The Effect of Graphene Nanoplatelets on the Mechanical Properties and Electrical Conductivity of Epoxy Resin Nanocomposites

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Contents

1 Introduction ................................................................................................................................. 26
  1.1 Background to the Project .................................................................................................. 27
  1.2 Aims of the Project .......................................................................................................... 30
  1.3 Challenges ......................................................................................................................... 31
  1.4 Outline of the Thesis ......................................................................................................... 33

2 Graphene and Epoxy Resins .................................................................................................... 34
  2.1 Introduction to Graphene .................................................................................................... 35
    2.1.1 Structure and Properties of Graphene ..................................................................... 35
    2.1.2 Manufacture of Graphene ......................................................................................... 36
  2.2 Characterisation of Graphene ............................................................................................. 37
    2.2.1 Optical Microscopy and Electron Microscopy ....................................................... 37
    2.2.2 Raman Spectroscopy ............................................................................................... 37
    2.2.3 Atomic Force Microscopy (AFM) ............................................................................ 38
  2.3 Graphene in Composite Materials ....................................................................................... 39
    2.3.1 Advantages of Graphene over Carbon Nanotubes (CNTs) .................................... 39
    2.3.2 Graphene Nanoplatelets (GNPs) .......................................................................... 40
  2.4 Introduction to Epoxy Resins ............................................................................................... 41

3 Literature Review ...................................................................................................................... 44
  3.1 The Dispersion of GNPs in Epoxy Resin .......................................................................... 45
  3.2 Methods of Dispersing GNPs in Epoxy Resin .................................................................. 47
    3.2.1 Three Roll Milling .................................................................................................. 47
    3.2.2 Sonication .............................................................................................................. 48
    3.2.3 Shear Mixing ........................................................................................................ 49
    3.2.4 The Effect of Solvents on the Exfoliation Process .................................................. 52
3.3 Chemical Functionalisation of GNPs ............................................................... 53
  3.3.1 Methods of Chemical Functionalisation .................................................. 54
3.4 Review of Mechanical Results from other Studies ........................................ 57
  3.4.1 Tensile Results ......................................................................................... 57
  3.4.2 Fracture Results ....................................................................................... 61
3.5 Electrical Properties of GNP Reinforced Epoxy Resin Composites ................ 66
  3.5.1 Electric Field Alignment of GNP .............................................................. 68
  3.5.2 Magnetic Field Alignment ....................................................................... 70
  3.5.3 Measuring Conductivity .......................................................................... 70
  3.5.4 Electrical Conductivity Results from other Research Studies .................. 72
4 Experimental ...................................................................................................... 75
  4.1 Materials ...................................................................................................... 76
    4.1.1 Unfunctionalised Graphene Nanoplatelets (GNPs) ................................... 76
    4.1.2 Functionalised GNPs ............................................................................ 76
    4.1.3 Multiwall Carbon Nanotubes (MWCNTs) .............................................. 79
    4.1.4 Expanded Graphite (EG) ..................................................................... 81
    4.1.5 Epoxy Resin ......................................................................................... 82
    4.1.6 Triton X-100 Surfactant ....................................................................... 82
    4.1.7 Silane Coupling Agent ......................................................................... 82
    4.1.8 Silver Conductive Epoxy Resin .............................................................. 82
  4.2 Equipment .................................................................................................... 83
    4.2.1 Silverson Shear Mixer ......................................................................... 83
    4.2.2 Mechanical Stirrer ............................................................................... 83
    4.2.3 QSonica Q700 Sonicator .................................................................... 83
    4.2.4 Heraeus Vacutherm Degassing Chamber ............................................ 83
    4.2.5 Heraeus Thermoscientific Curing Oven ............................................... 84
    4.2.6 Silicon Rubber Moulds ......................................................................... 84
4.2.7 Surface Grinder ................................................................. 84

4.3 Preparation of Samples ............................................................................. 85

4.3.1 Pure Epoxy Resin Investigation .......................................................... 86

4.3.2 GNP Reinforced Epoxy Resin Investigation ........................................ 87

4.3.3 Functionalised GNP Reinforced Epoxy Resin Investigation .................... 89

4.3.4 Surfactant Assisted Dispersion Investigation ........................................ 89

4.4 Testing ........................................................................................................... 91

4.4.1 Tensile Testing ......................................................................................... 91

4.4.2 Plane Strain Fracture Toughness Testing .................................................. 91

4.4.3 Electrical Conductivity Testing ................................................................. 93

4.4.4 Thermal Conductivity Testing ................................................................. 94

4.5 Characterisation of Composites ................................................................. 95

4.5.1 XPS (X-Ray Photoelectron Spectroscopy) .............................................. 95

4.5.2 FTIR (Fourier Transform Infrared Spectroscopy) .................................... 95

4.5.3 Raman Spectroscopy ............................................................................... 96

4.5.4 SEM (Scanning Electron Microscopy) ....................................................... 96

4.5.5 Optical Microscopy .................................................................................. 96

4.5.6 Modulated Differential Scanning Calorimeter (DSC) ............................... 96

4.5.7 Thermal Gravimetric Analysis (TGA) ........................................................ 97

4.5.8 Atomic Force Microscopy (AFM) ............................................................. 97

5 Tensile Properties Results and Discussion .................................................. 98

5.1 Pure Epoxy Resin Investigation ................................................................. 99

5.2 Unfunctionalised GNP Reinforced Epoxy Resin Investigation .................... 100

5.2.1 The Effect of Shear Mixing Speed and Time on the Mechanical Properties of GNP Reinforced Epoxy Resin ................................................................. 100

5.2.2 The Effect of GNP Loading Weight on the Mechanical Properties .......... 105

5.2.3 The Effect of MWCNTs and EG on the Mechanical Properties of Epoxy Resin .... 112
6

7.6 GNP Reinforced Epoxy Resin Composites ......................................................... 165
7.7 Modelling of GNP Reinforced Epoxy Resin Composites ................................. 167
7.8 Summary ........................................................................................................... 171

7.8.1 Comparison of Results with the Literature ..................................................... 171

8 Conclusions ......................................................................................................... 173

8.1 Overall Summary .............................................................................................. 174
8.2 Recommendations for Further work ................................................................. 175
8.3 Appendix ........................................................................................................... 177

8.3.1 Calculation of density of M25 grade GNPs .................................................... 177
8.3.2 AFM Measurements for the calculation of the aspect ratio of GNPs ............ 177

8.4 References ........................................................................................................ 187

Abbreviations

AC Alternating current
AFM Atomic force microscopy
ASTM American standards and testing methods
CB Carbon black
CFRP Carbon fibre reinforced plastic
CNT Carbon nanotube
CPS Counts per second
CVD Chemical vapour deposition
DC Direct current
DGEBA Diglycidyl Ether of Bisphenol A
DSC Differential scanning calorimetry
DWCNT Double wall carbon nanotube
EG Expanded graphite
FGS Functionalised graphene sheets
FTIR Fourier transform infrared spectroscopy
GNP Graphene nanoplatelet
GO Graphene oxide
IPA Isopropyl alcohol
IPD Inter particle distance
$K_{ic}$ Mode I Fracture toughness
MDI 4,4′-methylene diphenyl disocyanate
MWCNT Multiwall carbon nanotube
NDT Non-destructive testing
NMP N-Methyl-2-pyrrolidone
$P_c$ Percolation threshold
List of Tables

Table 1.1: Frequency of structural checks on aircraft. Checks can be timely, cost money and increase
down time ........................................................................................................................................... 29

Table 2.1: Summary of the physical properties of graphene ........................................................................ 36

Table 2.2: Comparison of CNT properties with Graphene ........................................................................ 40

Table 3.1: Fracture toughness results from other research groups .......................................................... 65

Table 3.2: Conductivity results from other research groups ......................................................................... 73

Table 4.1: Summary of the properties of different GNPs purchased from XG Sciences and ACS
Materials and the functional groups they contain according to the manufacturer ........................................... 76

Table 4.2: Table of the speeds and mixing times used to make the GNP reinforced epoxy resin
samples. In total 10 different samples were made........................................................................................ 87

Table 5.1: Tensile strength and modulus of the 7 neat epoxy resin specimens .............................................. 99

Table 5.2: Measurements of agglomerate sizes across five different optical micrographs shown in
Figure 5.6.................................................................................................................................................. 103

Table 5.3: Atomic concentration of oxygen and carbon from O1s and C1s peaks in various types of GNPs .................................................................................................................................. 126

Table 5.4: Quantities of resin and surfactant used in the effect of surfactant only investigation .... 136

Table 7.1: Dimensions of 17 agglomerates measured using AFM and their aspect ratios ................. 170
List of Figures

Figure 1.1: Use of different materials in the Airbus XWB. Composites make up 53% by weight of the aircraft with CFRP being the dominant composite. In volume terms this is about 80% of the total volume. The huge difference in weight percentage versus volume percentage is because CFRP is much lighter than other materials [3]................................................................. 28

Figure 1.2: Computerised image of the microstructure of carbon fibre epoxy resin composite. Fibres are arranged in layers stacked on top of one another and held together by epoxy resin. a) composites are strong when pulled along the plane of the fibres (x and y directions) b) composites are weak when subjected to through thickness stresses perpendicular to the fibres (z direction); c) Impact events such as hailstones birdstrikes and tool drops create through thickness stresses which result in microcracks forming in the epoxy resin beneath the surface of the composite. This can lead to delamination as shown in the SEM image. (Adapted from [6])................................................................. 28

Figure 1.3: A 33 ply CFRP laminate. Although the surface damage is small the damage that has occurred beneath the surface is extensive. This demonstrates the difficulties in inspection [1]....... 29

Figure 1.4: A representation of two microstructures of a graphene reinforced epoxy resin composite illustrating a good and a poor dispersion from a crack stopping perspective a) Representation of a poor microstructure. Graphene flakes are in the form of agglomerates and there are clear paths for cracks to grow through the weak epoxy resin. b) Representation of a good microstructure. Graphene flakes are distributed in such a way that there are no clear paths for cracks to move through epoxy resin. The graphene is therefore an effective crack stopper ................................................................. 32

Figure 1.5: A representation of two microstructures of a graphene reinforced epoxy resin composite illustrating a good and a poor dispersion from an electrical conductivity perspective a) Representation of a poor microstructure. Graphene flakes are in the form of agglomerates and there are no connections to transfer electrical current. b) Representation of a good microstructure. The graphene flakes are connected meaning current can be transferred through the thickness of the composite. This would be good for damage sensing purposes ................................................................. 32

Figure 2.1 (a) A low magnification transmission electron microscopy image of a graphene flake. Scale bar is 100nm (b) higher resolution image with an arrow pointing to the edge of the flake. Scale bar is 4 Å. (c) an atomic resolution image of a graphene flake showing the C-C bond length [12] ............... 35

Figure 2.2: stages of manufacture of graphene oxide. GNPs are firstly oxidised by heating in a mixture of hydrochloric acid (HCl), nitric acid (HNO₃) and potassium chlorate (KClO₃) to make oxidised GNPs
with an increased interlayer spacing. Sonication is then employed to exfoliate layers to yield 
graphene oxide [47].

Figure 2.3: a) Optical microscopy image of graphene showing mono layer, bi layer and tri layer 
graphene [8] b) TEM image of a graphene flake. Scale is 500 nm [19] c) Raman spectrum of graphene 
in comparison to graphite showing the G and 2D peak [20] d) Raman spectra of different layers of 
graphene showing the shift in the 2D peak position [20] e) AFM topology plot showing the change in 
height when the cantilever encounters a graphene flake. The 2 red markers represent the height 
change from the position shown in the microscope image f) [21].

Figure 2.4: (left) graphical representation of a typical GNP showing dimensions. GNPs can consist of 
anywhere between 4 and 20 layers. (Right) TEM image showing number of graphitic layers in GNPs 
each 0.34 nm thick. In this image 5 layers can be seen [73].

Figure 2.5: Chemical structure of the active molecule (DGEBA) in epoxy resin used in this 
investigation. n is often zero but can be 1 or 2 in some molecules. Typically, greater than 85 of 
molecules have n=0.

Figure 2.6: The structure of DGEBA in the epoxy resin used in this system when n is equal to zero.

Figure 2.7: Chemical structure of the amine hardener used in the investigation called bis-
cyclohexylamine.

Figure 2.8: The primary reaction ($k_1$) which occurs between the epoxide group of the epoxy resin and 
the amine group of the hardener.

Figure 2.9: Secondary reaction ($k_2$) which can occur between the epoxide group of the epoxy resin 
and the secondary amino hydrogen (N-H) of the reaction product of the primary reaction.

Figure 3.1 (a) A fibre less than the critical length. The fibre is too short for stress to be fully 
transferred to the fibre (b) fibre equal to the critical length. Maximum stress is fully developed in the 
fibre but at one point only (c) A fibre longer than the critical length. Stress is fully transferred to the 
fibre and reaches a plateau in the middle. This is the most efficient length for strengthening of 
composites [83].

Figure 3.2: a) Picture of a three roll mill b) diagram of how the rollers move and how material is fed 
into the machine [2].

Figure 3.3: Histogram of the number of layers per flake as a function of sonication time. 100 flakes 
were measured in each case. The histogram shows that the longer the sonication time the more 
graphene is exfoliated [59].
Figure 3.4: Histogram of the flake length as a function of sonication time. 100 flakes were measured in each case. The histogram shows that the flake length decreases with longer sonication times [59].

Figure 3.5 a) Silverson LSM Mixer showing the rotating paddle and perforated grid; b) Agglomerates enter the shear head where they are broken up by the shear forces created by the rotating paddle; c) They are then pushed out through the holes in the perforated grid.

Figure 3.6 Concentration of graphene produced versus the shear rate produced by the mixer. The concentration only increases once a shear rate of $10^4$ s$^{-1}$ is produced [18].

Figure 3.7: A histogram of the number of layers per flake measured for 100 flakes [18]. The average is 7.2 layers per flake. In total 9 flakes were monolayer graphene.

Figure 3.8: A histogram of the flake length measured for 100 flakes. The average flake length was 0.38 µm. [18]

Figure 3.9: The chemical structure of NMP (left) and cyclopentanone (right). These two solvents help stabilise dispersions of graphene because their solubility parameters are similar to those of graphene.

Figure 3.10: (left) complete non wetting of a liquid droplet on a solid surface characterised by a contact angle ~0˚; (middle) intermediate wetting; (right) perfect wetting characterised by a contact angle of 180˚. [4]

Figure 3.11: The chemical structure of graphene oxide. The addition of epoxide, hydroxyl and carboxylic acid groups disrupts the conductivity of graphene [7].

Figure 3.12 The chemical structure of reduced graphene oxide showing that most functional groups restoring some of the conductivity.

Figure 3.13 Steps for the preparation of amine functionalised graphene. (a) oxidation using Hummer’s method (b) reaction with an alkylamine (c) reduction using hydrazine. Reduction partly restores the electrical conductivity of graphene whist still providing functional groups to form bonds with epoxy resin molecules [11].

Figure 3.14: Functionalisation of graphene oxide with APTS. The NH$_2$ groups (in red) of the silane molecules attached to the surface of the graphene oxide are capable of reacting with epoxide groups from the epoxy resin. The silane molecules act as a coupling agent which improves the interfacial adhesion of graphene with epoxy resin.
Figure 3.15 (a) The effect of different functional groups on GNPs on the modulus of epoxy resin (b) the effect of different functionalisations on the tensile strength of epoxy resin. UG=unfunctionalised GNPs, GO=Graphene oxide, G-NH$_2$= amino functionalised GNPs, G-Si=Silane functionalised GNPs [14] .................................................................................................................................................. 58

Figure 3.16: Tensile properties of GO epoxy resin. Tensile strength and modulus improve up to 0.1 – 0.125 wt% but then begin to decline again. (FGS = functionalised graphene sheet which is equivalent to GO) .................................................................................................................................................. 59

Figure 3.17: (a) CNT agglomerates become exfoliated after 3 roll milling leading to better wetting of the surface with epoxy resin (b) agglomerates after sonication have a closed structure[113] ............ 60

Figure 3.18: (a) comparison of the tensile strength of different types of CNT reinforced epoxy resin. CB= Carbon black. SWCNT = Single walled carbon nanotube, DWCNT=Double walled carbon nanotube; (b) Comparison with amino functionalised (NH$_2$) nanotubes and carbon black [114] ......... 60

Figure 3.19 Comparison of packing of graphene sheets in a monolayer graphene composite and a trilayer graphene composite. A higher volume fraction of graphene can be accommodated in the trilayer graphene composite [9].................................................................................................................................................. 61

Figure 3.20: Tails forming around GNPs in an epoxy resin due to crack pinning. The white arrow shows the direction of crack propagation [109] .................................................................................................................................................. 62

Figure 3.21 Crack deflection in a graphene reinforced glass composite [117]................................. 62

Figure 3.22 Fracture toughness (y axis) versus loading percentage of GO (x axis). The fracture toughness increases at low loadings but then deteriorates if more GNPs are added. This is a typical trend of most fracture toughness results with nano fillers [5]. Functionalised graphene sheet content weight % is equivalent to GO weight %. .................................................................................................................................................. 63

Figure 3.23: Comparison of the fracture toughness of three different fillers in epoxy resin. TRGO (thermally reduced graphene oxide) is the best performer. The oxygen atoms on the surface promote better bonding with epoxy resin [15] .................................................................................................................................................. 64

Figure 3.24: SEM images of fracture surfaces of failed specimens: (a) neat epoxy resin, (b) 0.1 wt. %, (c) 0.5 wt. %, and (d) 0.7 wt % GO-epoxy resin nanocomposites. The white arrows at the bottom of the corners indicate the crack growth direction. Black arrows indicate micro cracks [17]. ............... 64

Figure 3.25: Illustration of how the conductivity of an insulator rises as a function of the amount of conductive filler added to it according to percolation theory. The percolation threshold is ~ 0.2 wt%
at which point the conductivity of the composite rises several orders of magnitude. Below the percolation threshold the conductivity is so low that it is essentially zero. Adapted from [10].

Figure 3.26 (a) A microstructure which does not result in a percolated network. This material will be a poor conductor (b) microstructure showing a percolated network of GNP s resulting in DC conductivity.

Figure 3.27: Optical micrograph of GNP s dispersed in epoxy resin during the application of an AC electric field. (a) before the field was applied (b) after 4mins (c) after 10 minutes and (d) after 20 minutes. + and − represent positive and negative electrodes [13].

Figure 3.28: Comparison of electrical conductivity for aligned and randomly orientated GNP s in epoxy resin [13]. Alignment of GNP s can enhance the electrical conductivity compared to randomly orientated GNP s.

Figure 3.29: Typical conductivity responses as a function of frequency for three different materials. A metal such as aluminium which is a homogenous conductor has a conductivity which is independent of frequency ~10^6 S/m. For nanocomposites which have a mixture of conductive phases (GNPs) and capacitative phases (epoxy resin) two possible scenarios can exist. If GNP s form a connected network they will follow the percolated nanocomposites curve. In this case the conductivity becomes independent of frequency at low frequencies. The DC conductivity is equivalent to the value at which conductivity becomes constant ~10^{-1} S m^{-1} in this example. If the GNP s do not form a connected network the conductivity will follow the unpercolated nanocomposites line and the DC conductivity cannot be defined. Whether or not the GNP s form a percolating network depends on the processing and loading of the GNP s in epoxy resin.

Figure 3.30: SEM of graphene foam showing an interconnected 3D network of graphene [16].

Figure 3.31: CVD growth of graphene composites using a nickel foam scaffold a) Nickel foam scaffold used as a template to grow graphene b) Nickel foam heated in the presence of methane causes graphene to grow on Nickel c) PMMA coated on the graphene surface d) Nickel etched away using HCl leaving graphene foam coated with PMMA. e) Acetone used to dissolve away the PMMA layer leaving graphene foam f) Graphene foam infiltrated with PDMS to create a composite with an extremely high conductivity. [16]

Figure 4.1: Low magnification image of XG Sciences grade M25 GNP s. The dimensions of the GNP s appear quite varied although the manufacturer claims the lateral dimensions are on average 25 µm and the thickness is 6-8 nm.
Figure 4.2: High magnification SEM image of XG Sciences grade M25 GNPs. The image reveals the different sizes of the individual platelets and the presence of wrinkles where the sheets have become creased and folded.

Figure 4.3: SEM Image of C300 grade GNPs from XG Sciences. In comparison to the M25 grade GNPs the overall agglomerate size appears smaller.

Figure 4.4: SEM Image of C500 grade GNPs from XG sciences

Figure 4.5: SEM image of C750 grade GNPs from XG sciences. The size of the agglomerates appears smaller than the M25 grade. This is would concur with the manufacturer’s claims that the specific surface area of the C grade GNPs is higher than the M25 grade GNPs.

Figure 4.6: Low magnification SEM image of MWCNTs from Cheap Tubes. The MWCNTs can clearly be seen in the form of agglomerates. Individual MWCNTs be only be seen protruding from the agglomerates at high magnification (see Figure 4.7)

Figure 4.7: High magnification SEM Image of a MWCNT agglomerate. Individual MWCNTs can just be seen as fine thread like structures sticking out at the edge of the agglomerate

Figure 4.8: Low magnification SEM image of EG “worms”. The worms are on average 1 mm in length, much larger than GNP and CNTs.

Figure 4.9: High magnification SEM Image of EG showing the interlayer spacing between the graphitic sheets. In EG the interlayer spacing is on the order of micrometres whereas in conventional graphite the spacing between layers is 0.34 nm

Figure 4.10: Chemical structures of the active molecules in Araldite LY564 (DGEBA) and Aradur 2954 (bis-cyclohexylamine), and the chemical structure of surfactant Triton X-100 (where n=9-10) and silane coupling agent.

