of the SSF composite suggests that the section of the percolating cluster would require less connected particles to percolate. This also supports the idea, suggested earlier, that SSFs can form a more effective network than NCCF composites. Therefore, the number of voxels identified in the SSF composites is lower than for those identified in NCCF composites.

As mentioned previously, there was no sign of a significant reduction in 3D objects when the percolation threshold was reached for the SSF and the NCCF composites. This is because it was initially expected that when the percolation threshold have been reached, the formation of the percolating cluster would potentially connect many clusters into one 3D object. This was not the case because there was only one major cluster detected before and after the percolation threshold was reached. Therefore, as filler loading increases, additional fibres can either connect to the major cluster or to various other small clusters. As a result, the reduction in the number of 3D objects is not significant when the percolation threshold has been reached.
Figure 8.12: Example of 50 wt% NCCF composite stacks (left, 2089 total images) and 12 wt% SSF composite stacks (right, 2085 total images)

Summary

Although the quantitative analyses of the aspect ratio and the feret ratio of the SSF and the NCCF do not support the reason why the SSF composites exhibited a lower percolation threshold, many of the SEM images of the NCCF illustrate that there are many clusters, curved fibres and fines. All of these features exhibit an effective aspect ratio less than their equivalent straight fibres which would increase the percolation threshold. As these features were not observed in the SSF fibres, this suggests that the percolation threshold of the SSF composite would be lower than that of NCCF composites. The approximated value of waviness ratio suggested the presence of curvature in the NCCF. This would increase the percolation threshold. Furthermore, the number of contact point required to attain the percolation threshold would also increase which means the amount of filler material required would also increase.

The statistical analysis, F and G functions, suggests that the distribution of SSF is random while the distribution of NCCF is leaning toward clustering. This means that more than the expected amount of NCCF is required to attain the percolation threshold. This is another reason why the SSF composite exhibited a lower percolation threshold than the NCCF composite. However, this also means that it is possible to reduce the percolation threshold of an NCCF composite by modifying fibre distribution.
The 3D object counter analysis suggests that, for both the SSF and the NCCF composite, the number of 3D objects decreases and filler loading increases. This is because there are more fibres at higher filler loading so there is a greater chance for these fibres to connect to form clusters. For the SSF composites, an increase in 1 volume percent of SSF (121,000 reduction in 3D objects) corresponds to a greater reduction of 3D objects than an increase in 19.2 volume percent of NCCF (52,000 reduction in 3D objects). This suggests that SSFs are more effective at forming networks, which could potentially be another reason why the percolation threshold of the SSF composite is lower than that of the NCCF composite.

For both NCCF and SSF composites, although a lot of 3D objects were identified, there is only one major cluster. For composite with loading above the percolation threshold, this major cluster is part of the percolating cluster. As composites reach the percolation threshold, the amount of voxels found within the cluster increases at a slower rate.

The SSF composites exhibited a web-like microstructure, which is believed to occur once the aspect ratio of filler is high enough. No web-like microstructure was observed for the NCCF composites since the aspect ratio of NCCF is too low. The web-like microstructure of the SSF composite suggests that the section of the percolating cluster would require fewer connected particles to percolate. This also supports the idea which was suggested earlier, that SSFs can form a more effective network than NCCF composites. Therefore, the number of voxels identified in SSF composites is lower than the number identified in the NCCF composite.
Chapter 9

Conclusions and Recommendations

Nickel was successfully deposited as a uniform coating on cellulose fibres. Composites based on these nickel coated cellulose fibres (NCCF) have shown promising results as an electromagnetic interference (EMI) shielding material. The commercial standard of 40dB for electromagnetic interference shielding effectiveness (EMI SE) was not reached. However, an EMI SE of 15–20dB, as required for computers, has been achieved in the present study.

The incorporation of NCCF into the PP matrix, via a process of compression moulding, reinforces the material, resulting in an improvement in mechanical properties. Additionally, the compression moulding of these composites is quite feasible. NCCF composites will therefore be more attractive than composites containing commercially available stainless steel fibres (SSF) where mechanical strength is important. This study pointed out a number of opportunities for improving the EMI SE of NCCF composites towards feasible commercialisation.

In the optimisation process, sodium hydroxide solution was added manually to the electroless plating solution. If the addition of sodium hydroxide solution could be automated and the pH could be controlled more carefully, it might be possible to further reduce the phosphorus content of the nickel coating, which would increase the electrical conductivity of NCCF and further improve the EMI shielding capability of NCCF. The automation process could also reduce the variability of the EMI SE results as well as improve the production rate, which is important for mass production.

Alternatively, other natural fibres with longer aspect ratio should be investigated because increasing the aspect ratio decreases the percolation threshold of the composite. The
reduction of the percolation threshold will decrease the amount of material required to achieve acceptable EMI shielding requirement, thus making the composite cheaper to fabricate.

Another important finding was that the measurement of volume resistivity profile has shown a general trend which can assist in the determination of the percolation threshold of a composite containing either stiff or flexible conducting fibres, as well as having a suitable fibre loading for EMI shielding. This trend was such that, when the volume resistivity profile illustrated a mixture of electrically conductive and non-conductive regions, the composites are about to reach the percolation threshold. Volume resistivity is an important variable to consider as the mechanism of EMI shielding for both the SSF and the NCCF composites is believed to be absorption which depends on the thickness of the shielding material. Similarly, volume resistivity is measured through the thickness of the shielding material.

Statistical function, 2D and 3D image analysis provides an understanding between the microstructure and percolation threshold of the composite. Qualitative and quantitative analysis of SEM images suggests that NCCF has a shorter effective fibre aspect ratio than SSF, due to its curved fibres and fines. A Statistical functions analysis suggests that the distribution of SSF is random and the distribution of NCCF leans towards clustering. A 3D image analysis suggests that a high aspect ratio favours a web-like microstructure, as seen only in the SSF composites. All of these results in combination give rise to some of the reasons why the SSF composite exhibited a lower percolation threshold than the NCCF composite.

There are several recommendations for future research directions. The kinetics of the electroless deposition of nickel on cellulose fibres should be investigated. The electroless deposition of nickel on natural fibres has always been empirical. However, in order to be able to transfer the work on the electroless deposition of nickel on a type of natural fibre to another type of natural fibre, it is important to model the kinetics of the deposition process. The kinetics of nickel deposition on cellulose fibres have not been extensively investigated in this study because it has been of greater importance to create an NCCF with commercial standard EMI shielding capability. Therefore, once an acceptable EMI shielding NCCF has been fabricated, it is recommended that the kinetics of the nickel deposition process are investigated so that the experiment can be applied to other types of natural fibre.
The mechanical properties of NCCF composites have not been extensively investigated in this study because it was more important to create a composite that could shield EMI effectively. Therefore, once an NCCF composite with an acceptable commercial EMI shielding standard has been obtained, it is recommended that the moisture content, manufacturing techniques and processing parameters are extensively investigated to optimise the mechanical properties of natural fibre composites.

Thermal conductivity measurements for the SSF and NCCF composites were conducted but are not reported in this thesis because no clear relationship was found between the loading of the NCCF and the thermal conductivity of the composite. Further investigation/measurement should be carried out once a NCCF composite with an acceptable EMI shielding standard has been fabricated.

As longer (or thinner) cellulose fibres cannot be obtained, the only way to increase the aspect ratio is to use other types of natural fibre (for example: ramie, flax and hemp). An initial trial run on the electroless plating of ramie fibre demonstrated a poorly nickel-coated ramie fibre. As these fibres have a different surface chemistry from that of cellulose, the optimisation for a uniformly deposited nickel coating onto them should be investigated.

The compression pads were prepared by wet-blending of NCCF and PP fibres. The dry-blending technique should be used to investigate its effect on fibre dispersion. Additionally, the use of a dispersion agent could also be considered.