Figure 4.11: a) Shear mixer b) and c) mechanism of action of the shear mixer. GNPs enter the head and the shear forces generated by the rotating paddle break up the agglomerates and push them out of the perforated metal grid; d) mechanical stirrer; e) Q700 Sonicator; f) Degassing chamber; g) Curing oven h) silicon rubber moulds used to cast tensile specimens; i) surface grinder; j) tensile specimen before surface grinding; k) tensile specimen after surface grinding

Figure 4.12: Images showing steps in the manufacture of pure epoxy resin specimens a) 120 g of Araldite LY564 mixed with 42g of Aradur 2954 b) Mixture stirred at 500 rpm using the mechanical stirrer c) degassing of mixture to remove air bubbles d) Tensile moulds into which mixture was
poured and cured in an oven e) cured specimen removed from the mould before surface grinding f) specimen after surface grinding.

Figure 4.13: Images showing steps in the manufacture of shear mixed GNP reinforced epoxy resin samples a) Shear mixing of GNPs in Araldite LY564 to break up GNP agglomerates b) Mechanical stirring of GNPs in Araldite LY564 with the addition of hardener Aradur 2954 to ensure an even distribution of resin and hardener c) silicon rubber moulds filled with epoxy resin mixture after degassing ready to be cured d) removal of cured GNP reinforced epoxy resin specimens from the mould after surface grinding. Specimens were prepared for tensile, thermal conductivity, electrical conductivity and fracture toughness tests. (Note that the addition of GNPs to epoxy resin turns the epoxy resin black).

Figure 4.14 a) tensile specimen in mechanical grips of an Instron testing machine being loaded in tension b) shape of individual tensile specimen

Figure 4.15 a) Drop weight setup. The crack machine lies underneath a drop weight which when released pushes down the razor blade into the specimen. B) Close up of the crack machine showing the razor blade used to create a pre crack c) close up of the razor blade pushed into the specimen after the drop weight has been released.

Figure 4.16: Three point bending rig used to test fracture toughness specimens. The load cell applies a downwards force on the specimen causing a crack to grow from the notch until failure.

Figure 4.17: a) NumetriQ AC Impedance Analyser. Specimens were connected to the machine and AC current was supplied to the specimen. The resistance of the specimen was measured at each frequency. b) close up of the specimen showing conductive contacts bonded to wires which were secured in crocodile clips linked up to the NumetriQ AC impedance analyser c) circuit diagram of electrical conductivity set up.

Figure 4.18: a) thermal conductivity specimens. Both have diameters of 5 cm but one is 1 cm thick whereas the other is 0.5 cm thick. Two specimens are used for each test because the errors associated with contact resistance are reduced b) TA Fox 50 heat flow meter. Specimens are inserted into the blue compartment.

Figure 5.1: Tensile stress versus tensile strain for the 7 pure epoxy resin specimens. The average strength is 73.23 MPa and the average modulus is 2.71 GPa. All specimens failed in a relatively brittle manner.

Figure 5.2: Equal quantities of GNP dispersed in equal volumes of NMP, acetone and epoxy resin. a) Initial dispersion of GNPs; b) Dispersion of GNPs after 2 days. The three different images show how
sedimentation takes place in the NMP and acetone but not the epoxy resin which is stable over prolonged time. In fact the epoxy resin dispersion stayed stable indefinitely. Hence epoxy resin seems a suitable medium to carry out shear mixing in directly ........................................ 101

Figure 5.3: Tensile strength for 0.1 wt% GNPs in epoxy resin shear mixed at different speeds and different times. The 5000 rpm 1hour samples produce an increase in strength and the 3000 rpm 2 hour sample maintain the strength. All other samples produce decreases in tensile strength......... 101

Figure 5.4: Tensile moduli of 0.1 wt% GNPs in epoxy resin shear mixed at different speeds and different times. The 3000 rpm 2 hours samples produce an increase in modulus whereas other samples more or less maintain the modulus of neat epoxy resin ......................................................... 102

Figure 5.5: Stress strain curves for the 7 specimens which make up the 3000 rpm 2 hours sample which achieved the highest modulus in figure 5.4. The response is similar to the neat epoxy resin stress strain curves. All samples followed this same response........................................ 102

Figure 5.6: Optical microscopy images of samples shear mixed at the following speeds and times a) 1000rpm 1hour b) 1000 rpm 2 hours c) 3000 rpm 1 hour d) 3000 rpm 2 hours e) 9000 rpm 1 hour f) no shear mixing .................................................................................................................. 104

Figure 5.7: Comparison of microstructure before curing (left) and after curing (right). There is no difference between the micrographs so no reagglomeration occurs during curing ...................... 105

Figure 5.8: Variation of tensile strength with GNP loading weight with and without using acetone as a solvent. Increasing the loading weight reduces the strength of epoxy resin ......................... 106

Figure 5.9 Optical microscope image of GNP agglomerates taken from the 1000 rpm 1hour sample ................................................................................................................................. 106

Figure 5.10: DSC of uncured samples of pure epoxy resin and 5 wt% GNP reinforced epoxy resin. The areas under the curves are proportional to the amount of heat given out by the curing reaction (called the heat of cure). The heat of cure is higher for pure epoxy resin higher than for the 5 wt% GNP reinforced epoxy resin. However, the GNPs do not interfere with the cure reaction more than is expected as the addition of 5 wt% GNPs only reduces the heat of cure by ~5%. ......................... 108

Figure 5.11 DSC of cured samples of pure epoxy resin and 5 wt% GNP reinforced epoxy resin. No exothermic peak is visible. Therefore the cure cycle used in this investigation (80 °C for 2 hours followed by 140 °C for 8 hours) completely cures the samples. Incomplete curing can therefore be discounted as a reason for lower tensile strength of GNP reinforced epoxy resin ...................... 108
Figure 5.12: Variation of Young’s Modulus with loading wt% of GNPs with and without acetone as a solvent mixed at 5000 rpm for 1 hour. The addition of acetone and GNPs appears to have a positive effect on Young’s Modulus ................................................................. 110

Figure 5.13: Optical micrographs from GNPs mixed with and without acetone at 5000 rpm for 1 hour at 5 wt%. Without acetone the GNPs appear more evenly dispersed than with acetone ............... 110

Figure 5.14: Stress strain curves for the 5 wt% GNP reinforced epoxy resin sample with no acetone. The tensile strain at failure is 1-2% less than the neat epoxy resin specimens in figure 5.1........... 111

Figure 5.15: Stress strain curves for the 5wt% GNP reinforced epoxy resin sample mixed using acetone as a solvent. The tensile strain at failure is also 1-2% less than the neat epoxy resin specimens in figure 5.1 ................................................................................. 111

Figure 5.16: Tensile strength of MWCNT reinforced epoxy resin composites using 0.1 wt% MWCNTs shear mixed for different speeds and lengths of time. There is no clear pattern between speed or time and tensile properties............................................................................................................. 112

Figure 5.17: Young’s modulus of MWCNT reinforced epoxy resin using 0.1 wt% MWCNTs shear mixed for different speeds and lengths of time. In general the addition of MWCNTs neither significantly improves or reduces the tensile strength of epoxy resin ......................................................................................... 112

Figure 5.18: Comparison of microstructure of MWCNT reinforced epoxy resin composites shear mixed for different times. The micrographs show that the agglomerates become smaller and more spread out as the time increases. The differences in microstructure cannot be correlated to the tensile properties however. (scale bar is 100 µm)................................................................................. 113

Figure 5.19: The effect of shear mixing speed and time on the tensile strength of EG reinforced epoxy resin composites. All samples result in a decrease in tensile strength compared to neat epoxy resin. The worst performing samples are those shear mixed for 10 minutes. ........................................ 114

Figure 5.20: The effect of shear mixing speed and time on the Young’s modulus of EG reinforced epoxy resin composites. The addition of EG neither significantly improves or reduces the modulus of epoxy resin on average. .................................................................................................................. 114

Figure 5.21: Comparison of EG reinforced epoxy resin microstructures shear mixed at 1000 rpm for different times. The micrograph of the sample shear mixed for 10 mins shows much larger agglomerates than samples shear mixed for 1 hour and 2 hours. The agglomerates are also much larger than those of the MWCNT reinforced epoxy resin and GNP reinforced epoxy resin samples. Agglomerates of this size could act as defects rather than reinforcements and so damage the strength of the epoxy resin. (scale bar is 200µm)................................................................................. 115
Figure 5.22: The variation of tensile strength with sonication amplitude when 0.5 wt% GNPs were added to epoxy resin...

Figure 5.23: Variation of modulus with sonication amplitude when 0.5 wt% GNPs were added to epoxy resin...

Figure 5.24: Microstructures of the sonicated samples. Left micrograph is for the 20% amplitude sample. Middle micrograph is for the 50% amplitude sample. Right micrograph is the 80% amplitude sample. There are no noticeable differences between the micrographs. (Scale bar is 500 µm) ...

Figure 5.25: Variation of tensile strength of epoxy resin with increasing weight fractions of silane functionalised GNPs. All samples reduced the strength of epoxy resin. There was no clear difference in performance between the sonicated and unsonicated samples.

Figure 5.26: Variation of tensile modulus of epoxy resin with increasing weight fractions of silane functionalised GNPs. In general the modulus is maintained at the neat epoxy resin value apart from the 1 wt% sonicated sample.

Figure 5.27: FTIR of silane functionalised GNPs showing characteristic peaks (labelled on the spectrum) which confirm that proper functionalisation had taken place.

Figure 5.28: XPS of silane functionalised GNPs. The peaks at binding energies of 153 eV and 102 eV correspond to Silicon and would suggest successful functionalisation had taken place. Together with the evidence from the FTIR data this confirms that silane functionalisation was successful.

Figure 5.29: Comparison of tensile strength of samples cured using different cycles. Typically a lower curing temperature results in a lower tensile strength however in this case neat epoxy resin cured for 1 hour at 60 °C and 8 hours at 120 °C has a higher tensile strength than neat epoxy resin cured for 2 hours at 80 °C and 8 hours at 140 °C...

Figure 5.30: Stress strain response for epoxy resin cured at a lower temperature of 60 °C and 120 °C. The tensile strain at failure is 1-2% higher than neat epoxy resin specimens cured at 80 °C and 140 °C shown in figure 5.1...

Figure 5.31: TGA curve showing that decomposition of the epoxy resin begins to occur at ~350 °C as shown by a rapid loss of weight of the sample. Therefore decomposition of the sample cannot be a reason for reduced mechanical properties because it was cured at a maximum temperature of 140 °C which is well below the degradation temperature...

Figure 5.32: The oxygen 1s XPS spectra of the C grade GNPs and M25 grade from XG Sciences. The concentration of oxygen is highest in the C750 as shown by the tallest peak. The oxygen content is...
lowest in the M25 grade as it has the smallest peak. (CPS = Counts per second and is proportional to concentration).

Figure 5.33: The XPS carbon 1s Spectra of the C grade GNPs from XG Sciences. The presence of a small peak at a binding energy of 289 eV is evidence of C=O bonding. This peak is highest in the C750 grade and lowest in M25. (CPS = Counts per second and is proportional to concentration).

Figure 5.34: Comparison of strength of different grades of GNP reinforced epoxy resin. Whilst the addition of M25 grade GNPs reduces the strength of epoxy resin, the addition of C grade (oxygen functionalised) GNPs enhance or maintain the strength of epoxy resin. This is evidence that oxygen functionalisation has an important effect on the adhesion between the GNPs and epoxy resin.

Figure 5.35: Comparison of tensile modulus of different grades of GNP reinforced epoxy resin. There is no particular trend with all grades behaving similarly.

Figure 5.36: Stress strain responses for the specimens which make up the C750 0.1 wt% samples. The responses are the same shape as all other samples except that the strain at failure is around 1% higher than neat epoxy resin specimens.

Figure 5.37: Comparison of microstructures of four different grades of GNPs at a 1wt% loading. The microstructures are varied with the M25 grade similar to the C750 but different to the C300 and C500 grades. The fact that the microstructures of C300, C500 and C750 are different to one another yet all three improve the tensile strength of epoxy resin is evidence to suggest it is the oxygen functionalisation which is responsible for the improved performance not dispersion.

Figure 5.38: The carbon 1s spectrum of the Carboxyl functionalised GNPs from ACS materials. The peaks are characteristic of carboxyl functionalisation confirming that functionalisation was successful.

Figure 5.39: The XPS oxygen 1s spectrum of the carboxyl functionalised GNPs from ACS materials. The peak at 531 eV shows that oxygen atoms have successfully attached to the GNPs and would support the claim that successful carboxyl functionalisation has been achieved.

Figure 5.40: Tensile strength of carboxyl reinforced epoxy resin at 0.1 wt% and 0.25 wt%.

Figure 5.41: Variation of strength when 0.5 wt% GNPs were added to epoxy resin using different ratios of surfactant. Ratios 1:15 and 1:20 improve the strength compared to neat epoxy resin whereas 1:5 and 1:10 reduce the strength. A 1:15 ratio maintains the strength.
Figure 5.42: Variation of modulus when 0.5 wt% GNPs were added to epoxy resin with different ratios of surfactant. The modulus improves relative to neat epoxy resin in all cases. The ratio 1:15 produces the greatest improvement in modulus. ................................................................. 133

Figure 5.43: Effect of GNPs and surfactant on the strength of epoxy resin using a GNP to surfactant ratio of 1:15. The strength is maintained up until 0.5 wt% and then declines thereafter. ..................... 134

Figure 5.44: Effect of GNPs and surfactant on the Young’s modulus of epoxy resin using a GNP to surfactant ratio of 1:15 ........................................................................................................................................... 134

Figure 5.45: Comparison of strength of samples made with GNPs and surfactant and samples made with GNPs only. Both samples deteriorate in strength with the addition of GNPs. ...................... 135

Figure 5.46: Comparison of Young’s modulus of samples made with GNPs and surfactant and samples made with GNPs only. The modulus increases at first for the sample with GNPs and surfactant but then rapidly decreases after 0.5 wt%................................................................. 136

Figure 5.47: The variation of strength of epoxy resin with the addition of surfactant. A small amount of surfactant (2.1g) increases the strength of epoxy resin to 80 MPa but with the addition of more surfactant the strength rapidly decreases in a linear fashion................................................................. 137

Figure 5.48: The variation of Young’s modulus with the addition of surfactant weight. The Young’s modulus remains fairly constant until 105 g of surfactant is added and the Young’s modulus rapidly drops ........................................................................................................................................... 138

Figure 5.49: Comparison of microstructure of GNP reinforced epoxy resin with and without surfactant at different loadings of GNPs. The surfactant has a positive effect on the dispersion as there is a much more even coverage of GNPs in micrographs d) and f) compared to c) and e). Scale bar is 500 µm........................................................................................................................................... 139

Figure 6.1: fracture toughness results for the 7 specimens tested of pure epoxy resin. The average fracture toughness was 0.21 MPa m$^{1/2}$ with a standard deviation of 0.03......................................................... 144

Figure 6.2 a) two-dimensional diagram of fracture toughness specimen shape b) fracture toughness specimen after crack has been initiated c) three dimensional representation of the fracture surface of the specimen after failure. The red area depicts that the crack does not have the same depth across the thickness of the specimen. Instead the depth is greater around one edge of the specimen compared to the other (see figure 6.3 for real image). This is one of the limitations of this test and could be why the value of fracture toughness from this experiment does not match the value given on the data sheet by the manufacturer................................................................. 145
Figure 6.3: Optical microscope image of the fracture surface of an epoxy resin sample showing the initial crack depth highlighted in dashed red line. The crack depth is not uniform across the thickness of the specimen. It has a depth of 0.659 mm in the middle but towards the left edge the depth is zero. This highlights the difficulty of making specimens with carefully controlled crack depths. An uneven crack depth will affect the fracture toughness results. A better specimen is shown in figure 6.4

Figure 6.4: An epoxy resin specimen with a more uniform crack depth. The depth of the crack in the middle of the specimen is 0.553 mm and this depth remains fairly constant across the thickness of the specimen. This specimen would have given more reliable results.

Figure 6.5: The fracture toughness of epoxy resin reinforced with different types of GNPs at 0.1 wt% and 0.5 wt%. There is no obvious trend here. Due to unreliable nature of this test these results should be treated with caution.

Figure 6.6: Load vs extensions response for the C750 0.5 wt% samples. The relationship is fairly linear and fracture occurs suddenly. All of the samples responded in the same manner.

Figure 7.1: Resistance of three standard resistors of known resistance. The value of resistance is independent of frequency and is exactly the same value as the resistance quoted on the three resistors. Therefore this AC impedance technique is an accurate and reliable method of measurement for future samples.

Figure 7.2: Conductivity of three epoxy resin specimens in order to compare scatter in the sample. The three specimens show reasonable similarity to one another and confirm there is no percolating network due to an absence in a plateau in the conductivity. No data is recorded below 100 Hz because the conductivity was too small to measure and beyond the machines capability.

Figure 7.3: Conductivity of epoxy resin reinforced with 0.1 wt% EG shear mixed for 10 minutes at different speeds. Only the sample mixed at 5000 rpm achieves percolation and a DC conductivity $\sim 2.5 \times 10^{-6} \text{ S m}^{-1}$ as shown by the plateau region.

Figure 7.4: Conductivity of the 0.1 wt% EG reinforced epoxy resin samples shear mixed for 1 hour at different speeds. None of the samples achieve percolation illustrated by the fact none of the curves become independent of frequency.

Figure 7.5: Conductivity of 0.1 wt% EG reinforced epoxy resin samples shear mixed for 2 hours at different speeds. The 2000 rpm and the 4000 rpm samples reach percolation with DC conductivities of $10^{-6} \text{ S m}^{-1}$ and $10^{-5} \text{ S m}^{-1}$ respectively. The 3000 rpm and 2000 rpm samples come close to reaching percolation. The 5000 rpm sample is the furthest from reaching percolation.
Figure 7.6 a) Photograph of a dispersion droplet taken from the ‘EG 0.1 wt% 3000 rpm 10 mins’ sample showing the presence of a large unexfoliated EG particle; b) photograph of a dispersion droplet taken from the ‘EG 0.1 wt% 4000 rpm 2 hour’ sample showing the presence of fine black particles where EG has become exfoliated. This microstructure is better from a conductivity perspective because there is more chance of the exfoliated flakes touching one another to form a network; c) graphical representation of an unexfoliated EG particle d) graphical representation of an exfoliated EG particle. Exfoliation leads to more chance of a percolated network being formed..

Figure 7.7: Conductivity of the four specimens which make up the EG 2000 rpm 2 hours sample. There is a large degree of scatter. Specimens 1 and 4 reach percolation although their DC conductivities are an order of magnitude apart. Specimens 2 and 3 do not reach percolation. This is evidence that there is a random element to conductivity because the shear mixer is not capable of controlling the size of the particles within a tight range.

Figure 7.8: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 10 minutes at different speeds. Three samples reach percolation the 1000 rpm, 3000 rpm and 4000 rpm. The highest conductivity recorded was $1.05 \times 10^{-6} \text{ S m}^{-1}$ by the 1000 rpm sample.

Figure 7.9: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 1 hour. The samples here all reach percolation suggesting 1 hour is the optimum time for electrical conductivity enhancement. The highest conductivity achieved was $3.52 \times 10^{-5} \text{ S m}^{-1}$.

Figure 7.10: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 2 hours at different speeds. All samples except the 1000 rpm sample reach percolation. The highest conductivity was $1.13 \times 10^{-5} \text{ S m}^{-1}$.

Figure 7.11: a) SEM image of MWCNT agglomerates showing individual tubes protruding from them b) graphical representation of MWCNTs in epoxy resin showing how agglomerates could connect via protruding tubes to form a percolating network. This is a consequence of their high aspect ratio.

Figure 7.12: a) SEM image of EG particles with one highlighted showing they are much bigger than MWCNTs b) Graphical representation EG particles after exfoliation in epoxy resin. Due to the lower aspect ratio of EG compared to MWCNTs there are less likely to be connections made between individual particles leading to lower conductivity.

Figure 7.13: Conductivity of the four samples which make up the ‘CNT 0.1wt% 1000rpm 10 mins’ sample. There is a much higher degree of scatter than in Figure 7.14 which uses a 2 hour mixing time. Specimen 1 does not reach percolation and specimen 3 has conductivity an order of magnitude lower than specimens 2 and 4.
Figure 7.14: Conductivity of the four specimens which make up the 4000 rpm 2 hours sample. There is a small scatter and all of the specimens are on the same order of magnitude. The maximum conductivity is $1.69 \times 10^{-5}$ S m$^{-1}$ and the minimum is $1.03 \times 10^{-5}$ S m$^{-1}$. The scatter is much smaller than in figure 7.13 which uses a 10 minute shear mixing time.

Figure 7.15: Influence of MWCNT loading weight on the electrical conductivity of epoxy resin. The more MWCNTs are added to epoxy resin, the higher the conductivity.

Figure 7.16: a) First scenario where MWCNTs are dispersed as individual tubes; b) Second scenario when MWCNTs exist as entangled spherical agglomerates; c) Third scenario where there are a mixture of individual tubes and agglomerates.

Figure 7.17: The relationship between percolation threshold and aspect ratio of MWCNTs adapted from [150]. Different methods of dispersion will alter the values of $\varepsilon$ and $\xi$. For a shear mixing process used in my investigation the parameters should have values of 0.05-0.01 according to [150]. The aspect ratio of the MWCNTs used in this study was ~400. Reading off from the curve the percolation threshold should be between 0.05 and 0.2 vol% for MWCNTs with an aspect ratio of 400 when $0.05 < \varepsilon, \xi < 0.1$.

Figure 7.18: Conductivity of GNP reinforced epoxy resin shear mixed for 1 hour at different speeds. None of the samples reach percolation.

Figure 7.19: Conductivity of GNP reinforced epoxy resin shear mixed for 2 hours. None of the samples reach percolation and the curves appear very similar to neat epoxy resin. Thus GNPs appear ineffective at transferring conductivity to epoxy resin at 0.1 wt% loading regardless of shear mixing time.

Figure 7.20: Variation of conductivity with loading weight of GNPs. Even samples with 5 wt% GNPs did not reach percolation. GNPs therefore appear the least effective nanofiller for electrical conductivity enhancement.