A Monte Carlo simulation should be conducted to determine the percolation threshold of composite containing uniformly distributed fibres so that comparison can be made with composite containing randomly distributed fibres to identify the ideal fibre dispersion. Factors such as curved fibres and varying effective aspect ratios should also be incorporated into the Monte Carlo simulation for an accurate model prediction of the percolation threshold of composite containing NCCF.
References


159. Thumm, A., Recommended Compression Moulding Parameters. 2013.


Appendix – Permission for Reuse

Figure 2.1, Figure 2.2, Figure 2.7

Thank you for your RightsLink / Taylor and Francis Group LLC Books transaction

Copyright Clearance Center <rightslink@marketing.copyright.com>
Reply-To: Copyright Clearance Center <reply-fe4e107779f2057e7c7c1c-14153969_HTML-113483790-1144653-190806@info.copyright.com>
To: psil003@aucklanduni.ac.nz

To view this email as a web page, go here.

Do Not Reply Directly to This Email

To ensure that you continue to receive our emails, please add rightslink@marketing.copyright.com to your address book.

Thank You For Your Order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center's RightsLink service. Taylor and Francis Group LLC Books has partnered with RightsLink to license its content.

This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://e100.copyright.com/CustomerAdminPLF.jsp?ref=63d2bddd-ec5b-4341-b972-d201f6207d5c

Order Details
Licensee: Pongphat Sittisart
License Date: Apr 6, 2015
License Number: 3603410709705
Title: Advanced materials and design for electromagnetic interference shielding
Type Of Use: Thesis/Dissertation
Total: 0.00 USD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1:v4.2
RF Cafe: Permission to reuse figure - granted!

rfcafe@yahoo.com <rfcafe@yahoo.com> 4 April 2015 at 01:54
To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

April 3, 2015

Greetings Patrick:

Thank you for bothering to write to ask permission. You are welcome to use the Near and Far Field image. Please include an attribution to RFcafe.com.

It is ironic that you ask about this figure because just two days ago I update the image to make it larger than the original. FYI, the graph was created in Excel using the three equations presented on the page.

Take care.

Sincerely,

Kirt Blattenberger
RF Cafe

www.rfcafe.com
rfcafe@yahoo.com
Kernersville, NC 27284
KB3UON -73-

Please support RF Cafe advertisers and Follow me on LinkedIn, Twitter and Facebook!
Hi Kirt

I would like to request for permission to reuse the following graph on my thesis:

Title: Near and Far Field - from static to radiation

Figure 3: The wave impedance measures the relative strength of electric and magnetic fields. It is a function of source structure.

Regards

Patrick

Patrick Sittisart <psit003@aucklanduni.ac.nz> 4 April 2015 at 02:03
To: RFCafe <rfcafe@yahoo.com>

Will do, thank yo so much

Patrick

[Quoted text hidden]
request for permission
11 messages

Patrick Sittisart <psit003@aucklanduni.ac.nz>
To: Ned Bryant <nrbryant@nptcompany.com>

Hi Ned,

Hope you are doing well.

I would like to know how I could request for permission to reprint the figures from the presentation (see attachment) that you sent to me a long time ago on my thesis.

Regards,
Patrick

EMI Setup.ppt
1057K

Ned Bryant <nrbryant@nptcompany.com>
To: psit003@aucklanduni.ac.nz
Cc: Margaret Cox <mcox@nptcompany.com>

Hi Patrick,

I have added Margaret Cox, she is our head of Marketing and she would be the one who could release the slides to you.

Margaret – Patrick is a graduate student in New Zealand that we have been supporting for several years. The attached slides are part of the larger EMI presentation and do not contain any customer photographs. We routinely display them in public and distribute this presentation to anyone that asks for a copy. From my perspective, I do not see a reason to not allow this.

Patrick – It would probably help if you could explain how you would like to use them, is this part of your thesis?

Thanks,

Ned

From: Patrick Sittisart [mailto:psit003@aucklanduni.ac.nz]
Sent: Saturday, June 18, 2016 5:23 AM
To: Ned Bryant
Subject: request for permission

[Quoted text hidden]

EMI Setup.ppt
1057K

Patrick Sittisart <psi003@aucklanduni.ac.nz>  28 June 2016 at 09:59
To: Ned Bryant <nbryant@rtcompany.com>
Cc: Margaret Cox <mcox@rtcompany.com>

Hi Ned and Margaret,

I would like to reuse the diagram illustrating the setup of EMI shielding measurement on slide one of the presentation on my thesis so that the reader can better understand the setup.

Regards,
Patrick
[Quoted text hidden]

Margaret Cox <mcox@rtcompany.com>  28 June 2016 at 10:24
To: Patrick Sittisart <psi003@aucklanduni.ac.nz>, Ned Bryant <nbryant@rtcompany.com>

Hi Patrick,

Thanks for the clarification on which item you are seeking permission to use. We require that you cite RTP Company for the use of the diagram. In addition, please let us know which media type you plan to use to display the diagram (i.e., Powerpoint, printed literature, pdf, video, something else?)? We’d like to provide the correct resolution for you. Please advise.

 Thanks!
Margaret

Margaret Cox
Manager, Marketing Communications

RTP Company

phone: 507-454-6900
direct: 507-474-5475
toll-free: 800-433-4787
mcox@rtcompany.com
www.rtcompany.com
580 E. Front Street
Winona, MN 55987

Disclaimer: No information supplied by RTP Company constitutes a warranty regarding product performance or use. Any information regarding performance or use is only offered as suggestion for investigation for use, based upon RTP Company or other customer experience. RTP Company makes no warranties, expressed or implied, concerning the suitability or fitness of any of its products for any particular purpose. It is the responsibility of the customer to determine that the product is safe, lawful and technically suitable for the intended use. The disclosure of information herein is not a license to operate under, or a recommendation to infringe any patents.

From: Patrick Sittisart [mailto:ps003@aucklanduni.ac.nz]
Sent: Monday, June 27, 2016 4:59 PM
To: Ned Bryant
Cc: Margaret Cox
Subject: Re: request for permission

[Quoted text Hidden]

Patrick Sittisart <ps003@aucklanduni.ac.nz> 28 June 2016 at 10:32
To: Margaret Cox <mcox@rtcompany.com>
Cc: Ned Bryant <nbryant@rtcompany.com>

Hi Margaret,

I will definitely cite RTP for the diagram. If you have a preference on how the citation should be then please provide a full citation for me so I can put it my references. Otherwise I will try to cite it to the best of my ability.

I am planning to use the diagram for powerpoint and pdf.

Regards,
Patrick
[Quoted text Hidden]

Margaret Cox <mcox@rtcompany.com> 29 June 2016 at 08:40
To: Patrick Sittisart <ps003@aucklanduni.ac.nz>
Cc: Ned Bryant <nbryant@rtcompany.com>

Hello, Patrick,

I am attaching the artwork in high resolution. As for the citation, please use the following:
Figure (xx) "Coaxial Transmission Line Test," RTP Company technical presentation 2014-09-05, Spectrum Analyzer/Tracking Generator illustration provided as a courtesy by RTP Company

Please let me know if you have any questions or concerns. Thanks!
Margaret

Margaret Cox
Manager, Marketing Communications
RTP Company

phone: 507-454-6900
direct: 507-474-5475
toll-free: 800-433-4787
mcox@rtpcompany.com
www.rtpcompany.com
580 E. Front Street
Winona, MN 55987

From: Patrick Sittisart [mailto:psit003@aucklanduni.ac.nz]
Sent: Monday, June 27, 2016 5:33 PM
To: Margaret Cox
Cc: Ned Bryant

[Quoted text hidden]

[Quoted text hidden]
Hi Margaret,

I would like to request for permission to reprint the surface resistivity image from your website.

http://www.rtpcompany.com/products/conductive/

I hope you can help me again,

Regards,
Patrick

---

Hello, Patrick,

I am traveling this week, but will take a look at this request when I return to the office next week.

Thanks,
Margaret

---

Hi Margaret,

May I please get an update on the request for permission to reprint?

Regards,
Patrick
Patrick Sittisart <psit003@aucklanduni.ac.nz> 24 March 2017 at 01:30
To: Margaret Cox <mcox@rtcompany.com>

Hi Margaret,

I would like to follow up on the request for permission to reprint please.