Figure 7.21: AFM image of a GNP agglomerate on a silicon wafer substrate after being shear mixed at 5000 rpm for 1 hour in epoxy resin. The agglomerate is number 16 from table 7.1. The height profile of the flake in the x and y profiles below the AFM image shows the flake is approximately 0.17 µm.
Abstract

The aim of this investigation was to enhance the tensile strength and fracture toughness of epoxy resin matrices for carbon fibre epoxy composites in an effort to reduce a type of mechanical failure called inter-laminar cracking or delamination. The second objective was to increase the electrical conductivity of epoxy resin matrices for carbon fibre epoxy composites as a means of sensing structural damage if delamination occurred.

The weak link of carbon fibre composites is the insulating and relatively brittle epoxy resin which is used to bind the carbon fibres together. In order to improve its performance the epoxy resin was reinforced using highly conductive and strong graphene nanoplatelets (GNPs).

In the first instance un-functionalised (chemically unmodified) GNPs were shear mixed in epoxy resin at a range of different speeds and time durations at 0.1 wt% loading. There appeared to be no trend between the processing conditions and the mechanical properties of the epoxy resin. The addition of 5 wt% un-functionalised GNPs to epoxy resin reduced the tensile strength by up to 50%. The lack of bonding between the un-functionalised GNPs and the epoxy resin created a weak interface that was responsible for the deterioration of tensile properties. This was followed by adding functionalised (chemically modified) GNPs to epoxy resin. The results show that oxygen functionalised GNPs improved the tensile strength of epoxy resin due to better interfacial bonding between the GNPs and the polymer. An increase in tensile strength of up 7% was seen using a 0.1 wt% loading of oxygen functionalised GNPs.

In terms of electrical conductivity the addition of GNPs to epoxy resin yielded barely any improvement. Adding 0.1 wt% GNPs to epoxy resin did not create a percolating network irrespective of the processing method used. The electrical conductivity was predicted using a model and AFM measurements of the dimensions of the GNPs. The model matched the experimental results reasonably. By contrast 0.1 wt% of multiwall carbon nanotubes (MWCNTs) did create a percolating network and was capable of enhancing the conductivity from $\sim 10^{-12}$ S m$^{-1}$ to 3.5x$10^{-5}$ S m$^{-1}$. The addition of 1 wt% MWCNTs to epoxy resin enhanced the electrical conductivity up 2.0x$10^{-4}$ S m$^{-1}$.

Overall the results of this investigation have shown that chemical modification of GNPs is essential in order to increase the strength of the epoxy resin. Shear mixing as a technique appears to be too simplistic to control the distribution and dispersion of GNPs on the nanoscale. Carbon nanotubes are more efficient at creating a percolating network compared to GNPs but in order to significantly improve the conductivity of epoxy resin the distribution of MWCNTs need to be manipulated, for instance by an electromagnetic field, at the nanoscale to form a connected network of nanoparticles.
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1 Introduction

This chapter introduces the reader to the background and motivation for conducting this research. It highlights the aims and objectives of the project as well as challenges that will be faced. An outline of subsequent chapters will also be summarised.
1.1 Background to the Project

In the aerospace industry, there is a drive to reduce fuel consumption and greenhouse gas emissions. The replacement of metallic alloys with composite materials has allowed manufacturers to make lightweight and fuel efficient planes whilst maintaining structural integrity. For example, the modern Airbus A350XWB and Boeing 787 are composed of more than 50% by weight composite materials primarily used in the fuselage and the wings [3][see Figure 1.1] which has resulted in a 25% improvement in fuel efficiency. Added benefits of using composite materials are their resistance to corrosion and their good thermal stability which is important when service temperatures can fluctuate between hot and cold environments [23]. Aerospace is the main market for composite materials but they are increasingly being used in cars, wind turbines, sporting equipment and the oil and gas industry and will become even more important in the future [3, 22, 24-28].

Composites used in aircraft are typically made from carbon fibre reinforced plastic (CFRP) and consist of reinforcing carbon fibres held together with an adhesive thermosetting plastic called epoxy resin [24, 29, 30]. The fibres are arranged in layers and the epoxy resin bonds the layers of fibre together to make a laminate. Composites are strong in tension, and when the load is applied along the plane of the fibres (x and y directions) their specific strength out performs metals (see Figure 1.2(a)), however their strength perpendicular to the plane of the fibres (z direction) is relatively weak. In fact, the through thickness strength can be 10% or less than the strength in the x and y directions [22]. The reason for this, is because there are no reinforcing fibres aligned in the through thickness direction (z direction). Consequently, composites have poor impact resistance and they are susceptible to a type of fracture called delamination which can seriously weaken the structure of an aircraft. Delamination starts off as a small crack below the surface of the composite which can grow rapidly leading to material failure (see figure 1.2 c)). It happens when a composite is subjected to through thickness stresses such as an impact event when aeroplanes are hit with hailstones, runway debris, bird strikes or tool drops during maintenance[31]. In addition, once a crack has developed the compressional and tensile strength of the composite in plane is also drastically reduced. For this reason aircraft structures using composite materials are designed conservatively and undergo rigorous and time consuming safety checks. Even then defects can be missed, for example in January 2012 Boeing detected delamination in the composite stringers which run the length of the fuselage in three of their aircraft [32]. Although the repairs were simple it required the aircraft to be temporarily put out of service. This is only one example and undoubtedly there may be more which airline companies do not disclose. If composite materials are to truly fulfil their potential and be used in more load bearing parts of an aeroplane then their through thickness strength must be improved.
Figure 1.1: Use of different materials in the Airbus XWB. Composites make up 53% by weight of the aircraft with CFRP being the dominant composite. In volume terms this is about 80% of the total volume. The huge difference in weight percentage versus volume percentage is because CFRP is much lighter than other materials [3].

Figure 1.2: Computerised image of the microstructure of carbon fibre epoxy resin composite. Fibres are arranged in layers stacked on top of one another and held together by epoxy resin. a) composites are strong when pulled along the plane of the fibres (x and y directions) b) composites are weak when subjected to through thickness stresses perpendicular to the fibres (z direction); c) impact events such as hailstones birdstrikes and tool drops create through thickness stresses which result in microcracks forming in the epoxy resin beneath the surface of the composite. This can lead to delamination as shown in the SEM image. (Adapted from [6])
A second issue which is hampering the use of composite materials is that damage detection is harder and not as well standardised as it is in metals [33]. Structural Health Monitoring (SHM) is set of techniques which are used to detect cracks within structural materials of an airplane. Currently SHM relies on non-destructive testing (NDT) but there are several drawbacks to this technique. For example, it requires components to be disassembled; it requires trained personnel and significant man hours, and it requires significant downtime and has to be performed when the aircraft is grounded. Current structural assessments are graded from A (being the least stringent) to D (being the most stringent)[34]. Table 1.1 shows the frequency and the time taken for each type of check.

There is also difficulty in detecting the damage. Composite parts can appear undamaged from the surface and can remain undetected by a visual inspection. However beneath the surface there can be significant delamination. In addition delaminations can spread across a far greater area than a surface dent would suggest (see Figure 1.3) [1]. The through thickness conductivity of composites is restrictive for damage detection. Composites are conductive along the fibre direction; however the insulating epoxy resin matrix restricts the flow of electric charge in the z direction. Therefore, techniques such as the Eddy current method or voltage drop are not capable of detecting damage beneath the surface of the composite. If the through thickness conductivity can be improved then damage detection would be easier. The true goal for SHM would be to build a ‘nervous system’ into the aircraft with real time sensing equipment to eliminate downtime and ensure safer flights.

*Table 1.1: Frequency of structural checks on aircraft. Checks can be timely, cost money and increase downtime.*

<table>
<thead>
<tr>
<th>Check</th>
<th>Frequency of Check</th>
<th>Time per Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>500-800 flight hours</td>
<td>6 hours</td>
</tr>
<tr>
<td>B</td>
<td>4-6 months</td>
<td>1-3 days</td>
</tr>
<tr>
<td>C</td>
<td>20-24 months</td>
<td>1-2 days</td>
</tr>
<tr>
<td>D</td>
<td>6 years</td>
<td>2 months</td>
</tr>
</tbody>
</table>

*Figure 1.3: A 33 ply CFRP laminate. Although the surface damage is small the damage that has occurred beneath the surface is extensive. This demonstrates the difficulties in inspection [1]*
1.2 Aims of the Project

This project aims to tackle the issue of delamination and damage detection simultaneously through the use of a highly conductive and strong nanomaterial called graphene. Graphene is a single atomic layer of carbon atoms with a thickness of 0.34 nm. In its purest form, it is the strongest, stiffest material known to man with a tensile strength five times more than steel. In addition, it is the most thermally conductive material that is known to exist and its electrical conductivity rivals that of copper [19, 20, 35].

Research is underway to try and impart the strength and conductivity of graphene to composites. The weakest part of the composite where damage occurs first is the epoxy resin matrix. Epoxy resin is a highly cross linked thermosetting polymer [22, 23]. Although the crosslinking provides stiffness and strength it also makes it relatively brittle. During impact events, cracks first appear in the epoxy resin perpendicular to the fibres and spread to the interface with the carbon fibres causing delamination. Therefore, in order to improve the composite as a whole we must improve the properties of the epoxy resin, as here lies the weak link where damage initiates.

In the last five years, small additions of graphene have been shown to improve the fracture resistance of epoxy resin by blocking moving cracks [5, 15, 17, 36]. This translates to improved impact resistance. However, improvements have been small and only occur when a tiny amount of graphene is used (less than 0.5% by weight) and if more graphene is added the fracture resistance begins to deteriorate. For graphene to have an engineering impact these improvements must be more significant and continue at higher loadings. The first aim of this research will therefore focus on reinforcing the epoxy resin with graphene to improve its mechanical properties and build on the progress of prior research.

The epoxy resin also restricts the through thickness conductivity of the composite since it acts as an insulating barrier between carbon fibres. Graphene has been shown to enhance the electrical conductivity of polymers by creating conducting pathways for charge to travel along [37-42]. Once again however, improvements have been lower than expected and do not enhance the conductivity enough for damage sensing purposes. The second aim of the project is therefore to focus on improving the conductivity of epoxy resin using the knowledge gained from other research groups.

If both of these aims are achieved then graphene reinforced epoxy resin will be used to make a modified CFRP and the performance will be compared to a conventional CFRP with unreinforced epoxy resin.

In summary, the aims of the project in order are:
• To try and improve the fracture toughness and tensile strength of epoxy resin using graphene
• To try and make epoxy resin electrically conductive by creating a pathway of graphene for current to flow as this would be useful for SHM.
• If the epoxy resin is successfully strengthened and improved electrical conductivity is achieved then the reinforced epoxy resin will be used to manufacture CFRP laminates. The resistance to delamination and damage detection using electrical methods shall then be tested.

It is worth pointing out that there are other methods of improving the fracture toughness of epoxy resin. For example the fracture toughness can be improved through the incorporation of micro sized thermoplastic particles or rubber [43]. However, these additions do not improve the conductivity. Carbon micro sized ‘Z pins’ can also reinforce the through thickness direction of carbon fibre composites but they only resist delamination on a larger scale [44]. Alternatively, 3D woven fibres can be used but these reduce the in plane tensile properties of the composite [45]. Graphene has the potential to tackle the delamination and conductivity problem in one due to its multi-functional nature, providing opportunity for this research.

1.3 Challenges

There are many challenges to overcome to achieve these goals. In order to be effective crack stoppers the graphene flakes must be carefully distributed amongst the epoxy resin polymer chains. This is a difficult task because graphene likes to restack to form micro sized graphite agglomerates which can act as stress raisers and actually initiate crack growth rather than prevent it. Agglomerates also present less of an obstruction to crack growth compared to well dispersed graphene since the mean distance a crack has to travel before it hits an obstruction is much larger. This is illustrated in Figure 1.4 a) and b) which show a good dispersion and a poor dispersion respectively. Good dispersions could be achieved through different mixing techniques and solvents.

Another challenge is to ensure a good interface between the graphene and the epoxy resin so that stress can be transferred to the graphene during loading of the composite. A weak interface will result in crack initiation at the interface and reduced mechanical properties. The surface chemistry of graphene could be modified to enhance its compatibility with epoxy resin and improve the interface.

From the electrical perspective, graphene flakes must touch one another to form a continuous conductive path through the epoxy resin. Trying to create architecture of this kind on the microscale
could be achieved through electric or magnetic fields which could align the graphene. Agglomeration will also be detrimental to the conductivity as is shown in Figure 1.5 a) and b).

Overall the key challenges in this project are as follows:

- Overcoming agglomeration of graphene and making an even dispersion of graphene in epoxy resin to transfer the properties of graphene to the epoxy resin
- Creating an optimum bond between the graphene and epoxy resin to improve the strength of the interface in a way that load is transferred effectively from graphene to the epoxy resin.
- Creating a network of graphene which touch one another to create a conductive path as shown in Figure 1.5 b).

Overall the aim of the investigation will be to make a microstructure like Figure 1.4b) and 1.5b)

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*Figure 1.4:* A representation of two microstructures of a graphene reinforced epoxy resin composite illustrating a good and a poor dispersion from a crack stopping perspective a) Representation of a poor microstructure. Graphene flakes are in the form of agglomerates and there are clear paths for cracks to grow through the weak epoxy resin. b) Representation of a good microstructure. Graphene flakes are distributed in such a way that there are no clear paths for cracks to move through epoxy resin. The graphene is therefore an effective crack stopper.

*Figure 1.5:* A representation of two microstructures of a graphene reinforced epoxy resin composite illustrating a good and a poor dispersion from an electrical conductivity perspective a) Representation of a poor microstructure. Graphene flakes are in the form of agglomerates and there are no connections to transfer electrical current. b) Representation of a good microstructure. The graphene flakes are connected meaning current can be transferred through the thickness of the composite. This would be good for damage sensing purposes.
1.4 Outline of the Thesis

The next chapter will introduce the two main materials used in this investigation: graphene and epoxy resin. Background information on the structure of graphene, its electrical and mechanical properties as well as methods of production and its use as a reinforcement in composite materials will be described. In addition, the chemical structure of epoxy resin and its mechanical and electrical properties will also be described.

Chapter 3 will critically review and examine published literature in the field of mechanical and electrical conductivity enhancement of graphene reinforced epoxy resin. In particular it will focus on processing and dispersion methods which can improve tensile strength, Young’s modulus and fracture toughness and novel methods of creating conducting networks. Gaps in research which need to be addressed will also be highlighted.

Chapter 4 describes the experimental methods, materials and equipment used in the study. The experimental method is split into four separate investigations. In the first investigation pure epoxy resin specimens were manufactured and tests on tensile strength and electrical conductivity were made. These specimens represented a bench mark onto which all subsequent investigations (where epoxy resin was reinforced with graphene) could be judged. In the second investigation the effect of processing conditions on the properties of graphene reinforced epoxy resin were examined. The third investigation examined the effect of chemically functionalised graphene on the properties of epoxy resin. Finally, the effect of surfactant on the dispersion of graphene in epoxy resin and its effect on mechanical and electrical properties was investigated.

Chapter 5 presents the tensile test results from the four investigations and chapter 6 presents the fracture toughness results. Chapter 7 summarises the electrical conductivity test results and compares them to mathematical models which have been derived from other research groups.

The conclusions of the project and an assessment of whether aims were achieved are included in Chapter 8. Opportunities for further work are also suggested.
This chapter describes the two main materials which will be used in the investigation: graphene and epoxy resin. In the first part of the chapter the physical properties, manufacturing techniques, characterisation of graphene as well as its potential in composites is discussed. In the second part of the chapter, background information on epoxy resin is discussed.
2.1 Introduction to Graphene

In the past decade one material has stood out in terms of its physical properties and impact on science. This material called graphene was discovered in 2004. It is simply a single atomic layer of graphite; however its properties are markedly different from those of graphite. Many materials have one superlative property but graphene has a number of superlative properties ranging from mechanical to electrical to thermal. The multi functionality of graphene is why it has caught the attention of so many researchers. There are high expectations to bring graphene into commercial products. However, before commercial products can appear the fundamental science of graphene and how to make it on an industrial scale must be understood. [19, 20, 35, 46, 47]

2.1.1 Structure and Properties of Graphene

Graphene is a single layer of sp² bonded carbon atoms. It is essentially one layer of graphite. Its thickness is that of one carbon atom ~0.14 nm but its lateral dimensions can span on the order of micrometres [12](figure 2.1). Graphene is therefore considered the first two-dimensional material.

Although graphene is the building block of graphite its properties are massively different. Some of the properties which are important from a composites perspective are summarised in Table 2.1. Graphene has one of the highest tensile strengths, modulus and thermal conductivity of any material measured [48]. Electron mobility is a measure of how quickly electrons can move through materials. For graphene, the electron mobility is also the highest known of any material [49]. The conductivity of materials is proportional to the electron mobility and the charge carrier concentration so high conductivity can come from a small number of electrons which travel quickly or a large number of electrons which travel slowly. It is an important characteristic for semiconductor devices such as transistors which normally perform better when there is high mobility. In addition graphene’s specific surface area is enormous. One gram of the material would cover an entire football pitch [51].

Figure 2.1 (a) A low magnification transmission electron microscopy image of a graphene flake. Scale bar is 100nm (b) higher resolution image with an arrow pointing to the edge of the flake. Scale bar is 4 Å. (c) an atomic resolution image of a graphene flake showing the C-C bond length [12]
2.1.2 Manufacture of Graphene

There are three main methods of manufacturing graphene. These are chemical vapour deposition (CVD), mechanical exfoliation from graphite and reduction of graphite oxide [35, 52, 53].

In chemical vapour deposition a copper sheet is used as a catalyst on which to grow graphene. Methane gas at room temperature and very low pressure is passed over the sheet and graphene grows on the copper. Once one layer has formed it automatically stops growing further layers. This technique produces high quality graphene with the properties reported in the table but it is highly expensive with 1 cm² costing £100 or more. This technique is scalable however [52].

Alternatively graphene can be made from graphite. In the mechanical exfoliation technique layers of graphite are stripped off until only one remains. This is achieved using scotch tape which can peel off layers of graphene. High quality graphene can be made with this process but it is not scalable [54].

A top down approach which is scalable is the reduction of graphite oxide. In this approach graphite is oxidised in a mixture of strong hydrochloric acid and nitric acid via the Hummer’s method (see Figure 2.2). During oxidation the interlayer spacing is increased from 0.34 nm to 0.7 nm. Therefore, the van der Waals forces in graphite oxide are weaker than in graphite which makes it easier to separate them. Graphite oxide can be sonicated in water which separates the layers in single sheets of graphene oxide. A reducing agent is then employed to remove the oxygen atoms on the graphene atoms. In reality not all the oxygen atoms are removed and there is also restacking of the graphene sheets to form graphene nanoplatelets (GNPs) which are stacks of 4-20 graphene sheets on top of one another [55].

Table 2.1: Summary of the physical properties of graphene

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>1000 GPa[48]</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>130 GPa[48]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>5300 W m⁻¹ K⁻¹ [50]</td>
</tr>
<tr>
<td>Charge carrier mobility</td>
<td>200,000 cm² V⁻¹ s⁻¹ [49]</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>2600 m² g⁻¹ [51]</td>
</tr>
</tbody>
</table>
Figure 2.2: stages of manufacture of graphene oxide. GNPs are firstly oxidised by heating in a mixture of hydrochloric acid (HCl), nitric acid (HNO₃) and potassium chlorate (KClO₃) to make oxidised GNPs with an increased interlayer spacing. Sonication is then employed to exfoliate layers to yield graphene oxide [47]

2.2 Characterisation of Graphene

Several methods are available to probe the structure of graphene. Microscopy is used to see the structure from low magnifications up to very high magnifications. Spectroscopy is used to understand the chemical nature of the graphene for example the bonding, impurities or intentionally added functional groups. Several methods of characterisation are shown in figure 2.3 and discussed below.

2.2.1 Optical Microscopy and Electron Microscopy

Graphene can be detected using an optical microscope although this takes a trained eye as it appears as a very subtle colour and 97% of light passes through it. In order to determine the structure at much higher magnifications transmission electron microscopy (TEM) and scanning electron microscopy (SEM) can be used. Wrinkles and holes in the sheets of graphene can be clearly imaged.

2.2.2 Raman Spectroscopy

Raman spectroscopy is a useful tool for determining exactly the number of graphitic layers there are in a sample and if single layer graphene has truly been manufactured. In this technique the surface of graphene is activated by using a laser causing the atoms to vibrate at certain wavenumbers. Typically a laser of wavelength of 514 nm or 633 nm is used. There are distinctive modes of vibration in graphene giving rise to characteristic peaks. Two characteristic peaks are called the G and 2D bands. These occur at 1581 cm⁻¹ and 2680 cm⁻¹ respectively using a 514nm wavelength laser. When there are more layers than one the wavenumbers of the G and 2D bands shift. The shift in the 2D peak position is the most obvious to see. As the number of layers of graphene increases the wavenumber shifts to higher numbers. Raman spectroscopy can therefore be used to distinguish graphene from multiple layers and graphite [56].
2.2.3 Atomic Force Microscopy (AFM)

AFM can be used to measure the thickness of graphene flakes. It uses a microscopic cantilever which scans across the surface of the sample. The cantilever is bought extremely close to the surface of the graphene where it interacts with the surface. As the cantilever scans across the surface of the graphene flake it moves up and down to maintain a constant distance between itself and the sample. The displacement of the cantilever in the vertical direction gives a topological image of graphene which can be used to calculate how many layers exist.