Regards,
Patrick

Margaret Cox <mcox@rtcompany.com> 24 March 2017 at 02:34
To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

Hello Patrick,

I apologize for the long delay. The artwork is attached – it's small and I am a bit concerned that the resolution will not be high enough for printing purposes, but please let me know on that. Please use the following information for the citation:

Figure (xx) "Surface Resistivity," RTP Company technical brochure 2009-01-14, Surface Resistivity illustration provided as a courtesy by RTP Company

Thanks,
Margaret

Margaret Cox
Manager, Marketing Communications
RTP Company
phone: 507-454-6900
direct: 507-474-5475
toll-free: 800-433-4787
mcox@rtcompany.com
www.rtcompany.com
580 E. Front Street
Winona, MN 55987
Disclaimer: No information supplied by RTP Company constitutes a warranty regarding product performance or use. Any information regarding performance or use is only offered as suggestion for investigation for use, based upon RTP Company or other customer experience. RTP Company makes no warranties, expressed or implied, concerning the suitability or fitness of any of its products for any particular purpose. It is the responsibility of the customer to determine that the product is safe, lawful and technically suitable for the intended use. The disclosure of information herein is not a license to operate under, or a recommendation to infringe any patents.

From: Patrick Sittisart [mailto:psit003@aucklanduni.ac.nz]
Sent: Thursday, March 23, 2017 7:31 AM

[Quoted text hidden]

[Quoted text hidden]

RTP Co_Surface resistivity of Conductive Products_02262017.jpg
205K
permission to reuse figure

Patrick Sittisart <psit003@aucklanduni.ac.nz>
To: bstas@item-media.net

Hi Belinda

I would like to request for permission to reuse the following figure in my thesis:

Title: Electromagnetic shielding (1988)
Author: White, D.R.J
Figure caption, shielding effectiveness vs. volume resistivity.

Regards
Patrick

Belinda Stas <bstas@item-media.net>
To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

Hi Patrick. Sure, you can use the figure, as long as you credit Interference Technology.

Belinda

Patrick Sittisart <psit003@aucklanduni.ac.nz>
To: Belinda Stas <bstas@item-media.net>

Will do, thank you so much

Patrick
Table 2.3, 2.4, 2.5, 2.6, 2.8

The University of Auckland Mail - Thank you for your RightsLink / JIn... https://mail.google.com/mail/u/0/?ui=2&ik=9e8b5b5f1e&jwver=9FXdY...

Patrick Sittisart <psit003@aucklanduni.ac.nz>

Thank you for your RightsLink / John Wiley and Sons transaction
1 message
Copyright Clearance Center <rightlink@marketing.copyright.com> 4 April 2015 at 02:46
Reply-To: Copyright Clearance Center <reply-fe4e107770652037e7c1c-14153369_HTML-
1134863790-114453-169040@info.copyright.com>
To: psit003@aucklanduni.ac.nz

To view this email as a web page, go here.

Do Not Reply Directly to This Email

To ensure that you continue to receive our emails,
please add rightlink@marketing.copyright.com to your address book.

Thank You For Your Order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center’s RightsLink service. John Wiley and Sons has partnered with RightsLink to license its content. This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://x100.copyright.com/CustomerAdmin/PLF.jsp?ref=6493112e-3686-4aeo-9c89-b3ac34972f6ea

Order Details
Licensee: Pongphat Sittisart
License Date: Apr 3, 2015
License Number: 380137042642
Publication: Journal of Applied Polymer Science
Title: EMI shielding: Methods and materials-A review
Type Of Use: Dissertation/Thesis
Total: 0.00 AUD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1:v4.2
Table 3.1, 3.2, 3.3, 3.4, 3.5 and Figure 3.4

---

**Table 3.1, 3.2, 3.3, 3.4, 3.5 and Figure 3.4**

---

**Request for permission to reprint**

5 messages

---

**Patrick Sittisart** <psit003@aucklanduni.ac.nz> 28 January 2017 at 19:30

To: MARK.WEBER2@mccgill.ca

Dear Dr. Weber,

My name is Patrick, I am a PhD student at the University of Auckland.

I would like to request your permission to reprint the following tables from your thesis "The processing and properties of electrically conductive fiber composites" please.

Table 4.1, 4.2, 4.3, 4.4 and 4.5

Regards,

Patrick

---

**Mark Weber, Dr.** <mark.weber2@mccgill.ca> 4 February 2017 at 10:41

To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

Hi Patrick,

Thanks for the note. I’m glad my research still has value. Please go ahead with the reprints as requested.

Best regards,

Mark

---

**Mark Weber, Ph.D., P.Eng.**

Associate Director | IDEA

McGill University | **Office of Innovation and Partnerships** | James Administration Building, room 429 | 845 Sherbrooke Street West | Montreal, QC H3A 0G4

T: 514-398-8649 | F: 514-398-4853

mark.weber2@mccgill.ca | http://www.mcgill.ca/research
From: Patrick Sittisart [mailto:pslt003@aucklanduni.ac.nz]
Sent: Saturday, January 28, 2017 1:30 AM
To: Mark Weber, Dr. <mark.weber2@mcgill.ca>
Subject: request for permission to reprint

Patrick Sittisart <pslt003@aucklanduni.ac.nz>
To: "Mark Weber, Dr." <mark.weber2@mcgill.ca>

Hi Mark,

Thank you for your permission.

Could you please clarify for me, Figure 4.1 on page 64 of your thesis (attached for your reference), my understanding is that you have redrawn the graph based on two references. If yes, I would like to request for permission to reprint Figure 4.1 as well please.

Regards,
Patrick

[Quoted text hidden]

THE PROCESSING AND PROPERTIES OF ELECTRICALLY CONDUCTIVE FIBRE COMPOSITES.pdf
5871K

Mark Weber, Dr. <mark.weber2@mcgill.ca>
To: Patrick Sittisart <pslt003@aucklanduni.ac.nz>

Hi Patrick,

Yes, you are correct. I used an old plotting software (Sigmaplot) to redraw the data from the two references. I am fine with you reprinting Figure 4.1.

Thanks.

Mark

From: Patrick Sittisart [mailto:pslt003@aucklanduni.ac.nz]
Sent: Wednesday, February 08, 2017 5:17 AM
To: Mark Weber, Dr. <mark.weber2@mcgill.ca>
Subject: Re: request for permission to reprint

Patrick Sittisart <pslt003@aucklanduni.ac.nz>
To: "Mark Weber, Dr." <mark.weber2@mcgill.ca>

178
Figure 3.1

Thank you for your RightsLink / Springer transaction

6 April 2015 at 23:37

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center’s RightsLink service. Springer has partnered with RightsLink to license its content. This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=b34e790e-179e-45bd-a547-e5752dc0c664

Order Details
Licensee: Pongphat Sittisart
License Date: Apr 6, 2015
License Number: 36303051232340
Publication: Journal of Electroceramics
Title: FEATURE ARTICLE Conducting Polymer Composites
Type Of Use: Thesis/Dissertation
Total: 0.00 USD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1:v4.2
Thank you for your RightsLink / John Wiley and Sons transaction

Copyright Clearance Center <rightlink@marketing.copyright.com>
Reply-To: Copyright Clearance Center <reply-fe4e10777052037e7c1c-14153369_HTML-1134883790-114453-169683@info.copyright.com>
To: psit003@aucklanduni.ac.nz

5 April 2015 at 15:02

Thank You For Your Order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center's RightsLink service. John Wiley and Sons has partnered with RightsLink to license its content. This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=554fb0c3:43ff-4242-6d20-d25262aced296

Order Details
Licensee: Pongphat Sittisart
License Date: Apr 4, 2015
License Number: 360260335096
Publication: Advances in Polymer Technology
Title: The effect of compounding on the conductive properties of EMI shielding compounds
Type Of Use: Dissertation/Thesis
Total: 0.00 AUD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1.4.2
Thank you for your order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center’s RightsLink® service.