Figure 2.3: a) Optical microscopy image of graphene showing mono layer, bi layer and tri layer graphene[8] b) TEM image of a graphene flake. Scale is 500 nm [19] c) Raman spectrum of graphene in comparison to graphite showing the G and 2D peak[20] d) Raman spectra of different layers of graphene showing the shift in the 2D peak position[20] e) AFM topology plot showing the change in height when the cantilever encounters a graphene flake. The 2 red markers represent the height change from the position shown in the microscope image f)[21]
2.3 Graphene in Composite Materials

Graphene has many outstanding properties. The question is can we use the properties of graphene (which exists only on the nanoscale) and transfer them to the microscale and macroscale to make useful engineering materials? One method of doing this is to make composite materials using graphene. With respect to composites there are several reasons why graphene would be good reinforcement:

- Graphene is a 2D material. It is only one atom thick and therefore it has a very high surface area, theoretically 2630 g m$^{-2}$. If all of the atoms of carbon in graphene can form chemical bonds with an epoxy resin matrix a strong adhesion and an efficient stress transfer between the epoxy resin and the graphene can be achieved [57].
- Graphene itself is one of the strongest material ever measured with a tensile strength of 130 GPa [48]. If stress can be transferred to the graphene during loading it would enhance the overall strength of the composite.
- Finally graphene has a high aspect ratio. It has been shown that high aspect ratio particles cause cracks to tilt absorbing more energy and increasing toughness [58].

Transferring the properties of graphene to epoxy resin is not an easy task and not as simple as mixing in graphene with the epoxy resin. There remain several hurdles which must be overcome before graphene can become an efficient reinforcement in composite materials. The first is the even distribution of graphene amongst the epoxy resin polymer chains. Graphene has a high tendency to re-agglomerate into graphite particles which act as stress raisers resulting in premature failure during loading [18, 21, 37, 39, 53, 59, 60]. Secondly, the surface of graphene must be chemically modified so that it forms a strong bond with epoxy resin [39, 53, 61-65]. Even if graphene has a high surface area and is extremely strong, if no bond is formed with the epoxy resin then stress cannot be transferred during loading rendering the graphene ineffective.

2.3.1 Advantages of Graphene over Carbon Nanotubes (CNTs)

CNTs possess very similar properties to graphene in many respects and have been around for over 20 years. The simplest type of carbon nanotube can be thought of as a layer of graphene rolled up into a seamless cylinder. These are called single walled carbon nanotubes (SWCNTs). Often however, there are several cylinders stacked inside one another much like a Russian doll. These are called multiwall carbon nanotubes (MWCNTs). In MWCNTs the interlayer spacing is around 3.4 Å slightly smaller than in graphite which is 3.35 Å. The nanotube ends can be left open or sometimes they are capped. They have diameters ranging from 20-40 nm and lengths several hundred microns [66]. In one paper an
extraordinary length to diameter ratios up to 132000000:1 were manufactured [67]. CNTs also have extraordinary physical properties shown in the table 2.2.

From the table it can be seen that both graphene and CNTs have extremely high tensile strengths, modulus, thermal conductivity and electron mobility. So what could make graphene any better than CNTs from a composites perspective? There are two reasons. One crucial benefit of using graphene compared to carbon nanotubes is the ease of processing of graphene composites compared to CNT composites. The viscosity of Graphene polymer composites do not increase significantly during processing unlike CNT polymer composites. This means larger amounts of graphene can be added to the polymer during processing. In the case of epoxy resin, 10 wt% of graphene can be added before it become too viscous to process. Conversely for CNTs processing becomes difficult when more than 2 wt% is added to epoxy resin. Higher amounts of graphene mean more of its properties could be transferred to the epoxy resin.

The second reason relates to the manufacture of graphene. Graphene exists in nature (as part of graphite). Graphene can therefore be made from top down processes which tend to be cheaper, easier and less expensive than bottom up processes. CNTs on the other hand do not exist in nature and must be made from expensive bottom up processes.

Table 2.2: Comparison of CNT properties with Graphene

<table>
<thead>
<tr>
<th>Property</th>
<th>CNTs</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>Up to 950 GPa [68]</td>
<td>1000 GPa[48]</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Up to 150 GPa [69]</td>
<td>130 GPa[48]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>Up to 3500 W m$^{-1}$ K$^{-1}$[70]</td>
<td>5300 W m$^{-1}$ K$^{-1}$[50]</td>
</tr>
<tr>
<td>Charge carrier mobility</td>
<td>100,000 cm$^2$ V$^{-1}$ s$^{-1}$[71]</td>
<td>200,000 cm$^2$ V$^{-1}$ s$^{-1}$[49]</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>1300 m$^2$ g$^{-1}$[72]</td>
<td>2600 m$^2$ g$^{-1}$[51]</td>
</tr>
</tbody>
</table>

2.3.2 Graphene Nanoplatelets (GNPs)

Single layer graphene is still currently expensive to manufacture and it would not be practical to use it in experiments. In addition, there is no certainty that using high quality single layer graphene would make any better composites because the problems of agglomeration and bonding the graphene to epoxy resin still exist. A less expensive form of graphene called graphene nanoplatelets (GNPs) are available for around $1/g [73]. GNPs consist of about 4-20 layers of graphene stacked on top of one another (see figure 2.4). The properties of GNPs are not the same as graphene but GNPs could be used as a starting point from which to make graphene. GNPs can be further processed and chemically functionalised so that they become compatible with the host matrix.
The dividing line between what is described as graphene, GNP s and graphite has become blurred. Graphene is strictly one layer of carbon however, there is a lot of literature which also describes two or three layers of carbon as graphene which is misleading [74]. There is still no consensus on graphene nomenclature and for this reason I have created my own definitions based on other studies. In this thesis I will refer to graphene as one layer of carbon only. Two and three layers of carbon will be called bilayer graphene and tri layer graphene respectively. Anything from 4-20 layers will be described as GNP s (see figure 2.4) and anything above twenty layers will be called graphite.

Figure 2.4: (left) graphical representation of a typical GNP showing dimensions. GNP s can consist of anywhere between 4 and 20 layers. (Right) TEM image showing number of graphitic layers in GNP s each 0.34 nm thick. In this image 5 layers can be seen [73]

2.4 Introduction to Epoxy Resins

In carbon fibre composite materials, epoxy resin is the adhesive which binds together carbon fibres to make a solid and rigid laminate which is strong and lightweight. For a plastic material epoxies have good mechanical strength and dimensional stability, excellent corrosion resistance and low moisture absorption [75-78]. However, epoxy resin is relatively brittle [76, 79]. In carbon fibre composite structures the epoxy resin which holds plies of carbon fibre together can crack when subjected to through thickness stress or impact events [62]. Therefore a solution is sought to strengthen the resistance of epoxy resin to cracking through the addition of graphene. The electrical conductivity may also be improved through the addition of graphene which would be useful for SHM.

Epoxy resin is a thermosetting polymer and comprises of two parts. It is the reaction product of one chemical called an epoxy resin and a co-reactant often called a hardener. When these two chemicals are mixed together and heat is applied a chemical reaction occurs and a solid product called epoxy resin is made [77].
Epoxy resins all consist of active molecules which contain at least one epoxide group. Epoxy resin is typically a blend of a diglycidylether of bisphenol A (DGEBA) and butane diol-diglycidyl ether. In this investigation, epoxy resin based on DGEBA with 2 reactive epoxide groups will be used with the chemical structure shown in figure 2.5. The more epoxide groups present in the resin the more chemical cross linking can form and the stiffer and stronger the resulting epoxy resin. However, the presence of more epoxide groups also makes the resin very viscous which can make processing hard.

![Figure 2.5: Chemical structure of the active molecule (DGEBA) in epoxy resin used in this investigation. n is often zero but can be 1 or 2 in some molecules. Typically, greater than 85 of molecules have n=0](image)

The average value of n is typically very low for these types of resins. In fact n=0 for >85% of all epoxy resin monomers. Some molecules may have n=1 or n=2 but the majority of monomers can be simplified to the structure shown in figure 2.6 below.

![Figure 2.6: The structure of DGEBA in the epoxy resin used in this system when n is equal to zero](image)

The second reactant required to make epoxy resin is called the hardener shown in figure 2.7, which is a bis-cyclohexylamine. It contains two amine groups which are capable of reacting with the epoxy groups of the resin.

![Figure 2.7: Chemical structure of the amine hardener used in the investigation called bis-cyclohexylamine](image)

During a chemical reaction one of the primary amine groups (NH$_2$) of the hardener attacks the epoxy resin group of the resin. The epoxy resin ring is broken and a single product is formed consisting of a hydroxyl group and a secondary amino hydrogen (NH-A) [80][see figure 2.8].

![Figure 2.8: The primary reaction ($k_1$) which occurs between the epoxide group of the epoxy resin and the amine group of the hardener](image)
The secondary amino hydrogen can also react with more epoxy resin monomers via the following reaction shown in figure 2.9.

\[
\begin{align*}
\text{E} \cdot \text{CH} \cdot \text{CH}_2 & + \ E \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{A} \xrightarrow{k_2} (\text{E} \cdot \text{CH} \cdot \text{CH}_2)^2 \text{N} \cdot \text{A} \\
\end{align*}
\]

*Figure 2.9: Secondary reaction \((k_2)\) which can occur between the epoxide group of the epoxy resin and the secondary amino hydrogen \((N-H)\) of the reaction product of the primary reaction*

The result of the chemical reactions is a cross-linked network of chemical bonds called epoxy resin. The network is entirely made of chemical bonds rather than physical bonds and so epoxy resin does not melt and the reaction is irreversible. The process of chemical reactions taking place to create epoxy resin is called curing [81].

Typically heat is required to initiate curing. Higher curing temperatures result in more reactions taking place and more crosslinks being formed. In turn this makes epoxies with higher tensile strengths and modulus but lower flexibility. However, beyond a certain temperature (dependent on the particular epoxy resin) thermal degradation can take place [82]. Therefore, the thermal degradation temperature must not be exceeding during curing.

There are many different types of epoxy resin that are commercially available. In this investigation a low viscosity (1-2 Pa s) epoxy resin will be used with two reactive epoxide groups. The reason for using a low viscosity resin is for ease of processing. In industry, typical aerospace grade epoxy resin resins have higher viscosities (on the order of 90 Pa s) however this would require special processing which is not available in my laboratory. The higher viscosity of aerospace grade epoxy resins is because their monomers contain four reactive epoxide groups compared to two. This results in more chemical cross linking and higher tensile strengths compared to lower viscosity resins. However, if mechanical and electrical properties can be improved for low viscosity resins then this can act as a proof of principle which could be extended to more viscous aerospace grade epoxy resins.

In the next chapter, a critical review of literature in the field of GNP reinforced epoxy resin and CNT reinforced epoxy resin composites will be reviewed in terms of their mechanical and electrical properties.
3 Literature Review

This chapter begins with a more in depth discussion of the challenges required to ensure efficient dispersion and reinforcement of GNPs in epoxy resin. The current methods of processing and dispersing GNPs into epoxy resin will be reviewed. Processing is important because it directly affects the properties of nanocomposites. Subsequently, the current research carried out on the tensile, fracture and electrical properties of GNP reinforced epoxy resin composites will be examined. This chapter includes the results of work from other research studies and will critically analyse them.
3.1 The Dispersion of GNPs in Epoxy Resin

One of the key challenges outlined in section 1.3 was the dispersion and distribution of graphene amongst the epoxy resin polymer chains [18, 21, 37, 39, 53, 59, 60]. In order for graphene to be effective as a mechanical reinforcement it must be prevented from agglomerating into graphite particles. This is a hard task because graphene has a high surface area resulting in strong van der Waals interactions between neighbouring flakes which make them stick together. Although graphene manufacturing companies advertise their product as graphene it is normally supplied as GNPs which comes as a powder consisting of particles of platelets 4-20 layers thick, stacked on top of one another. GNPs also stick to one another forming agglomerates which can be tens of micrometres in thickness. In order to make a composite with improved properties the GNPs need to be well dispersed in the epoxy resin. As part of a good dispersion three requirements should be fulfilled.

1. **Graphene should be well exfoliated from GNPs so that the entire surface of the graphene is available to bond with the epoxy resin.** This is important because the middle layers in GNPs are not in contact with the epoxy resin, take up space and are effectively redundant. The layers in the middle of GNPs can slide past one other easily which weakens the composite. The maximum surface area free to bond with epoxy resin is achieved when there are monolayers of graphene which are distributed evenly.

2. **Graphene must be homogenously distributed in the epoxy resin.** This is so that the properties of graphene are evenly transferred across the whole volume of the composite and composite properties become homogenous.

3. **Graphene flakes must have lateral dimensions greater than the critical length for reinforcement.** According to the shear lag theory, graphene will only become an efficient reinforcement if its lateral dimensions are above a critical length [24]. Although shear lag theory was intended to describe fibre composites it can be extended to describe nanocomposites. Consider a fibre embedded in an epoxy resin matrix subjected to tensile stress. Assuming there is a good bond between the epoxy resin and fibre the tensile stress in the fibre builds up from the ends of the fibre and increases towards the middle [83]. If the fibre is too short then the stress is not fully developed in the fibre (Figure 3.1(a)). If the fibre is long enough the tensile stress reaches a plateau at \( \sigma^* \) (See Figure 3.1(c)). The length of fibre at which this maximum stress is reached is called the critical length for reinforcement (See Figure 3.1(b)). The critical length can be calculated using the equation 3.1

\[
l_c = \frac{d\sigma_f}{2t_c} \quad (3.1)
\]
Where \( l_c \) is the critical fibre length; \( d \) is the diameter of the fibre; \( \sigma_f^* \) is the tensile strength of the fibre and is \( \tau_c \) the fibre matrix bond strength or matrix shear strength whichever is smaller.

\[ l_c = \frac{0.34 \times 130000}{2 \times 60} = 368 \text{ nm} \]

This would be the critical length given perfect dispersion and perfect bonding. In reality this is a huge underestimate because the assumptions made are completely unrealistic. Firstly, the thickness used in the calculation is too small. The thickness of graphene is 0.34 nm but it is unlikely that monolayers can be exfoliated from GNPs and prevented from agglomerating meaning the actual thickness is a lot more. GNPs are likely to agglomerate and perhaps become on the order of micrometres in thickness.

Although this formula was originally intended for calculating the critical length of carbon fibre it can be extended to calculate an estimate for the critical length for effective reinforcement of graphene. In the case of graphene, the diameter of the fibre is replaced by the thickness of the graphene (0.34 nm). The tensile strength of graphene \( \sigma_f^* \) (if the maximum theoretical value is taken) is 130 GPa. Assuming a perfect bond between the graphene and epoxy resin the matrix shear strength should be taken as the value for \( \tau_c \) which for the epoxy resin used in this investigation is \( \sim 60 \) MPa. Therefore using equation 3.2 the critical length can be estimated as:

\[ l_c = \frac{0.34 \times 130000}{2 \times 60} = 368 \text{ nm} \]
Secondly, the strength used in the calculation is unrealistic. 130 GPa represents the tensile strength of perfect monolayers of graphene. However, no research has been conducted on how the strength varies in bilayer graphene, trilayer graphene and GNPs of four or more layers. GNPs do not have the same tensile strength as graphene and they undoubtedly have a tensile strength less than 130 GPa. Thirdly, it is likely that the interface between graphene and epoxy resin is much weaker than the shear strength of epoxy resin. Therefore the graphene matrix bond strength should be used in the calculation instead of 60 MPa which is the shear strength of the epoxy resin used in this investigation.

With these three requirements in mind, the methods of achieving a good dispersion of GNPs in epoxy resin are discussed in the next section.

3.2 Methods of Dispersing GNPs in Epoxy Resin

There are 3 common techniques used to try and ensure a good dispersion of GNPs in epoxy resin. These techniques are three roll milling, sonication and shear mixing which are discussed next [84-87].

3.2.1 Three Roll Milling

In this technique 3 rollers rotate in opposite directions to one another with a small gap in between each roller as shown in figure 3.2. The gaps between the rollers can be reduced down to 0.2 µm and the speed of the rollers can be varied typically between 0-200 rpm. GNPs are mixed with epoxy resin by hand and then fed through the rollers. The rollers create very high shear forces which can break down agglomerates [88]. The drawback to this technique is that it can only be used on very high viscosity epoxy resin resins. Lower viscosity resins such as the one used in this study fall in between the gaps in the rollers and a lot of material gets wasted. Therefore this technique will not be used in this study and will not be discussed further.

![Figure 3.2: a) Picture of a three roll mill b) diagram of how the rollers move and how material is fed into the machine [2]](image-url)
3.2.2 Sonication

A sonicator is a probe which has a piezoelectric material at its tip. The tip of the sonicator is placed in the liquid to be processed. When electrical current is applied to the sonicator the piezoelectric tip starts to vibrate which causes cavitation in the liquid. In cavitation, air bubbles grow within the liquid until they become unstable and collapse. As they collapse they send out shock waves through the liquid and give off tremendous heat very locally. The combination of shock waves and heat break down agglomerates of GNPs in solution and exfoliate layers of graphene [89-91]. The advantage of this technique is that large volumes of material can be processed. The amount of energy put into the liquid can also be varied. The disadvantages are that sonication is only effective on low viscosity liquids and it can damage the graphene. Sonication cannot be used directly on epoxy resin because the sonicator produces a chemical change in the resin which turns it pink. Instead the graphene must be sonicated in a low viscosity solvent such as acetone and then mixed in with the resin separately.

Studies have shown that sonicating for longer periods of time can exfoliate more graphene from GNPs. In [59] powdered graphite was added to a solvent called NMP at a concentration of 3.3 mg ml\(^{-1}\) and sonicated from 0.5 hrs to 343 hrs at a constant temperature of \(\sim 50 \, ^\circ C\). Using TEM, 100 flakes were analysed in terms of thickness and lateral size. The results are presented in figure 3.3 and show the amount of exfoliation which takes place increases as the time of sonication increases. However, from figure 3.4 the lateral dimensions of the flakes become smaller as the time of sonication increases. For mechanical reinforcement this is not ideal because better stress transfer is achieved when the lateral dimensions of GNPs are large [92]. Although sonication has produced some promising results another dispersion method called shear mixing is seen as a more efficient and industrially applicable method.

![Figure 3.3](image)

*Figure 3.3: Histogram of the number of layers per flake as a function of sonication time. 100 flakes were measured in each case. The histogram shows that the longer the sonication time the more graphene is exfoliated [59].*
3.2.3 Shear Mixing

Shear mixing is similar to a blender designed for breaking down particles of micrometre size [93]. A Silverson shear mixer, as used in this study, consists of a rotating paddle inside a perforated metal grid (see figure 3.5). The distance between the paddle and the perforated grid is small (~100 µm) and this creates high shear forces when it rotates. GNPs can be directly mixed in epoxy resin using this technique. It also works with a variety of viscosity solvents. The speed of mixing can be increased typically up to 10,000 rpm.

Research has shown that shear mixing is a more effective and scalable technique than sonication. Shear mixers are more energy efficient using ~100 Watts per litre compared to sonicators which can use thousands of Watts per litre. Production rates of graphene are also higher using shear mixing. The maximum reported production rate using a shear mixing process was 5.3 g hr\(^{-1}\) of graphene compared to less than 0.4 g hr\(^{-1}\) for sonication [18]. According to research, there exists a critical shear rate (10\(^4\) s\(^{-1}\)) which is required to exfoliate graphene from GNPs [18]. In the study graphite particles were dispersed in a mixture of a solvent and a surfactant N-Methyl-2-pyrrolidone (NMP) and sodium cholate (NaC) respectively.
The shear rate produced by the shear mixer was calculated as $\dot{\gamma} = \frac{\pi ND}{\Delta R}$

$\dot{\gamma}$ = shear rate

N = speed of shear mixer

D = rotor diameter

$\Delta R$ = gap between rotor and perforated grid (100µm)

Figure 3.5 a) Silverson L5M Mixer showing the rotating paddle and perforated grid; b) Agglomerates enter the shear head where they are broken up by the shear forces created by the rotating paddle; c) They are then pushed out through the holes in the perforated grid.

The shear rate produced by the shear mixer was calculated as $\dot{\gamma} = \frac{\pi ND}{\Delta R}$

$\dot{\gamma}$ = shear rate

N = speed of shear mixer

D = rotor diameter

$\Delta R$ = gap between rotor and perforated grid (100µm)

Figure 3.6 Concentration of graphene produced versus the shear rate produced by the mixer. The concentration only increases once a shear rate of $10^4$ s$^{-1}$ is produced [18]
In order for exfoliation to take place the shear rate must be greater than $10^4$ s$^{-1}$ (see Figure 3.6)

The concentration of graphene produced was proportional to the following variables:

$$C \propto C_i^{0.66} N^{1.13} D^{2.28} V^{-0.68}$$

Where $C_i$ = initial concentration of graphite in solvent (g l$^{-1}$), $t$ = time (mins), $N$=speed of mixer (rpm), $D$=diameter of rotor (mm), $V$ = volume of container (ml).

The exponents are applicable to the solvents used which were NMP and NaC. Other solvents will alter the exponents.

The following conditions were used: $C_i$ = 80 g l$^{-1}$, $N$=5700 rpm, $D$=32 mm and $V$=1500 ml and the dimensions of 100 flakes were measured by TEM. The average length of each flake was 0.382 µm and the average number of layers per flake was 7.2. Histograms of the number of layers per flake and the length of the flakes are presented in figure 3.7 and 3.8 respectively. Raman spectroscopy and XPS confirmed that the flakes did not have basal plane defects and had not been oxidised during the shear mixing process.

![Figure 3.7](image1.png)

*Figure 3.7: A histogram of the number of layers per flake measured for 100 flakes [18]. The average is 7.2 layers per flake. In total 9 flakes were monolayer graphene.*

![Figure 3.8](image2.png)

*Figure 3.8: A histogram of the flake length measured for 100 flakes. The average flake length was 0.38 µm. [18]
Other studies have shown that using a simple kitchen blender can exfoliate graphene\cite{94} \cite{95}. In \cite{95} graphite powder was dispersed in Fairy Liquid (a common household washing up detergent) and blended for periods of up to 240 minutes. A maximum production rate of 0.15 g hr\(^{-1}\) was reported which is higher than any reported sonication technique. In addition sonicators can cost thousands of pounds whereas a simple kitchen blender can be purchased for around 20 pounds so it is more economical.