Order Summary

Licensee: Pongphat Sittisart
Order Date: Oct 8, 2017
Order Number: 4204380752227
Publication: RSC Advances
Title: Novel approach to percolation threshold on electrical conductivity of carbon nanotube reinforced nanocomposites
Type of Use: Thesis/Dissertation
Order Total: 0.00 AUD

View or print complete details of your order and the publisher's terms and conditions.

Sincerely,

Copyright Clearance Center
Figure 3.5

permission to reuse figure

Patrick Sittisart <psit003@aucklanduni.ac.nz>

To: rights@wspc.com.sg

5 April 2015 at 15:14

Hi

I would like to request for permission to reuse the following figure in my thesis:

Title: PERCOLATION AND TUNNELING IN COMPOSITE MATERIALS
Fig 1: An illustration of a system of "metallic" particles that are embedded in an insulating matrix....

Regards
Patrick

rights@wspc.com <rights@wspc.com>

To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

7 April 2015 at 21:17

Hi Patrick

Please let us have the ISBN/ISSN of our publication where the below figure is from.

Kind regards
Tu Ning
[Quoted text hidden]

Patrick Sittisart <psit003@aucklanduni.ac.nz>

To: "rights@wspc.com" <rights@wspc.com>

7 April 2015 at 22:11

Hi Tu Ning

Only the DOI is available. DOI: 10.1142/S02179792064025336

Regards
Patrick
[Quoted text hidden]

rights@wspc.com <rights@wspc.com>

To: Patrick Sittisart <psit003@aucklanduni.ac.nz>

9 April 2015 at 19:42

Hi Patrick

We are pleased to grant you the permission of reproducing Fig 1 from the title "PERCOLATION AND TUNNELING IN COMPOSITE MATERIALS", International Journal of Modern Physics B, Vol. 18, No. 15 (2004) 2091/2121 in your thesis, provided that full credit given to the original source in the following format:

Title of the Work, Author(s) and/or Editor(s) Name(s), Title of the Journal, Vol and Issue No., Copyright @ year and name of the publisher

Kind regards
Thank You For Your Order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center's RightsLink service. John Wiley and Sons has partnered with RightsLink to license its content. This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://e100.copyright.com/CustomerAdmin/PLF.jsp?ref=18f5e5c9-cb32-4e34-af22-d687bc74a6d6

Order Details

Licensee: Pongphat Sittisart
License Date: Apr 4, 2015
License Number: 3602270066429
Publication: Polymer Engineering & Science
Title: Electron transport processes in conductor-filled polymers
Type Of Use: Dissertation/Thesis
Total: 0.00 AUD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1:v4.2

+1-855-239-3415 / Tel: +1-978-646-2777
customercare@copyright.com
http://www.copyright.com

Copyright Clearance Center <rightslnk@marketing.copyright.com>
Reply-To: Copyright Clearance Center <reply-fe4e107770620327e7c1c-14153369_HTML-1134883790-114453-169696@info.copyright.com>
To: psit003@aucklanduni.ac.nz

To view this email as a web page, go here.
Figure 3.7

The University of Auckland Mail - permission for reprint

Patrick Stittisart <psit003@aucklanduni.ac.nz>

184
Figure 3.8, 3.9

Thank You For Your Order!

Dear Mr. Pongphat Sittisart,

Thank you for placing your order through Copyright Clearance Center's RightsLink service. John Wiley and Sons has partnered with RightsLink to license its content. This notice is a confirmation that your order was successful.

Your order details and publisher terms and conditions are available by clicking the link below:
http://x100.copyright.com/CustomerAdmin/PLF.jsp?ref=ad1f6a39-f50c-4852-ad93-c8331a851d9

Order Details
Licensee: Pongphat Sittisart
License Date: Apr 5, 2015
License Number: 3602290216288
Publication: Polymer Composites
Title: Microstructure and volume resistivity of composites of isotactic polypropylene reinforced with electrically conductive fibers
Type Of Use: Dissertation/Thesis
Total: 0.00 AUD

To access your account, please visit https://myaccount.copyright.com.

Please note: Online payments are charged immediately after order confirmation; invoices are issued daily and are payable immediately upon receipt.

To ensure that we are continuously improving our services, please take a moment to complete our customer satisfaction survey.