3.2.4 The Effect of Solvents on the Exfoliation Process

Sonication and shear mixing are commonly carried out in a solvent. Some solvents are much better at exfoliating graphene from GNPs than others. Two parameters are used to measure the compatibility of graphene with the solvent. They are called the Hildenbrand Solubility parameter (\(\delta_T\)) and the Hansen solubility parameters (\(\delta_D\), \(\delta_P\), \(\delta_H\))\cite{96}. The two parameters are linked by equation 3.2:

\[
\delta_T = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (3.2)
\]

Good solvents for dispersing graphene should have a Hildebrand solubility parameter of \(\delta_T \approx 23\) MPa\(^{1/2}\) and Hansen Solubility parameters of \(\delta_D \approx 18\) MPa\(^{1/2}\), \(\delta_P \approx 9.3\) MPa\(^{1/2}\) and \(\delta_H \approx 7.7\) MPa\(^{1/2}\) \cite{97}. Solvents which are near to these values help in the production rate because they stabilise the exfoliated flakes and prevent re-agglomeration. If there is a big mismatch in these parameters between the solvent and graphene the stabilisation will not be as effective. Choosing a solvent is crucial therefore to effective dispersion. Solvents like NMP are excellent for exfoliating graphene. They have a Hildebrand Parameter of \(\delta_T = 23\) MPa\(^{1/2}\) and Hansen Solubility Parameters of \(\delta_D = 18\) MPa\(^{1/2}\), \(\delta_P = 12.3\) MPa\(^{1/2}\) and \(\delta_H = 7.2\) MPa\(^{1/2}\) which is very close to the ideal values for stabilising graphene. However, NMP has a high boiling point of 205\(^\circ\)C which makes it difficult to remove from epoxy resin in the final composite. Another suitable solvent with a lower boiling point is cyclopentanone (131\(^\circ\)C) which has a Hildebrand parameter \(\delta_T = 22.1\) and Hansen solubility parameters of \(\delta_D = 17.9\) MPa\(^{1/2}\), \(\delta_P = 11.9\) MPa\(^{1/2}\) and \(\delta_H = 5.2\) MPa\(^{1/2}\). The chemical structure of NMP and cyclopentanone is shown in figure 3.9.

![Chemical structure of NMP and cyclopentanone](image)

*Figure 3.9: The chemical structure of NMP (left) and cyclopentanone (right). These two solvents help stabilise dispersions of graphene because their solubility parameters are similar to those of graphene.*
When looking for an ideal solvent not only should the solubility parameters be as close to the ideal values but it should also have a boiling point as low as possible to make it easy to remove from epoxy resin. The effect of different solvents on the curing of epoxy resin has not been well studied so it is important to avoid residual solvent becoming trapped in the epoxy resin. Acetone has a much lower boiling point of 56 °C compared to other solvents so it is much easier to remove from epoxy resin. However, its solubility parameters ($\delta_T = 19.9 \text{ MPa}^{1/2}, \delta_D = 15.5 \text{ MPa}^{1/2}, \delta_P = 10.4 \text{ MPa}^{1/2}$ and $\delta_H = 7.0 \text{ MPa}^{1/2}$) are not as good as some others. In spite of this, acetone was still capable of producing 63% of flakes with 1-5 layers [18]. Therefore although acetone is not the best solvent for exfoliation, it may be more practical to use as it can be easily removed and still produces reasonable exfoliation.

Whilst many studies have focussed on using solvents help stabilise a dispersion of GNPs, there are very few studies on directly mixing GNPs in epoxy resin. This provides me with an opportunity to carry out novel research. Solvents can be difficult to remove from the final composite and could affect the properties of epoxy resin so if they can be avoided completely this would make processing more efficient. Therefore in section 4.1.1 an experiment has been designed to test if shear mixing GNPs directly into epoxy resin without solvents can have a positive impact on mechanical properties.

### 3.3 Chemical Functionalisation of GNPs

As well as a good dispersion, the other important factor for efficient mechanical reinforcement is the interface between graphene and epoxy resin [39, 53, 61-65]. No matter how strong graphene is and how well dispersed it is, if it cannot be bonded to the epoxy resin then its strength will be redundant. The better the bond between the graphene and the epoxy resin, the more efficiently stress can be transferred during loading. A poor bond will result in premature failure at the interface and also means that the critical length of graphene for reinforcement is longer. There are many mechanisms occurring at the interface which promote good bonding.

The first mechanism is wetting of the surface of graphene by the epoxy resin. At a micro or nanoscale the surface of graphene is not perfectly smooth but consists of many ridges. When the resin comes into contact with the graphene it must cover every hill and valley on the surface displacing all the air in the process [24]. The wetting of a liquid on a solid can be measured by the contact angle shown in figure 3.10. A contact angle of 180° represents perfect wetting where the interaction between the solid and the liquid is very strong in comparison to the liquid-liquid interaction. Imperfect wetting would be represented by a contact angle of 0°.
The Young Equation (equation 3.3) can be used to calculate the contact angle of a liquid on a solid

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]  (3.3)

\( \gamma_{SV}, \gamma_{SL} \) and \( \gamma_{LV} \) are the surface free energies of the solid-vapour, solid-liquid and liquid-vapour interfaces and \( \theta \) is the contact angle. The surface free energies can be calculated from experiments. In general, better wetting occurs when the surface energy of the solid is much higher than the surface energy of the liquid.

For graphite, the surface energy has been calculated as \(~70 \text{ mJ m}^{-2}\)[98]. However the surface energy of graphene has not been thoroughly researched. There have been values published from \(46 \text{ mJ m}^{-2}\) for graphene to \(62 \text{ mJ m}^{-2}\) for graphene oxide [99]. In order to enhance wettability the surface energy of the graphene should be enhanced as much as possible. Functionalisation of the surface with polar groups could be one way to achieve this.

Chemical bonding is the second mechanism which can enhance the strength of the graphene epoxy resin interface [11, 100, 101]. The bonds can be covalent or ionic. The edge of the graphitic planes is where most chemical bonding to the matrix takes place, because the carbon atoms at the edges have valence electrons. Holes and defects in the graphitic planes are also active sites where chemical bonding to the matrix takes place. Chemical modification of graphene also helps in the dispersion of graphene since it can increase the interlayer separation and reduce the van der Waals forces holding the layers together. A drawback of chemical modification is that it disrupts the electrical conductivity of graphene. For this reason if both mechanical reinforcement and improved electrical conductivity is required simultaneously it may be better to use a hybrid composite consisting of chemically functionalised and unfunctionalised graphene.

### 3.3.1 Methods of Chemical Functionalisation

Effective functional groups to attach to the surface of graphene from a mechanical reinforcement perspective are amine and epoxide groups because both of these can react with the epoxide groups of the epoxy resin and the amine groups of the hardener. A classical way to introduce oxygen functionality to the surface of graphene is the Hummer’s method [102]. By this method, graphite is...
bathed in a mixture of nitric acid, sulphuric acid and potassium permanganate solution for 96 hours. This introduces oxygen containing functional groups onto the surface of the graphite such as hydroxyl, epoxide and carboxylic acid groups. The oxidised graphite can be exfoliated to produce graphene oxide (GO) whose structure is shown in figure 3.11. GO is insulating so in order to restore some conductivity it can be reduced to remove some of the functional groups [103] and increase the carbon to oxygen ratio, thus restoring the sp² hybridised network. Reduction can be achieved using a reducing agent called hydrazine. GO which has been reduced is called reduced graphene oxide and its structure is shown in figure 3.12.

GO can also be used as the building block to make amine functionalised graphene. Oxygen atoms act as active sites on which to chemically bond other functional groups. In [11] it was shown that graphene oxide can be reacted with alkyamines and then reduced with hydrazine to make amine functionalised graphene (see figure 3.13).

Silane coupling agents have been employed to improve the interface with epoxy resin. The functional groups on silane molecules (such as epoxy resin, amine and hydroxyl) act as a chemical bridge connecting graphene and epoxy resin. In [104] 3- amino triethoxysilane (APTS) was grafted onto the surface of graphene oxide by sonicating it with GO for 1 hour, followed by heating with N,N'-dicyclohexyl-carbodiimide at 75 °C for 12 hours (see figure 3.14). In [105] a silane coupling agent called 3-(Glycidoxypropyl)trimethoxysilane was grafted on to the surface of GO by heating it with graphene oxide for 3 hours at 300 °C in the presence of toluene. In both cases XPS and FTIR analysis demonstrated successful functionalisation.

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**Figure 3.11:** The chemical structure of graphene oxide. The addition of epoxide, hydroxyl and carboxylic acid groups disrupts the conductivity of graphene [7]

**Figure 3.12** The chemical structure of reduced graphene oxide showing that most functional groups restoring some of the conductivity.
Figure 3.13 Steps for the preparation of amine functionalised graphene. (a) oxidation using Hummer’s method (b) reaction with an alkylamine (c) reduction using hydrazine. Reduction partly restores the electrical conductivity of graphene whilst still providing functional groups to form bonds with epoxy resin molecules [11].

Figure 3.14: Functionalisation of graphene oxide with APTS. The \( \text{NH}_2 \) groups (in red) of the silane molecules attached to the surface of the graphene oxide are capable of reacting with epoxide groups from the epoxy resin. The silane molecules act as a coupling agent which improves the interfacial adhesion of graphene with epoxy resin.
The addition of functional groups to CNTs has also had a positive impact on CNT reinforced epoxy resin composites [101, 106, 107]. Since the chemistry of CNTs is the same as GNPs this is further evidence that functionalisation can help with mechanical reinforcement of epoxy resin.

Whilst many studies have investigated the effect of different functional groups on the mechanical properties of epoxy resin, there has not been any work to my knowledge on how the concentration of functional groups affects the mechanical properties of epoxy resin. Therefore a study on the effect of the concentration of oxygen functionalisation is described in experimental section 4.1.2 and results section 5.3.2.

3.4 Review of Mechanical Results from other Studies

3.4.1 Tensile Results

The addition of unfunctionalised GNPs to epoxy resin has had mixed results. Some research groups have reported improvements in strength and modulus of epoxy resin. For example [14] have reported \(\sim 20\%\) improvement in strength and a \(\sim 2.5\%\) increase in modulus when loaded with 0.5 wt% GNPs (see figure 3.15). The GNPs were purchased from XG Sciences (the same supplier used for this study) and was dispersed directly into epoxy resin using a three roll mill. (The same epoxy resin system was used in [14] as in my experiments). However, no error bars are provided with the data so it is impossible to know about the variability of the results. In the same experiment, GNPs functionalised with Oxygen, NH\(_2\) groups, and silane were also added to epoxy resin and tested. The results in figure 3.15 show that functionalised GNPs performed better than unfunctionalised GNPs.

The curing cycle used by [14] was 1 hour at 60 °C followed by 8 hours at 120 °C. For optimum mechanical properties the manufacturer suggests curing at a higher temperature of 80 °C for 2 hours followed by 140 °C for 8 hours. Using the manufacturer’s guidelines the epoxy resin should have a tensile strength of 70-77 MPa. Curing at a lower temperature reduces the strength of the neat epoxy resin to \(\sim 50\) MPa as shown in figure 3.16 a). Therefore although improvements have been reported by [14] they are relative to 50 MPa. Curing temperature is an important factor in the properties of epoxies and the paper does not discuss if the improvements continue when epoxy resin is cured using the cycle recommended by the manufacturer. This provides me with an opportunity to investigate if this is true in section 5.3.1.
Other studies however, have reported that unfunctionalised GNP s reduce the tensile strength of epoxy resin. In [108] the tensile strength of epoxy resin was reduced from 77 MPa to 56 MPa, with the addition of 1 wt% of GNP s. The addition of more GNP s reduced the strength even more. The GNP s were purchased from XG sciences and were dispersed using a high shear mixer at 2500 rpm for 40 mins. The reason why one group [14] showed an improvement in tensile strength whilst another group [108] showed a reduction in tensile strength is not clear. Perhaps it is because the three roll mill is more effective at breaking down the agglomerates than a high shear mixer, when GNP s are added directly to the resin. High shear mixing has proved useful for breaking apart agglomerates when the GNP s are dispersed in solvent [18], but no work has been carried out on the effect of shear mixing of GNP s directly in epoxy resin which provides me opportunity to research this.

Figure 3.15 (a) The effect of different functional groups on GNP s on the modulus of epoxy resin (b) the effect of different functionalisations on the tensile strength of epoxy resin. UG=unfunctionalised GNP s, GO=Graphene oxide, G-NH2= amino functionalised GNP s, G-Si=Silane functionalised GNP s [14]
Most research studies have made improvements to the strength and modulus of epoxy resin by using graphene oxide (GO) which is graphene functionalised with oxygen atoms [5, 17, 36, 109-112]. Graphene oxide has outperformed CNTs, for example a 0.1 wt% addition of GO to epoxy resin resulted in a 40% increase in tensile strength compared to an 11% increase for SWCNT reinforced epoxy resin and a 14% increase for MWCNT reinforced epoxy resin [109]. A 40% improvement is impressive given that only 0.1 wt% loading of GO was used. However, because epoxy resin is so weak to begin with it makes very little difference from an engineering materials perspective. In order for nano-reinforcements to be fully effective, the improvements must continue at higher loadings. However currently, improvements only occur at small loadings, typically less than 0.5 wt%, and adding more GO does not make the epoxy resin stronger. In fact, adding more GO can make epoxy resin weaker. For example, [5] has shown that the tensile properties improved up to 0.125 wt% addition of GO, but then declined when greater than 0.125 wt% was added (see figure 3.16). The reason suggested for this is that at higher loadings it becomes harder to prevent agglomeration from occurring because the graphene flakes are forced nearer to one another.

The knowledge gained from experiments using CNTs could help exploit the potential of graphene. The chemistry of CNTs and graphene is almost identical so processing methods which work for CNTs should also work for graphene. In [113] both sonication and a three roll mill were used to disperse CNTs into epoxy resin. Figure 3.17 (a) shows that the three roll mill was effective at breaking down agglomerates and exfoliating the CNTs whereas sonication only made the agglomerates smaller figure 3.17 (b). Unfortunately the paper did not compare the two samples by mechanical testing to determine whether the exfoliated structure resulted in better mechanical properties than the closed structure.

![Figure 3.16: Tensile properties of GO epoxy resin. Tensile strength and modulus improve up to 0.1 – 0.125 wt% but then begin to decline again. (FGS = functionalised graphene sheet which is equivalent to GO)](image-url)
Research has also shown that the type of CNTs is important for improvement of mechanical properties. In [114] it was shown that SWCNTs and double walled nanotubes (DWCNTs) significantly outperform MWCNTs (see figure 3.18(a)). It is hypothesised that MWCNTs do not perform as well as the SWCNTs or DWCNTs because the internal layers of the MWCNTs are not in contact with the epoxy resin and are therefore redundant in taking up stress during loading. For a MWCNT with an outer diameter of 15 nm, an inner diameter of 4 nm and an interlayer distance of 0.32 nm, the surface area which could contribute to reinforcement was calculated as 9% of the total weight of the MWCNT. The inner layers do not ‘see’ the polymer and slide within one another contributing to early failure of the composite. From this point of view, GNPs with fewer layers should be more effective than GNPs with more layers, and single layer graphene should be the most effective. In addition, when the CNTs were functionalised with NH$_2$ groups they also performed better than without functionalisation (see figure 3.18(b)). This shows the importance of the interface between the CNTs and the epoxy resin. NH$_2$ groups can directly react with epoxide groups in the resin to form chemical bonds linking the CNTs to the epoxy resin.
However unlike SWCNTs, research from [57] has suggested that monolayer graphene may not be the most effective reinforcement and that bi-layer or tri-layer graphene could be more effective. The reasoning behind this, is that if bi-layer or tri-layer graphene is used then the volume fraction of graphene in the polymer can be increased which in turn can increase the strength and modulus of the composite. Graphene layers are separated by polymer chains which are usually several nanometres long [9]. By contrast the distance between two layers of graphene in bi-layer or tri-layer graphene is 0.34 nm. From figure 3.19 it can be seen that the packing density of graphene is much greater in the case of a trilayer graphene composite than in a monolayer graphene composite. With bi-layer graphene it has been shown that there is no slippage between the layers if both are fully encapsulated by the polymer. With tri-layer graphene there is some slippage of the middle layer but this is offset by the fact that higher volume fractions of graphene can be accommodated in the structure. Therefore although tri-layer graphene is not as strong as monolayer graphene it could be more effective when used in a composite.

![Figure 3.19](image) Comparison of packing of graphene sheets in a monolayer graphene composite and a trilayer graphene composite. A higher volume fraction of graphene can be accommodated in the trilayer graphene composite [9]

### 3.4.2 Fracture Results

The ability of a material to resist fracture when it contains a crack is called the fracture toughness of a material. It is a critical design parameter for engineers. Epoxy resin has a low fracture toughness because of its brittle nature. The theory of why fillers such as graphene can improve the fracture toughness of polymers have been explained by [58]. Two mechanisms have been proposed: crack pinning and crack deflection. In crack pinning, the crack front is forced to bow out as it passes impenetrable particles. This is seen on a micrograph as tails forming around the particles as shown in figure 3.20. In crack deflection, the crack front is forced to change the orientation of the plane it is travelling in [115]. In both cases, cracks are forced to deflect from their normal path which absorbs
more energy and increases the toughness of the material (see Figure 3.21). However, there have been a number of papers that suggest for thermosetting matrices the toughening effect from secondary phase particles is insignificant and that only in thermoplastic polymers is the effect noticeable [116].

Figure 3.20: Tails forming around GNP s in an epoxy resin due to crack pinning. The white arrow shows the direction of crack propagation [109]

Figure 3.21 Crack deflection in a graphene reinforced glass composite [117]

Additions of GO have produced improvements in fracture toughness. One study has shown that 0.1 wt% GO improved the $K_{IC}$ by 53% compared to 14% for SWCNT reinforced epoxy resin and 20% for MWCNT reinforced epoxy resin [109]. As well as outperforming CNTs, GO has also outperformed other nanofillers such as SiO$_2$ and nanoclays which required loadings between 5-10 wt% to produce similar improvements in fracture toughness. Similar to tensile strength, fracture toughness improvements do not continue on adding more graphene. In another paper by the same researchers 0.125 wt% GO reinforced epoxy resin showed an improved $K_{IC}$ by 65% [5]. However, once again these improvements did not continue at higher loadings of GO (see figure 3.22.)
Another study has seen improvements when using acetone as a dispersion aid to mix GNPs with epoxy resin [118]. GNPs were sonicated in acetone for 30 minutes. The GNP acetone mixture was then added to epoxy resin and sonicated for a further 60 minutes. The mixture was then heated to evaporate the acetone before curing agent was added and then it was poured into a mould. The results reported a 128% improvement in $K_{IC}$ when 0.1 wt% of GNPs were added. However, the report only tested one loading percentage so it did not show if the improvements continued at higher loadings. In addition there was no proper control experiment. Fracture toughness samples of epoxy resin were made to compare their performance against the graphene reinforced epoxy resin. However, the epoxy resin samples were not made using the same procedure as the GNP reinforced epoxy resin samples. The epoxy resin was made by adding the resin and the hardener but no acetone was added and no sonication took place. Therefore it is impossible to say whether the improvement was because of the acetone, the sonication or whether it was due to the GNPs.

In [15] the performance of GO reinforced epoxy resin and GNP reinforced epoxy resin were compared alongside MWCNT reinforced epoxy resin composites (see figure 3.23). GO was prepared by oxidising GNPs using the Hummer’s method and then heating the GNPs rapidly to split the layers. GNPs were purchased from a company which according to the manufacturers had lateral dimensions of 20-50 µm. Interestingly, the maximum $K_{IC}$ value for the GNP reinforced epoxy resin composite was achieved at 1 wt% loading which is much higher than [5] where it peaked at 0.125 wt%. The best performing filler in [15] was the GO reinforced epoxy resin composite and the highest $K_{IC}$ was achieved at 0.5 wt%. This once again shows the importance of oxygen functionalisation for improving mechanical properties.
Fracture surfaces of GO reinforced epoxy resin composites were examined in [17]. Samples ranging from 0.1 wt% GO to 0.7 wt% GO were made by firstly sonicating GO in acetone for 1 hour. Subsequently, epoxy resin was added to the mixture and the acetone was evaporated off. The samples were then poured into a mould and cured. Micrographs are shown in figure 3.24. As the percentage of GO in the composite increased the surfaces became rougher. Higher surface roughness has been attributed to higher fracture toughness [60]. At the same time however, microcracks can be seen as indicated by the black arrows in figure 3.24(d). This could be the reason why the fracture toughness only increases up to a certain weight percentage and then begins to fall again.

Figure 3.23: Comparison of the fracture toughness of three different fillers in epoxy resin. TRGO (thermally reduced graphene oxide) is the best performer. The oxygen atoms on the surface promote better bonding with epoxy resin [15]

Figure 3.24: SEM images of fracture surfaces of failed specimens: (a) neat epoxy resin, (b) 0.1 wt. %, (c) 0.5 wt. %, and (d) 0.7 wt.% GO-epoxy resin nanocomposites. The white arrows at the bottom of the corners indicate the crack growth direction. Black arrows indicate micro cracks [17].
One study managed to show the effect of chemical modification (other than oxygen functionalisation) on the fracture properties of GNP reinforced epoxy resin composites [65]. They grafted 4,4′-methylene diphenyl diisocyanate (MDI) to the surface of GNPs which reacted with epoxy resin during curing. Improvements of ~85% in fracture toughness were made at loadings up to 4 wt% [65]. Normally, properties start deteriorating above 1 wt%, so to be able to add 4 wt% is unusual. An improvement of 85% is not significantly better than other groups, however. In addition, although the $K_{IC}$ improved, the tensile strength dramatically decreased. The objective in my work is to at least maintain strength while improving toughness.

Aligning the GNPs in the epoxy resin can have a profound effect on the fracture properties of the composite. In [13] GNPs were aligned transverse to the direction of crack growth using an AC electric field. The mode I fracture energy increased by 900%. In the randomly orientated GNP sample the increase was 600%. In the same experiment, GNPs were aligned parallel to the crack growth resulting in an improvement in fracture energy of 550%. These results sound more impressive than other groups but it should be noted that the ASTM standard was not followed and also only the fracture energy is reported whereas most other groups have reported the fracture toughness. The two properties are similar but not the same so it is hard to compare results, which is why they are not included in table 3.1. What can be concluded however is that orientation does have a significant effect on the fracture properties of epoxy resin. The intrinsic toughening mechanisms were delamination between the nanosheets of GNPs, interfacial debonding of the GNPs from the matrix and crack pinning. GNP fracture and pull out are the effective extrinsic toughening mechanisms. A table summarising a number of fracture toughness results from other research groups for GNP and CNT reinforced epoxies is shown in table 3.1.

**Table 3.1: Fracture toughness results from other research groups**

<table>
<thead>
<tr>
<th>Nanofiller type</th>
<th>Wt% added to Epoxy resin</th>
<th>Dispersion method</th>
<th>% Improvement in $K_{IC}$</th>
<th>Reference</th>
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<td>0.1</td>
<td>Three Roll Mill</td>
<td>53</td>
<td>[119]</td>
</tr>
<tr>
<td>GNPs</td>
<td>0.1</td>
<td>Sonication</td>
<td>54</td>
<td>[109]</td>
</tr>
<tr>
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<td>Three Roll Mill</td>
<td>60</td>
<td>[36]</td>
</tr>
<tr>
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<td>Sonication</td>
<td>85</td>
<td>[65]</td>
</tr>
<tr>
<td>GNPs</td>
<td>0.1</td>
<td>Sonication</td>
<td>128</td>
<td>[118]</td>
</tr>
<tr>
<td>MWCNTs</td>
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<td>Three Roll Mill</td>
<td>17</td>
<td>[120]</td>
</tr>
<tr>
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<td>Sonication</td>
<td>18</td>
<td>[109]</td>
</tr>
<tr>
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<td>Sonication</td>
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<td>[121]</td>
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<td>Three Roll Mill</td>
<td>73</td>
<td>[122]</td>
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3.5 Electrical Properties of GNP Reinforced Epoxy Resin Composites

Graphene can be added to insulating polymers to enhance their electrical conductivity. This happens when GNPs or agglomerates touch one another and create an electrically conducting path through the insulating polymer. Sometimes the GNPs do not touch one another because they are separated by a thin layer of polymer, however conduction can still occur through quantum mechanical tunnelling. For tunnelling to take place the tunnelling distance must be extremely small and on the order of 1 nm. The smaller the distance the more current can be transferred by tunnelling [123].

The electrical behaviour of random arrangements of GNPs in insulating matrices can be described by percolation theory [124]. In percolation theory, the conductivity of a composite increases in the manner shown in figure 3.25. Initially, when the concentration of GNPs is low the conductivity is essentially zero. At a critical concentration of GNPs, called the percolation threshold, the conductivity jumps up several orders of magnitude. The percolation threshold occurs when the concentration of GNPs is high enough that the individual agglomerates or platelets begin to touch one another. A network of GNPs in the polymer is created. After the percolation threshold, adding more GNPs enhances the conductivity but at a slower rate than before. The electrical conductivity of the composite obeys the following law:

$$\sigma \propto \sigma_f (\phi - \phi_c)^\nu$$  \hspace{1cm} (3.3)

Where $\sigma$ is the filler conductivity, $\phi$ is the filler volume fraction and $\nu$ is a critical exponent describing the variation in the conductivity near the percolation threshold $\phi_c$.

Percolation theory describes the behaviour not just of GNPs in composites but also of other conductive micro and nanofillers in insulating matrices. The key to achieving a low percolation threshold and to enhancing the conductivity as much as possible is to arrange the GNPs in an efficient network. An inefficient distribution of GNPs will result in the microstructure of figure 3.26 (a). Electrons cannot travel through the sample because the GNPs do not connect to transfer current. In figure 3.26 (b) GNPs have been distributed in such a way that electrons can travel from one GNP to another. Figure 3.26(b) represents efficient structure for electrical conductivity. In order to achieve a microstructure like Figure 3.26(b) graphene agglomerates must first be broken up and exfoliated to individual platelets and then be arranged to form a network. Here lies the challenge with creating conductive nanocomposites. Manipulating the graphene flakes to form a network such as figure 3.20(b) is a tricky task. Modifications to the graphene’s surface as well as using electric fields and
magnetic fields could be a way to align flakes so that they touch one another and this will be discussed next.

![Graph illustrating the conductivity of an insulator as a function of the amount of conductive filler added, according to percolation theory. The percolation threshold is \( \sim 0.2 \) wt% at which point the conductivity of the composite rises several orders of magnitude. Below the percolation threshold the conductivity is so low that it is essentially zero. Adapted from [10].](image)

**Figure 3.25:** Illustration of how the conductivity of an insulator rises as a function of the amount of conductive filler added to it according to percolation theory. The percolation threshold is \( \sim 0.2 \) wt% at which point the conductivity of the composite rises several orders of magnitude. Below the percolation threshold the conductivity is so low that it is essentially zero. Adapted from [10].

![Microstructures illustrating a percolated network of GNPs resulting in DC conductivity.](image)

**Figure 3.26 (a)** A microstructure which does not result in a percolated network. This material will be a poor conductor. **(b)** Microstructure showing a percolated network of GNPs resulting in DC conductivity.
3.5.1 Electric Field Alignment of GNP

Researchers have created nanocomposites where GNP s have been aligned in an electric field with significantly improved electrical properties. In [13] GNP s were added to epoxy resin and an AC electric field of 25 V mm\(^{-1}\) at 10 kHz was applied across the sample using electrodes whilst the sample cured. As time progressed the GNP s aligned themselves in the direction of the electrical field (see figure 3.27 (a-d)).

The electrical conductivity of the aligned sample was measured and compared to a sample where there was no alignment. The results are shown in figure 3.27. Parallel to the alignment the conductivity was much higher than the randomly oriented sample. This is because the GNP s in the aligned sample are more connected and can pass electrical current from one platelet to another.

![Optical micrograph of GNPs dispersed in epoxy resin during the application of an AC electric field.](image)

*Figure 3.27: Optical micrograph of GNPs dispersed in epoxy resin during the application of an AC electric field. (a) before the field was applied (b) after 4mins (c) after 10 minutes and (d) after 20 minutes. + and – represent positive and negative electrodes [13].*
The mechanism for the orientation of the GNP\textsubscript{s} is as follows. A solid inclusion dispersed in a dielectric medium such as a polymer can be polarised by an alternating electric field. This induces a dipole moment in the GNP\textsubscript{s} causing them to line up end to end with the positive polarised end of one flake attracting the negatively charged polarised end of the neighbouring flake. It was discovered that the frequency of the AC current did not have a significant effect on the overall alignment and conductivity of the composite. A bulk conductivity on the order of $10^{-5} \text{ S m}^{-1}$ was achieved using 1.6 volume\% of GNP.

The drawback of this technique is that the electric field will only work across small distances in the centimetre range and so sample size is limited. In order to make larger composites with aligned GNP\textsubscript{s}, the electric field must be much stronger which becomes impractical. In addition, if this technique is used on composites which also include carbon fibres, it almost becomes impossible because the contact of carbon fibres results in short circuiting and weakening of the electric field. Furthermore, the electric field cannot always pass through carbon fibre composites due to a build-up of surface charge on the outer plies. A promising alternative alignment technique uses magnetic fields [125] which do not suffer this problem since they can penetrate through carbon fibre more easily.

![Figure 3.28: Comparison of electrical conductivity for aligned and randomly orientated GNP\textsubscript{s} in epoxy resin [13].](image)

Alignment of GNP\textsubscript{s} can enhance the electrical conductivity compared to randomly orientated GNP\textsubscript{s}. 

69
3.5.2 Magnetic Field Alignment

Magnetic Fields can also be used to align GNRs. GNRs and CNTs have an anisotropic magnetic susceptibility and in low viscosity solvents they can overcome Brownian motion and orientate themselves parallel to the magnetic field. If the GNRs or CNTs are being dispersed in a more viscous polymeric matrix then a higher magnetic field can be used on the order of 25T. However, using high strength magnets limit the practicality of such a technique. Heating the host polymer to reduce its viscosity reduces the need for such a high strength field, since GNRs and CNTs are more easily able to align themselves. Even so, there may be a more practical way to align nanoparticles in a magnetic field by functionalising the surface of the nanoparticles with magnetic functional groups. Magnetite (Fe₃O₄) can be attached onto CNTs and has led to successful alignment using a magnetic field of 0.3T [125]. The external magnetic field causes the nanotubes to form a chain like structure with the south pole of one nanotube attracting the north pole of the next.

3.5.3 Measuring Conductivity

Conductivity measurements fall into two categories: DC conductivity measurements and AC conductivity measurements. Most people are familiar with DC conductivity measurements from school where a sample is connected into a circuit, a current of constant frequency is applied and the voltage drop across the sample is measured. The resistance of the sample can be calculated from $R = \frac{V}{I}$. The conductivity which is dependent on the dimensions of the sample can then be calculated using equation 3.4

$$\sigma = \frac{l}{Rwt} \quad (3.4)$$

Where $l$ is the length of the sample, $w$ is the width of the sample, $t$ is the thickness of the sample and $R$ is the resistance calculated from $V/I$. Typically for a DC conductivity measurement the four probe technique is used which minimises the contact resistance. This is useful for making very sensitive measurements if the contact resistance is a considerable proportion of the actual resistance of the sample. Typically, nanocomposite samples have very high resistances so the use of a four probe technique may not be necessary. However, there is another measuring technique which is useful for measuring nanocomposites’ conductivity. This is called the AC conductivity technique.

3.5.3.1 AC Conductivity Measurements

In addition to DC conductivity measurements which use one frequency of current, tests on composite materials are often carried out using an AC conductivity test, which is also the test that will be used in this investigation as it is capable of detecting lower conductivities compared to the DC electrical
measurement, and it can determine whether a percolated network has been formed. In essence, the sample is supplied with a current which increases in frequency and the resistance of the sample is measured as a function of the frequency.

A GNP reinforced epoxy resin composite can be thought of as a network of resistors (conductive GNPs) connected to capacitors (insulating epoxy resin)[126]. Therefore composites consist of a resistive component and a capacitive component which respond differently to an alternating current than a direct current. The conductivity of a nanocomposites varies as a function of the frequency according to the universal dielectric response proposed by Jonscher in equation 3.5 [127].

\[
\sigma_{AC}(\omega) = \sigma_{DC} + A \omega^n \quad (3.5)
\]

where \( \omega \) is the angular frequency, \( n \) is an exponent usually between 0.6 and 1 and \( A \) is a constant for the particular material. The resistive component is represented by \( \sigma_{DC} \) which is the equivalent of the DC conductivity. The capacitative component is represented by \( A \omega^n \).

From this equation, it can be seen that as \( \omega \) approaches zero, \( A \omega^n \) becomes smaller and the AC conductivity tends towards \( \sigma_{DC} \). For good conductors such as aluminium, the capacitive component is negligible and the AC conductivity is the same as the DC conductivity regardless of frequency. This is shown in figure 3.29 as a straight line intercepting the y axis at 10^6 S m^-1.

However, for materials which consist of a mixture of conductive and insulating phases such as GNP nanocomposites, there is both a resistive component (from the GNPs) and a significant capacitive component (from the epoxy resin). In this case the conductivity is dependent on the frequency of the current supplied and one of two things can happen. In one scenario a percolated network of GNP could be formed. Then at low frequencies the conductivity becomes independent of frequency. This is because the resistive component of the conductivity becomes dominant at low frequencies. The equivalent DC conductivity of the composite is taken as the value of conductivity at which this independency from frequency is reached (~10^{-1} S m^{-1} from figure 3.29). However, in the other scenario if GNPs do not form a percolated network, the conductivity curve will be dependent on frequency even at low frequencies. The capacitive contribution to conductivity is dominant and the AC conductivity increases as the frequency increases even at low frequencies. Un-percolated networks do not have defined DC conductivity.
The benefit of using the AC conductivity technique is that it is more sensitive than DC measurements. This is necessary because GNP reinforced epoxy resin composites typically have very low conductivities which can be difficult to measure. Another advantage, is that it enables the user to see if a percolated network has been formed in the composite, by viewing whether the conductivity has become independent of frequency or not. In contrast DC conductivity measurements cannot do this.

3.5.4 Electrical Conductivity Results from other Research Studies

Many groups have reported improvements in conductivity with the addition of GNPs to epoxy resin. Typically percolation thresholds are ~0.1-1 wt% and maximum conductivities achieved are between ~$10^5$ and 1 S m$^{-1}$. The limiting factors for conductivity are the lack of orientation of the GNPs, poor exfoliation and high contact resistance of touching GNPs. A summary of maximum conductivities for GNP reinforced epoxy resin composites is shown in table 3.2 As a comparison some results for CNT reinforced epoxy resin composites are also shown.

If higher conductivities are to be achieved a novel approach could be used. One group has succeeded in making composite with a much higher conductivity (1000 S m$^{-1}$) than any others [16]. In
their research they created a 3D scaffold of interconnected graphene by CVD using Nickel foam as a template see figure 3.30. The big benefit with the technique is that the network is continuous whereas other techniques suffer from high contact resistance where the GNPs touch each other or are separated by a thin layer of polymer. The basic procedure was as follows and is summarised in figure 3.31. A nickel foam template was used to grow graphene by CVD. The nickel was then etched away leaving a scaffold of graphene which was then infused with PDMS. If this could be recreated with epoxy resin and the scaffold formed a good bond with epoxy resin then this could be a promising way to enhance electrical, thermal and tensile properties of GNP reinforced epoxy resin composites.

![Figure 3.30: SEM of graphene foam showing an interconnected 3D network of graphene [16]](image)

Table 3.2: Conductivity results from other research groups

<table>
<thead>
<tr>
<th>Nano filler</th>
<th>Wt % of filler in epoxy resin</th>
<th>Type of processing</th>
<th>Maximum DC conductivity ($S \cdot m^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNPs</td>
<td>0.5wt%</td>
<td>Sonication</td>
<td>$10^{-5}$</td>
<td>[128]</td>
</tr>
<tr>
<td>GNPs</td>
<td>4wt%</td>
<td>Sonication and shear mixing</td>
<td>$10^{-3}$</td>
<td>[38]</td>
</tr>
<tr>
<td>CNTs</td>
<td>3wt%</td>
<td>Sonication and three roll Mill</td>
<td>$10^{-3}$</td>
<td>[129]</td>
</tr>
<tr>
<td>GNPs</td>
<td>2wt%</td>
<td>Sonication</td>
<td>$10^{-3}$</td>
<td>[39]</td>
</tr>
<tr>
<td>GNPs</td>
<td>2wt%</td>
<td>Three roll mill</td>
<td>$10^{-3}$</td>
<td>[37]</td>
</tr>
<tr>
<td>GNPs/CNTs</td>
<td>5wt%</td>
<td>Sonication</td>
<td>$10^{-2}$</td>
<td>[130]</td>
</tr>
<tr>
<td>CNTs</td>
<td>1wt%</td>
<td>Sonication</td>
<td>$10^{-3}$</td>
<td>[63]</td>
</tr>
<tr>
<td>CNTs</td>
<td>2.5wt%</td>
<td>Sonication</td>
<td>$10^{-4}$</td>
<td>[40]</td>
</tr>
<tr>
<td>CNTs</td>
<td>4wt%</td>
<td>Sonication</td>
<td>0.1</td>
<td>[131]</td>
</tr>
</tbody>
</table>
Figure 3.31: CVD growth of graphene composites using a nickel foam scaffold a) Nickel foam scaffold used as a template to grow graphene b) Nickel foam heated in the presence of methane causes graphene to grow on Nickel c) PMMA coated on the graphene surface d) Nickel etched away using HCl leaving graphene foam coated with PMMA. e) Acetone used to dissolve away the PMMA layer leaving graphene foam f) Graphene foam infiltrated with PDMS to create a composite with an extremely high conductivity. [16]
4 Experimental

This chapter describes all aspects of the experimental procedures used in this project. The materials and equipment used in the project are described first of all. The experimental method used to make samples is then outlined followed by the methods of testing. In the final section the methods of characterisation are described.
4.1 Materials

The nanoparticles used in the experiments are described in this section. These include graphene nanoplatelets (GNPs), carbon nanotubes (CNTs) and expanded graphite (EG). Other materials used for making samples such as epoxy resin, surfactant (to assist dispersion of nanoparticles) and silane (to functionalise the GNPs) are also described. The supplier of all the materials is detailed as well as the properties of the materials according to the manufacturer.

4.1.1 Unfunctionalised Graphene Nanoplatelets (GNPs)

GNPs were purchased from XG Sciences and were Grade M25 [73]. According to the manufacturer they have a thickness of 6-8 nm (approximately 17-20 layers) and an average lateral dimension of 25 µm. The lateral dimension is described as the longest dimension of the graphene flakes. The manufacturer claims that the specific surface area of the grade M25 GNPs is 150-200 m² g⁻¹. Low and high magnification SEM images are shown in Figure 4.1 and 4.2 respectively. They show that the lateral dimensions of the sheets are quite varied and the flakes are also wrinkled.

4.1.2 Functionalised GNPs

Functionalised nanoplatelets were purchased from two suppliers: XG Sciences and ACS Materials [132]. Oxygen functionalised GNPs were purchased from XG Sciences and came in three grades C300, C500 and C750. According to the manufacturer specific surface area of each grade was 300, 500 and 750 m² g⁻¹ respectively. The manufacturer also claimed there was oxygen functionalisation which was proportional to the specific surface area as shown in Table 4.1. SEM images are illustrated in figures 4.3, 4.4 and 4.5 for C300, C500 and C750 grades respectively.

Carboxyl functionalised GNPs were purchased from ACS materials. No SEM images of this grade are shown because only a small quantity was available which was used to make tensile samples.

<table>
<thead>
<tr>
<th>Type of GNP</th>
<th>Specific Surface Area (m² g⁻¹)</th>
<th>Functionalisation</th>
<th>% Functionalisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>M25</td>
<td>150-200</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>C300</td>
<td>300</td>
<td>Oxygen</td>
<td>4</td>
</tr>
<tr>
<td>C500</td>
<td>500</td>
<td>Oxygen</td>
<td>6</td>
</tr>
<tr>
<td>C750</td>
<td>750</td>
<td>Oxygen</td>
<td>8</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>No info</td>
<td>Carboxyl (COOH)</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 4.1: Low magnification image of XG Sciences grade M25 GNP. The dimensions of the GNP appear quite varied although the manufacturer claims the lateral dimensions are on average 25 µm and the thickness is 6-8 nm.

Figure 4.2: High magnification SEM image of XG Sciences grade M25 GNP. The image reveals the different sizes of the individual platelets and the presence of wrinkles where the sheets have become creased and folded.
Figure 4.3: SEM Image of C300 grade GNP\textsubscript{s} from XG Sciences. In comparison to the M25 grade GNP\textsubscript{s} the overall agglomerate size appears smaller.

Figure 4.4: SEM Image of C500 grade GNP\textsubscript{s} from XG sciences
4.1.3 Multiwall Carbon Nanotubes (MWCNTs)

Multi walled carbon nanotubes were purchased from Cheap Tubes [133]. According to the data sheet the outer diameter is 30-50 nm, the inner diameter is 5-10 nm and the length 10-20 μm. High and low magnification SEM images (figure 4.6 and 4.7 respectively) show that the MWCNTs existed as agglomerates ranging from 10-100 μm in diameter. In the highest magnification image, thin thread like structures can be seen protruding from the agglomerates which are individual MWCNTs.
Figure 4.6: Low magnification SEM image of MWCNTs from Cheap Tubes. The MWCNTs can clearly be seen in the form of agglomerates. Individual MWCNTs be only be seen protruding from the agglomerates at high magnification (see Figure 4.7)

Figure 4.7: High magnification SEM Image of a MWCNT agglomerate. Individual MWCNTs can just be seen as fine thread like structures sticking out at the edge of the agglomerate
4.1.4 Expanded Graphite (EG)

Expanded graphite was manufactured in house and supplied by another research group. It consisted of graphitic layers with a larger interlayer spacing than in conventional graphite. Individual EG particles consisted of worm like structures around 1 mm in length (see Figure 4.8). In brief, EG was manufactured as follows. Natural graphite flakes were bathed in sulphuric acid which diffused into the spacing between the layers. The graphite was then dried and microwaved for a minute causing the residual sulphuric acid trapped between the layers to vaporise. This resulted in a pressure increase which pushed the layers of graphite apart causing the graphite to expand (see Figure 4.9).

![Figure 4.8: Low magnification SEM image of EG "worms". The worms are on average 1 mm in length, much larger than GNP and CNTs.](image1)

![Figure 4.9: High magnification SEM image of EG showing the interlayer spacing between the graphitic sheets. In EG the interlayer spacing is on the order of micrometres whereas in conventional graphite the spacing between layers is 0.34 nm](image2)
4.1.5 Epoxy Resin

The epoxy resin system purchased from Huntsman Advanced Materials [134] was a 2 part system consisting of an epoxy resin (Araldite LY564) and a co-reactant hardener (Aradur 2954). The active molecules of Araldite LY564 and Aradur 2954 are DGEBA and bis-cyclohexylamine respectively, which are shown in figure 4.10. When mixed together in the ratio 100 g of Araldite to 35 g Aradur the resin cures and forms a cross-linked network of epoxy resin. According to the manufacture’s data sheet, when the system is cured for 2 hours at 80°C followed by 8 hours at 140°C the tensile strength of the epoxy resin is 70-77 MPa and the modulus is 2.55 – 2.65 GPa.