B.1:v4.2

+1-855-239-3415 / Tel: +1-978-648-2777
customercare@copyright.com
http://www.copyright.com
Figure 3.10, 3.11
FW: New Contact Us submission from Patrick

Clare Richardson <CRichardson@nickelinstitute.org>
To: "psit003@aucklanduni.ac.nz" <psit003@aucklanduni.ac.nz>

16 October 2017 at 22:47

Dear Patrick,

Thank you for your message.

You may reprint it with reference:

Parkinson R., Properties and applications of electroless nickel, Nickel Development Institute, NIDI Technical Series No. 10081, (1997) Link: https://nickelinstitute.org/~Files/Technical_literature/PropertiesAndApplicationsOf/Ele
crolessNickel_10081_.pdf

Courtesy of Nickel Institute

(NIDI was incorporated into the Nickel Institute in 2004).

Thanks and kind regards

Clare

Clare Richardson
Director, Communications & Member Services
Nickel Institute
Rue Belliard 12, 3rd floor
B-1040 Brussels-Belgium
Telephone: +32 2 290 3206

Mobile: +32 477 675 228
E-mail: crichardson@nickelinstitute.org
Web: www.nickelinstitute.org ; www.nickelconsortia.eu

Twitter: @nickelinstitute
From: Brussels  
Sent: maandag 16 oktober 2017 11:26  
To: Clare Richardson <CRichardson@nickelInstitute.org>  
Subject: FW: New Contact Us submission from Patrick

Hi Clare,

FYI,

KR,

IB

From: noreply@nickelInstitute.org [mailto:noreply@nickelInstitute.org]  
Sent: vrijdag 13 oktober 2017 11:29  
To: Brussels <Brussels@nickelInstitute.org>  
Subject: New Contact Us submission from Patrick

Good Day Nickel User,

A new Contact Us submission has been made by: Patrick  
Email: psw003@aucklanduni.ac.nz  
Phone:  
Inquiry type: General Inquiry

Message:
I would like to request for permission to reprint the following figure in my thesis please. Figure 4 Effect of composition on electrical resistivity. This is from the article: Parkinson R., Properties and applications of electroless nickel, Nickel Development Institute, NIDI Technical Series No. 10081, (1997) Link: https://nickelInstitute.org/~Media/Files/TechnicalLiterature/PropertiesAndApplicationsOfElectrolessNickel_10081_.pdf

end

This message, including any attachments, is privileged and may contain confidential information intended only for the person(s) named above. Any other distribution, copying or disclosure is strictly prohibited. Communication by email is not a secure medium and, as part of the transmission process, this message may be copied to servers operated by third parties while in transit. Unless you advise us to the contrary, by accepting communications that may contain your personal information from us via email, you are deemed to provide your consent to our transmission of the contents of this message in this manner. If you are not the intended recipient or have received this message in error, please notify us immediately by reply email and permanently delete the original transmission from us, including any attachments, without making a copy.
Figure 8.7

Permission to Reuse Figure

2 messages

Patrick Sittisart <psilt003@aucklanduni.ac.nz>
To: Thomas Boudier <thomas.boudier@upmc.fr>

3 October 2017 at 22:23

Hi Thomas,

I would like to request for permission to reprint the below figure in my thesis please. I will be using this figure as an example.

Regards,
Patrick

---

Thomas Boudier <thomas.boudier@upmc.fr>
To: Patrick Sittisart <psilt003@aucklanduni.ac.nz>

4 October 2017 at 15:07

Hi Patrick,

Sure you can use the figure, please cite the reference papers:

https://www.ncbi.nlm.nih.gov/pubmed/223836354, application of spatial statistics to P-bodies

http://journals.plos.org/ploscompbiol/article?id=10.1371/journal.pcbi.1000053, methodology paper for spatial statistics used


Good luck with your PhD.

Best

Thomas [Quoted text hidden]

="/*******************************************************************/
 * Thomas Boudier. Associate Professor, UPMC,
 * Université Pierre et Marie Curie, Paris, France.
 * Bioinformatics Institute (BII)/IPAL, Singapore.
="/**********************************************************************/"