4.1.6 Triton X-100 Surfactant

Triton X-100 was purchased from Sigma Aldrich [135]. It was used as a surfactant to try and improve the dispersion of nanoparticles in the epoxy resin. The chemical structure is shown in figure 4.10. It consists of a hydrophilic polyethylene oxide chain and an aromatic hydrophobic group.

4.1.7 Silane Coupling Agent

Silane coupling agent (3-Glycidyloxypropyl-trimethoxysilane) was purchased from Sigma Aldrich [136]. It was used to functionalise the surface of the GNPs in order to improve its adhesion to the epoxy resin matrix. (See figure 4.10)

4.1.8 Silver Conductive Epoxy Resin

Silver conducting epoxy resin was purchased from Chemtronics [137] and was used make conductive contacts so that samples could be placed in a circuit to measure electrical conductivity. It is a 2 part system consisting of a resin and hardener. The two parts were mixed in a 1:1 ratio and spread across the surface to be bonded. Curing took place at 80 °C for 10 minutes. The resistivity of the silver epoxy resin is <0.1 Ω m and insignificant compared to the resistivity of the samples. Therefore, the contact resistance can be considered negligible.

Figure 4.10: Chemical structures of the active molecules in Araldite LY564 (DGEBA) and Aradur 2954 (bis-cyclohexylamine), and the chemical structure of surfactant Triton X-100 (where n=9-10) and silane coupling agent.
4.2 Equipment

In this section, the equipment used to process nanocomposites and make samples is described.

4.2.1 Silverson Shear Mixer

The Silverson shear mixer [138], shown in figure 4.11(a) was used to break down agglomerates of nanoparticles in epoxy resin. It consists of a rotating paddle inside a perforated metal grid. The gap between the perforated grid and the rotating paddle is 100 µm and the speed of the paddle can be varied from 0-10000 rpm. Nanoparticles are sucked into the region of the rotating paddle where they experience very high shear forces where exfoliation can potentially take place see figure 4.11(b). Exfoliated nanoparticles are then ejected via the perforations in the metal grid see Figure 4.11(c).

4.2.2 Mechanical Stirrer

The mechanical stirrer (figure 4.11 (d)) was a simple mixing machine consisting of a rotating paddle with speeds from 0-1000 rpm. Unlike the shear mixer there was no perforated metal grid surrounding the paddle, and the maximum speed was much lower. The shear forces produced by the mechanical stirrer are lower than the shear mixer and it could not be used for breaking down and exfoliating agglomerates. The mechanical stirrer was used to homogenously mix resin and hardener to ensure they would chemically react during curing. Improper mixing of the resin and hardener leads to samples where curing is incomplete and which have reduced mechanical properties.

4.2.3 QSonica Q700 Sonicator

The Q700 sonicator [139] shown in figure 4.11 (e) was used to exfoliate layers of graphene from GNPs and break down large agglomerates of nanoparticles. Sonicators use ultrasound to produce areas of high and low pressure in a liquid. This creates vacuum bubbles in the liquid which grow until they reach a critical size and then collapse. The collapse of the bubbles produces a very high local pressure and temperature which is used to break down agglomerates of nanoparticles and exfoliate GNPs. The amplitude of vibration could be altered from 100% down to 1%. The energy given to the system could therefore be controlled by altering the amplitude.

4.2.4 Heraeus Vacutherm Degassing Chamber

The degassing chamber (see figure 4.11(f)) was used to remove air bubbles from the resin since trapped air bubbles in the final composite adversely affect the mechanical properties of the final composite. Once all air bubbles had been removed the resin could be cured.
4.2.5 Heraeus Thermoscientific Curing Oven

The oven was used to cure the resin and hardener to form epoxy resin. The cure cycle used was 2 hours at 80 °C followed by 8 hours at 140 °C using a ramp rate of 1 °C per minute. (See fig 4.11 g))

4.2.6 Silicon Rubber Moulds

Silicon rubber moulds were made so that epoxy resin could be cast into dog bone shaped specimens for tensile tests. Other moulds were made for fracture toughness specimens and electrical and thermal specimens. The silicon rubber was sprayed with silicon oil before the epoxy resin was cast to ensure that the specimens could be easily removed after curing. (See figure 4.11 h))

4.2.7 Surface Grinder

In order to ensure all tensile specimens were of uniform thickness a surface grinder was used to smooth off any unevenness or remove surface air bubbles from the as cast specimens. The surface grinder was capable of smoothing off the surface to within 0.25 mm. Tensile strength measurements are sensitive to flaws in the specimen and unevenness in the dimensions and this step was therefore essential to ensure reliability of results. (See figure 4.11 j) and k))

Figure 4.11: a) Shear mixer b) and c) mechanism of action of the shear mixer. GNPs enter the head and the shear forces generated by the rotating paddle break up the agglomerates and push them out of the perforated metal grid; d) mechanical stirrer; e) Q700 Sonicator; f) Degassing chamber; g) Curing oven h) silicon rubber moulds used to cast tensile specimens; i) surface grinder; j) tensile specimen before surface grinding; k) tensile specimen after surface grinding
4.3 Preparation of Samples

In this section the method of manufacturing samples is presented. This project consisted of four scientific investigations and each investigation consisted of different studies which used various methods of preparing samples. The investigations were as follows:

1. **Pure Epoxy Resin Investigation.** The first part of the investigation was to manufacture pure epoxy resin specimens which would represent a benchmark to measure improvements against in subsequent experiments. Mechanical and electrical properties were tested.

2. **Unfunctionalised GNP Reinforced Epoxy Resin Investigation.** The second part of the investigation was to reinforce epoxy resin with unfunctionalised GNP and determine its effect on the mechanical and electrical properties. Four separate studies were conducted.
   - The Effect of Shear Mixing Speed and Time on the Mechanical and Electrical Properties of GNP Reinforced Epoxy Resin
   - The Effect of GNP Loading on the Mechanical and Electrical Properties of Epoxy Resin
   - The Effect of Carbon Nanotubes and Expanded Graphite on the Mechanical and Electrical Properties of Epoxy Resin.
   - The Effect of Sonication Amplitude on Mechanical Properties of GNP Reinforced Epoxy Resin

3. **Functionalised GNP Reinforced Epoxy Resin Investigation.** GNP were functionalised with various chemical groups and their effect on the mechanical properties of epoxy resin was studied. Three separate studies were conducted:
   - The Effect of Silane Functionalised GNPs on the Mechanical Properties of Epoxy Resin
   - The Effect of Oxygen Functionalised GNPs on the Mechanical Properties of Epoxy Resin
   - The Effect of Carboxyl Functionalised GNPs on the Mechanical Properties of Epoxy Resin

4. **Surfactant Assisted GNP Reinforced Epoxy Resin Investigation.** In the final part of the investigation the effect of surfactant and GNP on the mechanical properties of epoxy resin was measured. The surfactant was used as a means of improving the dispersion of GNP. Three studies formed part of the investigation:
   - The Effect of GNP to Surfactant Ratio on the Mechanical Properties of Epoxy Resin
   - The Effect of GNP Loading Using the Best Ratio of GNPs to Surfactant
   - The Effect of Surfactant Addition Only on the Mechanical Properties of Epoxy Resin

The method of manufacturing the samples in each investigation is described in the following sections.
4.3.1 Pure Epoxy Resin Investigation

Step 1: 100 g of Araldite LY564 was poured into a beaker (figure 4.12 a)).

Step 2: 35 g of hardener Aradur 2954 was added to the beaker and the mixture was then stirred using the mechanical stirrer at 500 rpm for 3 minutes (figure 4.12 b)). Preliminary experiments had shown that 3 minutes of mixing at this speed was sufficient to result in an even blend of Araldite and Aradur. In this preliminary experiment, blue dye was dropped into Araldite LY564 and stirred at a range of speeds and times. It was determined that stirring at 500 rpm for 3 minutes ensured an even distribution of the dye. Therefore this time and speed was chosen for stirring.

Step 3: The mixture was transferred to the Hereus Vacutherm degassing chamber where air bubbles were removed until none remained by eye (figure 4.12 c)). The time taken for this was on the order of 2 hours but was variable depending on how much air was in the resin to begin with.

Step 4: The mixture was poured in silicon rubber moulds which had been sprayed with silicon oil (figure 4.12 d)). The moulds were placed in the Hereus Thermostcientific Oven where they were cured using the following cycle: 2 hours at 80 °C followed by 8 hours at 140 °C. The ramp rate was 1 °C per minute.

Step 5: The cured specimens were removed from the moulds (figure 4.12 e)) and the surface was ground to ensure it was flat and smooth (figure 4.12 f))

Steps 2 to 5 were used as the standard curing procedure for all other remaining investigations. Whenever the samples were cured the method in steps 2 to 5 was used.

Figure 4.12: Images showing steps in the manufacture of pure epoxy resin specimens a) 120 g of Araldite LY564 mixed with 42g of Aradur 2954 b) Mixture stirred at 500 rpm using the mechanical stirrer c) degassing of mixture to remove air bubbles d) Tensile moulds into which mixture was poured and cured in an oven e) cured specimen removed from the mould before surface grinding f) specimen after surface grinding
4.3.2 GNP Reinforced Epoxy Resin Investigation

4.3.2.1 The Effect of Shear Mixing Speed and Time on the Mechanical and Electrical Properties of GNP Reinforced Epoxy Resin

GNP M25 from XG sciences weighing 0.10 g was added to 100 g of Araldite LY 564. The reinforced resin was shear mixed in the Silverson L5M shear mixer at 1000 rpm for 1 hour and then cured. The procedure was then repeated for a range of different speeds and times as shown in Table 4.2. In total 10 different samples were made. (See figure 4.13)

Table 4.2: Table of the speeds and mixing times used to make the GNP reinforced epoxy resin samples. In total 10 different samples were made

<table>
<thead>
<tr>
<th>Shear Mixing Speed</th>
<th>1 hour</th>
<th>2 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 rpm</td>
<td>Sample 1</td>
<td>Sample 6</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>Sample 2</td>
<td>Sample 7</td>
</tr>
<tr>
<td>3000 rpm</td>
<td>Sample 3</td>
<td>Sample 8</td>
</tr>
<tr>
<td>4000 rpm</td>
<td>Sample 4</td>
<td>Sample 9</td>
</tr>
<tr>
<td>5000 rpm</td>
<td>Sample 5</td>
<td>Sample 10</td>
</tr>
</tbody>
</table>

4.3.2.2 The Effect of GNP Loading on the Mechanical and Electrical Properties of Epoxy Resin

Samples were made with 0.5 g, 1.00 g, 2.00 g and 5.00 g of GNP M25 added to 100 g of Araldite LY564. They were shear mixed using a speed of 5000 rpm for 1 hour in order to determine the effect of filler loading on the properties of the composite. (see Figure 4.13)

4.3.2.3 The Effect of MWCNTs and EG on the Mechanical and Electrical Properties of Epoxy Resin.

MWCNTs from Cheap Tubes weighing 0.1 g were added to 100 g of Araldite LY 564. The reinforced resin was shear mixed in the Silverson L5M shear mixer at 1000 rpm for 1 hour and cured. The procedure was then repeated for a range of different speeds and times as shown in Table 4.2. In total 10 different samples were made. The process was repeated using the EG made in house.
Figure 4.13: Images showing steps in the manufacture of shear mixed GNP reinforced epoxy resin samples a) Shear mixing of GNPs in Araldite LY564 to break up GNP agglomerates b) Mechanical stirring of GNPs in Araldite LY564 with the addition of hardener Aradur 2954 to ensure an even distribution of resin and hardener c) silicon rubber moulds filled with epoxy resin mixture after degassing ready to be cured d) removal of cured GNP reinforced epoxy resin specimens from the mould after surface grinding. Specimens were prepared for tensile, thermal conductivity, electrical conductivity and fracture toughness tests. (Note that the addition of GNPs to epoxy resin turns the epoxy resin black)

4.3.2.4 The Effect of Sonication Amplitude on the Mechanical Properties of GNP Reinforced Epoxy Resin

GNPs grade M25 weighing 0.5 g were mixed with 100 ml of acetone and sonicated at amplitudes of 20%, 50% and 80% for 30 minutes. 100 g of resin was then added to the mixture which was stirred at 500 rpm for 3 minutes. The acetone was removed by heating at 80 °C over night to a constant mass and the samples were cured.
4.3.3 Functionalised GNP Reinforced Epoxy Resin Investigation

4.3.3.1 The Effect of Silane Functionalised GNP on the Mechanical Properties of Epoxy Resin

XG Sciences GNP grade M25 was used as a starting point for functionalisation. 0.25, 0.5, 0.75 and 1 wt% of GNPs was mixed with 200 ml of 40% nitric acid at 80 °C for 4 hours in order to make oxidised GNPs. The oxidised GNPs were washed with distilled water several times and filtered and dried at 80°C for 24 hours to obtain a powder. The powder was dissolved in 200 ml of toluene and sonicated in a QSonica Q700 sonicator (700 Watts) at 50% amplitude for 30 minutes [14].

15 g of methanol was mixed with 15 g of silane coupling agent and 75 ml of distilled water and 0.15 ml of glacial acetic acid. This mixture was added to the sonicated oxidised GNPs in toluene and stirred for 24 hours at 25 °C.

The mixture was then filtered and washed with more toluene and methanol and dried at 80 °C to obtain dried silane functionalised GNPs. This procedure was based on the work of [14].

Silane functionalised GNPs were added to Araldite LY564 in the following quantities: 0.25 g, 0.5 g, 0.75 g and 1 g and shear mixed for 1 hour at 5000 rpm and cured in the normal way.

4.3.3.2 The Effect of Oxygen Functionalised GNP on the Mechanical Properties of Epoxy Resin

XG Sciences GNP grades C300, C500 and C750 were added to 100 g of Araldite LY564 in the following quantities: 0.1 g, 0.25 g and 0.5 g. Samples were shear mixed at 5000 rpm for 1 hour and cured in the normal way.

4.3.4 Surfactant Assisted Dispersion Investigation

4.3.4.1 The Effect of GNP to Surfactant Ratio on the Mechanical Properties of Epoxy Resin

Samples were manufactured using the surfactant Triton X-100. 0.7 g of GNPs were mixed with 80 g acetone and sonicated at amplitude of 40% for 30 minutes. Afterwards 140 g of Araldite LY564 and Triton X-100 was added to the acetone. Different weight ratios of GNPs to surfactant were used (1:5, 1:10; 1:15, 1:20 and 1:30). Therefore the quantity of Triton X-100 used was 3.5 g, 7.0 g, 14 g, 10 g and 28 g respectively for each ratio. The mixture was then shear mixed for 2 hours at 3000 rpm causing the acetone to evaporate off. Any remaining acetone was evaporated by using a hot plate with a magnetic stirrer until the beaker and its contents reached a constant mass. The samples were cured using steps 2-5 from the procedure used to manufacture pure epoxy resin samples. (Note that this shear mixing speed and time was chosen as 3000 rpm for 2 hours compared to 5000 rpm used in
previous studies because it gave more time for the acetone to be evaporated off without the mixture overheating)

4.3.4.2  The Effect of GNP Loading Using the Best Ratio of GNP to Surfactant

The best ratio of GNP to surfactant obtained from the previous study was determined to be 1:15 by weight. The loading weight of GNP was increased and the loadings used were 0.14 g, 0.7 g, 1.4 g, 4.2 g and 7.0 g. The amount of surfactant added in each case was 2.1 g, 10.5 g, 21 g, 63 g and 105 g respectively. The same procedure was used as in the previous study and the samples were cured in the normal way.

4.3.4.3  The Effect of Surfactant Addition Only on the Mechanical Properties of Epoxy Resin

Triton X-100 only was added to 140 g Araldite LY564 in the following quantities 1.5 g, 7.5 g, 15 g, 45 g and 75 g. Samples were cured in the normal way.

Note that in the surfactant based investigations a higher mass of Araldite LY564 was used compared to other investigations (140 g compared to 100 g). This was because a larger beaker had to be used to accommodate both the surfactant and the resin and in order that the shear mixer head was fully submerged in the resin more had to be poured into the beaker.
4.4 Testing

Once the samples had been prepared they were tested. Three different types of tests were used during the investigation: tensile, fracture toughness and electrical conductivity.

4.4.1 Tensile Testing

Tensile testing was carried out in accordance with ASTM D638 on an Instron testing machine model 5659 (figure 4.14). All samples were smoothed off to a uniform thickness before testing. The samples were Type IV according to the standard. The thickness and width of the gauge length of the samples were measured using a digital micrometre. A loading rate of 5 mm/min was used during the test and the tensile strength and modulus was measured. In total 7 specimens were tested per sample. Values for strength and Young’s modulus were calculated automatically by Bluehill computer software by measuring the load and strain on the specimens using a mechanical extensometer.

4.4.2 Plane Strain Fracture Toughness Testing

Fracture toughness testing was carried out in accordance with ASTM D5045-99. Specimens were rectangular with a V-notch in the centre (figure 4.15). The nominal dimensions of the specimens were 88 mm in length, 20 mm in width and 10 mm in thickness. A pre-crack was created in the notch using a razor blade and a drop weight. Specimens were loaded in a 3 point bending rig on an Instron testing machine model 5659 and loaded until failure (Figure 4.16). The crack length was measured after fracture using an optical microscope.

Figure 4.14 a) tensile specimen in mechanical grips of an Instron testing machine being loaded in tension b) shape of individual tensile specimen
Figure 4.15 a) Drop weight setup. The crack machine lies underneath a drop weight which when released pushes down the razor blade into the specimen. B) Close up of the crack machine showing the razor blade used to create a pre crack c) close up of the razor blade pushed into the specimen after the drop weight has been released.
4.4.3 Electrical Conductivity Testing

The width, thickness and length of the specimens were measured using a digital micrometre. Nominally, the specimen dimensions were: length 20 mm, width 10 mm and thickness 5 mm. Opposite faces of the specimens were coated with silver conductive epoxy resin and two conductive wires were adhered. Crocodile clips were connected to the wires which were linked up to a NumetriQ AC Impedance Analyser. The frequency of the current supplied was 0 to $10^6$ Hz and the resistance of the sample was measured by the machine. In total 4 specimens were tested per sample. From the results the conductivity of the specimen could be calculated by the following equation where $\sigma$ is the conductivity, $l$ is the length of the specimen, $w$ is the width, $t$ is the thickness and $R$ is the resistance measured by the Numetric AC Impedance analyser. (see figure 4.17)

$$\sigma = \frac{l}{Rwt}$$
4.4.4 Thermal Conductivity Testing

A TA Fox 50 Heat flow meter (figure 4.18) was used to measure the thermal conductivity of the samples. For each sample two cylindrical specimens were made with two different thicknesses. Both specimens were 5 cm in diameter but one was 0.5 cm thick and the other was 1 cm thick. The two thickness method was used to reduce the error associated with contact resistance. Specimens were sandwiched between two conductive plates in the machine. One metal plate was heated up and the time taken to transfer the heat from one side through the specimen to the other was measured. Fourier’s’ law was used to calculate the thermal conductivity. \( Q = -k\frac{dT}{dx} \) where \( q \) is the heat flux, \( k \) is the thermal conductivity and \( \frac{dT}{dx} \) is the temperature difference across the sample.
4.5 Characterisation of Composites

In order to understand the chemical structure and morphology of the nanoparticles and composites several characterisation techniques were used. To chemically analyse the samples XPS and FTIR were used. For structural analysis Raman Spectroscopy, SEM and optical microscopy were used.

4.5.1 XPS (X-Ray Photoelectron Spectroscopy)

XPS is capable of identifying the types of chemical elements in a material and the quantity of those elements. The type of functionalisation on the surface of the graphene and how much functionalisation there is can be determined. It does not tell you the exact chemical bonds which have been formed and is therefore used as a complementary technique to FTIR. XPS was used to determine if functional groups had been successfully bonded to GNPs as claimed by the manufacturer and whether the percentage of the functionalisation claimed by the manufacturer was also correct (See section 5.3). A Kratos Axis Ultra DLD spectrometer was used in this investigation.

4.5.2 FTIR (Fourier Transform Infrared Spectroscopy)

FTIR is a technique which identifies the chemical bonds present in a material. It is useful because it can differentiate two elements bonded in different ways. For example –C=O and –C-O will have different characteristic absorption wavenumbers whereas XPS can only identify that there is carbon and oxygen present in the material. A Thermo Scientific Nicolet 5700 FTIR was used. FTIR was used to determine if functional groups had been successfully bonded to GNPs as claimed by the manufacturers (See section 5.3)
4.5.3 Raman Spectroscopy

Raman Spectroscopy was used to determine the number of graphitic layers present in the GNPs. This was useful in order to see if any exfoliation of the GNPs had taken place during sonication or shear mixing as exfoliation can have a marked influence on mechanical properties of composites. The number of layers could be determined by measuring the shift in wavenumber of the 2D band compared to monolayer graphene. The 2D peak occurs at 2680 cm\(^{-1}\) for monolayer graphene using a 514nm wavelength laser. When there are more layers than one, the wavenumber of the 2D band increases and the shape of the peak changes as shown in figure 2.2 d). Raman spectroscopy can therefore be used to distinguish graphene from multiple layers and graphite. A Renishaw RM System 2000 Mk1 Raman spectrometer with a HeNe laser of excitation wavelength of 514nm was used to characterise samples.

4.5.4 SEM (Scanning Electron Microscopy)

A Zeiss EVO 60 SEM was used to examine the fracture surface of tested tensile specimens. The roughness or smoothness of the fracture surface gave an indication of ductile or brittle fracture and whether the GNPs were efficient at taking up the stress during loading of the composite. In addition SEM could be used to see if exfoliation of GNPs had taken place. Samples were cut into small pieces and placed on adhesive stubs. They were coated with a thin layer of platinum in a sputtering machine prior to placing the samples in the SEM. Sputtering with a surface layer of metal was necessary to make the samples conductive because SEM does not work on insulating epoxy resin. SEM specimens are shown in figure 4.19.

4.5.5 Optical Microscopy

Optical microscopy was used to examine the overall dispersion of the nanoparticles in the epoxy resin at the micrometre length scale which has been shown to have an important influence on the mechanical properties of composites. For each sample a small dab of GNP/EG/CNT reinforced epoxy resin was placed on a glass slide before it had cured. A cover slip was placed on top of the dab forcing it to spread under the weight of the cover slip. The sample was then cured at 80 °C for 2 hours and 140 °C for 8 hours as normal. Measurements on the size of the agglomerates could be carried out on the microscope software. Optical microscopy specimens are shown in figure 4.19.

4.5.6 Modulated Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry (DSC) was used as a technique to measure the glass transition temperature (\(T_g\)) and also the heat of reaction during curing of epoxy resin. This was useful to
understand if the addition of GNPs adversely affected the curing of epoxy resin as incomplete curing would affect the mechanical properties of epoxy resin. Uncured specimens were weighed and placed in an aluminium pan which was sealed and heated using modulated DSC mode at 3 °C per minute from 0 °C to 250 °C. The heat of reaction of curing was calculated by integrating the area under the heat flow curve.

4.5.7 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was used to measure the decomposition temperature of the epoxy resin. It was useful to see if the addition of GNPs altered the decomposition temperature of epoxy resin as this affects the mechanical properties of epoxy resin. Cured epoxy resin was placed in an aluminium pan and heated to 500 °C. The machine measured the weight loss associated with the decomposition.

4.5.8 Atomic Force Microscopy (AFM)

AFM was used to measure the thickness of the GNPs as well as their lateral dimensions so that their aspect ratio could be calculated. The aspect ratio of GNPs is an important factor in whether the GNPs are efficient at taking up stress during loading of the composite. The GNPs in epoxy resin were dispersed on a silicon wafer using a spin coater set at 2500 rpm for 3 mins. Using a syringe, IPA was dropped slowly onto the silicon wafer as it was spinning to dissolve the resin but leave flakes of GNPs on the silicon wafer. The GNPs left on the silicon wafer were then analysed using the AFM.

Figure 4.19: SEM fracture surface specimens coated in a thin layer of platinum. The platinum acts as a conductor for the electron beam to pass through and was necessary to achieve a clear image. Also shown are the samples made for optical microscopy examination. A dab of the sample (which is not visible) was placed on the slide before curing and cover slip was placed on top. The sample was then cured and the microstructure observed.
5 Tensile Properties

Results and Discussion

In this chapter the tensile results of the four investigations outlined in chapter 4 will be analysed and discussed from a mechanical property perspective. In the first section, the tensile properties of pure epoxy resin specimens are plotted which represent a baseline to compare results in subsequent investigations. Secondly, results are presented from epoxy resin reinforced with unfunctionalised GNP. The mechanical properties of MWCNT reinforced epoxy resin and EG reinforced epoxy resin is also investigated for comparison. In the third section, results are discussed from epoxy resin reinforced with functionalised GNP, and in the final section, data is examined from the investigation using surfactant to promote the dispersion of GNP.
5.1 Pure Epoxy Resin Investigation

The first part of the investigation measured the tensile strength and Young’s modulus of unreinforced epoxy resin in accordance with ASTM D638. These results were used as a benchmark to measure improvements in future investigations. The results are presented in table 5.1 and figure 5.1.

The mean tensile strength and Young’s modulus of the 7 specimens tested is 73.23 MPa and 2.67 GPa respectively with the modulus calculated from the gradient of the chord between a strain of 0.1% and 0.3%. These lay within the values quoted from the manufacturer’s data sheet of 70-77 MPa for tensile strength and reasonably near to 2.55-2.65 GPa for the modulus. The stress strain curves show that epoxy resin is non-linear elastic which fails in a relatively brittle manner (at ~7% strain).

Table 5.1: Tensile strength and modulus of the 7 neat epoxy resin specimens

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78.14</td>
<td>2.58</td>
</tr>
<tr>
<td>2</td>
<td>71.05</td>
<td>2.64</td>
</tr>
<tr>
<td>3</td>
<td>72.37</td>
<td>2.70</td>
</tr>
<tr>
<td>4</td>
<td>66.99</td>
<td>2.99</td>
</tr>
<tr>
<td>5</td>
<td>78.31</td>
<td>2.86</td>
</tr>
<tr>
<td>6</td>
<td>74.35</td>
<td>2.37</td>
</tr>
<tr>
<td>7</td>
<td>71.43</td>
<td>2.86</td>
</tr>
<tr>
<td>Mean</td>
<td>73.23±3.76</td>
<td>2.713±0.19</td>
</tr>
</tbody>
</table>

Figure 5.1: Tensile stress versus tensile strain for the 7 pure epoxy resin specimens. The average strength is 73.23 MPa and the average modulus is 2.71 GPa. All specimens failed in a relatively brittle manner.
5.2 Unfunctionalised GNP Reinforced Epoxy Resin Investigation

In the second investigation the tensile strength and Young’s modulus of epoxy resin samples reinforced with unfunctionalised GNPs were tested. The investigation was split into several different studies which will be discussed in order:

1. **The Effect of Shear Mixing Speed and Time on the Mechanical Properties of GNP Reinforced Epoxy Resin.** Epoxy resin was reinforced with 0.1 wt% of unfunctionalised GNP and processed using the shear mixer using two different time settings (1 hour and 2 hours) and five different speeds (1000 rpm to 5000 rpm). This was investigated to understand how processing conditions affect the mechanical properties of the nanocomposites.

2. **The Effect of GNP Weight Percentage on the Mechanical Properties of GNP Reinforced Epoxy Resin.** Different weights of GNPs were added to epoxy resin ranging from 0.1 wt% to 5 wt% and mixed at a constant speed and time of 5000 rpm and 1 hour respectively.

3. **The Effect of Carbon Nanotubes and Expanded Graphite on the Mechanical properties of Epoxy Resin.** Samples were manufactured using MWCNTs and EG in order to compare their performance against the results of GNPs. Nanocomposites were processed using the shear mixer with the same speed settings and time settings as per the first study.

4. **The Effect of Sonication Amplitude on Mechanical Properties of Epoxy Resin.** In order to determine if sonication was a better processing method than shear mixing the nanocomposites were processed with the sonicator using three different amplitude (power) settings for a constant time period and quantity of GNPs.

5.2.1 The Effect of Shear Mixing Speed and Time on the Mechanical Properties of GNP Reinforced Epoxy Resin

The reason for conducting this study was based on the work of [18], in which graphite was shear mixed in a range of different solvents such as NMP and acetone. It was discovered that shear mixing was able to exfoliate graphene flakes from GNPs. The graphene was then used to make composites which had improvements in tensile strength. Their work was carried out in a solvent, however, could exfoliation be carried out directly in the resin without the need for solvents? It would be useful to know this because although solvents may aid dispersion they are difficult to remove from the final composite adding to complications with processing. In addition, little work has been carried out by directly shear mixing GNPs into epoxy resin. A trial was conducted where GNPs were mixed by hand
in epoxy resin (see figure 5.2). The results show GNPs in epoxy resin remain stable indefinitely whereas in solvents such as NMP and acetone which were used in [18] sedimentation took place after a few hours (see figure 5.2b)). This suggests that the resin is a stable medium to carry out exfoliation and that there may be no need for solvents.

In this study 0.1 wt% of GNPs were shear mixed with epoxy resin for different speeds and lengths of time and samples were cured in the conventional way. The results are presented in figures 5.3 and 5.4.

Figure 5.2: Equal quantities of GNP dispersed in equal volumes of NMP, acetone and epoxy resin. a) Initial dispersion of GNPs; b) Dispersion of GNPs after 2 days. The three different images show how sedimentation takes places in the NMP and acetone but not the epoxy resin which is stable over prolonged time. In fact the epoxy resin dispersion stayed stable indefinitely. Hence epoxy resin seems a suitable medium to carry out shear mixing in directly

Figure 5.3: Tensile strength for 0.1 wt% GNPs in epoxy resin shear mixed at different speeds and different times. The 5000 rpm 1hour samples produce an increase in strength and the 3000 rpm 2 hour sample maintain the strength. All other samples produce decreases in tensile strength
Figure 5.4: Tensile moduli of 0.1 wt% GNPs in epoxy resin shear mixed at different speeds and different times. The 3000 rpm 2 hours samples produce an increase in modulus whereas other samples more or less maintain the modulus of neat epoxy resin.

Several observations can be made from figures 5.3 and 5.4. In general, the addition of GNPs decreases the tensile strength of the epoxy resin. Secondly, there appears to be no trend between the tensile strength and the speed and time of shear mixing. The tensile strength does not decrease or increase linearly with speed or time, it appears to be random. However, there are improvements for example the 3000 rpm 2 hours sample achieves the highest Young’s Modulus averaging 3.02 MPa without reducing the tensile strength and with a small scatter. The highest strength is obtained by
the 5000 rpm 1 hour sample (76.68 MPa) and the modulus is maintained in this sample. In all other samples however, the modulus remains similar to the neat epoxy resin value. The stress strain responses for all samples are very similar to the neat epoxy resin specimens. Stress strain curves for the 3000 rpm 2 hour specimens are shown in figure 5.5

5.2.1.1 The Effect of Shear Mixing on the Agglomerate Size

An important observation is that shear mixing reduces the size of the agglomerates. Comparing Figure 5.6 f) (mixed by hand) with the figures 5.6 (a-e) we can see that the agglomerates in figure 5.6 f) are much bigger than in all the other optical microscope images. However, it also appears that changing the speed and time of shear mixing has very little impact on the size of agglomerates. When images 5.6 (a-e) are compared to each other there is very little difference between them. By eye it appears that shear mixing for 2 hours does not produce smaller agglomerates than shear mixing for 1 hour and shear mixing at 5000 rpm does not produce smaller agglomerates than mixing at 1000 rpm. This could explain why there is hardly any difference in mechanical properties between samples. An extra sample was made by shear mixing at a much higher speed of 9000 rpm as this should have made an obvious difference. Having examined the optical microscope image of this sample by eye the agglomerates again appear no smaller than any of the other shear mixed samples even at this significantly higher speed. In order to verify this, the sizes of the agglomerates for selected images were measured using the microscopy software and the results are recorded in Table 5.2.

There appears to be no relationship between speed and time and agglomerate size. For example, one would expect the average size of agglomerates to decrease with time but it can be seen that the 5000 rpm 2 hours sample has a bigger average size compared to the 5000 rpm 1 hour sample. Similarly, one would expect higher speeds such as the 9000 rpm 1 hour sample to have smaller agglomerates than the 5000 rpm 1 hour sample but this is not the case. The data was collected from one microscope image per sample and from observation across the whole microscope slide there was a huge variation in agglomerate size in each sample.

Table 5.2: Measurements of agglomerate sizes across five different optical micrographs shown in Figure 5.6

<table>
<thead>
<tr>
<th>Lateral dimensions of agglomerate (µm)</th>
<th>1000 rpm 1 hr</th>
<th>5000 rpm 1 hr</th>
<th>9000 rpm 1 hr</th>
<th>3000 rpm 2 hr</th>
<th>5000 rpm 2 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>38</td>
<td>20</td>
<td>26</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Biggest</td>
<td>169</td>
<td>73</td>
<td>56</td>
<td>123</td>
<td>94</td>
</tr>
<tr>
<td>Smallest</td>
<td>7</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 5.6: Optical microscopy images of samples shear mixed at the following speeds and times a) 1000rpm 1 hour b) 1000 rpm 2 hours c) 3000 rpm 1 hour d) 3000 rpm 2 hours e) 9000 rpm 1 hour f) no shear mixing

Perhaps some re-agglomeration occurs during curing which negates the exfoliation done by the shear mixer. In order to test this hypothesis optical micrographs were monitored during the curing process. The results are shown in Figure 5.7 and demonstrate there is no change in microstructure before and after curing so no re-agglomeration occurs during the curing process. The cover slip placed on top on the dab of reinforced resin could have restricted the re-agglomeration of GNPs during curing and give a misleading result. Therefore, another test was carried out whereby the dab of resin was examined under a microscope without a cover slip being placed on top of it. Once again however no re-agglomeration occurs upon curing.
Therefore, it appears that shear mixing is capable of breaking down primary agglomerates of GNPs but only down to a certain size. In addition, it is not effective at controlling the size distribution of the GNPs as there is a big spread in the size of the agglomerates.

5.2.2 The Effect of GNP Loading Weight on the Mechanical Properties

From the previous study the majority of samples experience a decrease in tensile strength and where improvements are reported they are minor. It appears as though in general the GNPs are acting as defects rather than strengthening the epoxy resin. This could be because the weight fraction of GNPs is so low that by the rule of mixtures it produces a decrease in strength. Therefore, in this study the quantity of GNPs added to the resin was increased from 0.1 wt% to 5 wt% to see if adding more GNPs improves the mechanical properties of the epoxy resin. Samples were shear mixed at 5000 rpm for 1 hour and cured in the normal way. The reason this speed and time were chosen was because from the previous experiment the strength was highest and the modulus was maintained using these conditions and also because of time constraints on using equipment.

5.2.2.1 The Effect of GNPs on Tensile Strength

Figure 5.8 shows that the tensile strength reduces linearly with the loading weight of the GNPs. Why is this trend observed? One reason why the strength decreases could be because the sizes of the GNP agglomerates are too large and act as stress raisers which cause premature failure. In Figure 5.9 a close up of an agglomerate from the 1000 rpm 1 hour optical microscope slide is shown measuring 169 µm and surrounded by smaller agglomerates. It has rough edges and sharp corners which could be big enough to act as stress raisers. It only requires one stress raiser to create a catastrophic crack which could lead to failure of the sample. However, there are other studies using functionalised graphene where agglomerates are similar sizes to the agglomerates in this study and yet there are improvements in tensile strength [60, 105]. Therefore, agglomerate size cannot be the sole reason for the reduction in strength there must be something else at play.
Figure 5.8: Variation of tensile strength with GNP loading weight with and without using acetone as a solvent. Increasing the loading weight reduces the strength of epoxy resin.

Figure 5.9 Optical microscope image of GNP agglomerates taken from the 1000 rpm 1 hour sample.

Another possible reason is because the GNPs are not effectively exfoliated during shear mixing. So rather than having graphene (or bi or tri layer graphene) in the composite it was in fact agglomerated GNPs which are weak in comparison. The thickness (number of layers) of the GNP flakes can be measured using AFM. Unfortunately AFM data could not be collected on GNPs in resin because the resin covers the GNPs and gives an inaccurate topological representation. The resin cannot be evaporated either, therefore AFM data can only be collected on GNPs dispersed in solvents which can be evaporated. Evidence from AFM in [18] has shown that shear mixing in solvents such as NMP, acetone and cyclopentanone are capable of exfoliating graphene from GNPs. Therefore the same should be true when shear mixing in resin. However, the crucial difference between their study and this study was that centrifuging was performed in [18] in order to separate heavier GNPs from exfoliated graphene whereas in this study no centrifuging was carried out. Therefore it was likely
there was a mixture of unexfoliated and exfoliated GNP s left in the same beaker which could explain the huge variation in agglomerate lateral size in the optical micrograph images. It is likely that there was a huge variation in flake thickness too. There is evidence from other research groups [140, 141] which would suggest that the level of exfoliation can significantly affect the mechanical properties. Two other research groups have used another type of unfunctionalised GNP which has a higher degree of exfoliation and has improved the tensile strength of epoxy resin. One group [141] purchased C grade GNP s from XG sciences. The difference between the C grade and the M grade used in this study is that the C grade has an average surface area of 300 m$^2$/g compared to 150 m$^2$/g for the M grade. This would suggest that C grade has fewer layers than M grade and therefore is better exfoliated. In [140] the GNPs were Asbury Carbons’ TC307 and had a specific surface area of 350 m$^2$/g which is once again higher than the M grade GNP s used in this project. In both studies the tensile strength of epoxy resin improved by ~5% by the addition of 1 wt% of GNPs. This would suggest specific surface area and exfoliation have a lot to do with the efficiency of the filler as a reinforcement. It may therefore be that if centrifuging had been carried out to separate exfoliated GNPs from the unexfoliated GNPs then better tensile properties would have been achieved.

However, this too cannot fully explain the decrease in properties since there are other reports of GNPs producing mechanical improvements in epoxy resin using shear mixing without centrifuging. Something else must also be at play. Another explanation for the reduction in properties could be the lack of a strong interface between the GNPs and the epoxy resin. There was no functionalisation on the surface of the GNPs when examined by FTIR so the bond with the epoxy resin could have been weak and the wetting of the surface could have been poor. Most research has shown there is improvement in the tensile properties when the surface of graphene has been functionalised with oxygen atoms. Therefore, functionalisation of the surface of graphene appears to be another factor for improvement of mechanical properties. Functionalisation is investigated in section 5.3.

The strength could also be lower because the GNPs affect the curing reaction between the resin and the hardener. In order to investigate this differential scanning calorimetry was performed on uncured samples of neat epoxy resin and 5 wt% GNP reinforced epoxy resin. The heat of cure was measured by calculating the integral under the curve between limits of 25 °C and 200 °C. One would expect that adding GNPs to epoxy resin would reduce the heat of cure because they would take up volume otherwise occupied by epoxy resin and hardener molecules preventing them from reacting. So if 5 wt% of GNPs is added to epoxy resin one would expect the heat of cure to be 5% less than that of neat epoxy resin. However, does the presence of GNPs reduce the heat of cure more than expected? Figure 5.10 compares the average heat of cure of neat epoxy resin against 5 wt% GNP reinforced epoxy resin. The average heat of cure of the neat epoxy resin sample is 374 J g$^{-1}$
compared to 353 J g\(^{-1}\) for 5 wt% GNP reinforced epoxy resin. Therefore, the presence of GNPs does reduce the heat of cure of epoxy resin but no more than would be expected because 353 J g\(^{-1}\) is ~5% less than 374 J g\(^{-1}\).

DSC was re-performed on cured samples to ensure that the curing reaction was complete and there was no residual heat of cure. The results are shown in figure 5.11 and illustrate that there is no exothermic peak in either the pure epoxy resin or 5 wt% GNP reinforced epoxy resin sample. Therefore GNPs do not affect the degree of cure of the samples and incomplete curing can be discounted as a reason for the lower tensile strength of GNP reinforced epoxy resin composites compared to neat epoxy resin.

**Figure 5.10:** DSC of uncured samples of pure epoxy resin and 5 wt% GNP reinforced epoxy resin. The areas under the curves are proportional to the amount of heat given out by the curing reaction (called the heat of cure). The heat of cure is higher for pure epoxy resin higher than for the 5 wt% GNP reinforced epoxy resin. However, the GNPs do not interfere with the cure reaction more than is expected as the addition of 5 wt% GNPs only reduces the heat of cure by ~5%.

**Figure 5.11** DSC of cured samples of pure epoxy resin and 5 wt% GNP reinforced epoxy resin. No exothermic peak is visible. Therefore the cure cycle used in this investigation (80 °C for 2 hours followed by 140 °C for 8 hours) completely cures the samples. Incomplete curing can therefore be discounted as a reason for lower tensile strength of GNP reinforced epoxy resin.
5.2.2.2 The Effect on Tensile Strength of using Acetone as a Solvent during Shear Mixing

An extra experiment was conducted using acetone as a solvent to see if it assisted the dispersion. GNPs were mixed with equal amounts of acetone and epoxy resin for 5000 rpm and 1 hour. The acetone was then evaporated off by heating the mixture to a constant mass. The results are also shown in figure 5.8 and are very similar to the epoxy resin samples without acetone, so from the tensile strength point of view the acetone does not have an effect.

5.2.2.3 The Effect of GNPs on Young’s Modulus

Figure 5.12 shows the results of Young’s modulus as a function of the loading weight of GNPs. As the weight percentage of GNPs increases there is no significant improvement in the Young’s Modulus. The lack of effect would be consistent with the finding that there is not a strong bond between the GNPs and the epoxy resin and therefore the GNPs do not contribute to the stiffness of the composite.

5.2.2.4 Effect of Using Acetone as a Solvent during Shear Mixing on Young’s Modulus

The results using acetone as a solvent are also shown in Figure 5.12. The results show that adding acetone improves the Young’s Modulus of the epoxy resin up to 3.11GPa at 5 wt% which is an improvement of ~17%. However, it is not clear whether it is the acetone which causes the improvement or because the GNPs are better dispersed. Therefore, a control was made where acetone was shear mixed in epoxy resin at 5000 rpm for 1 hour without GNPs. The acetone was then evaporated and the epoxy resin was cured in the normal way. An average of 2.68 MPa was recorded for the Young’s modulus which is pretty much the same as pure epoxy resin which suggests that it is not the acetone which is responsible for the improvement but the effect of the acetone on the dispersion of the GNPs. If the dispersion is better, then this should be visible on the optical microscopy slides for the samples shown in Figure 5.13. Having examined the micrographs there does not appear to be a better dispersion in the acetone samples than without acetone and in fact, the dispersion appears better without acetone. Therefore further work is required to understand why there is an improvement in modulus with the addition of acetone. Perhaps the acetone functionalised the surface of the GNPs leading to a better interface. Stress strain responses for specimens prepared with and without acetone are shown in figures 5.14 and 5.15 respectively. There appears to be no noticeable difference between them. However, comparing them to neat epoxy resin specimens shown in figure 5.1 the tensile strain at failure is 1-2% lower.
Figure 5.12: Variation of Young's Modulus with loading wt% of GNPs with and without acetone as a solvent mixed at 5000 rpm for 1 hour. The addition of acetone and GNPs appears to have a positive effect on Young's Modulus.

Figure 5.13: Optical micrographs from GNPs mixed with and without acetone at 5000 rpm for 1 hour at 5 wt%. Without acetone the GNPs appear more evenly dispersed than with acetone.
Figure 5.14: Stress strain curves for the 5 wt% GNP reinforced epoxy resin sample with no acetone. The tensile strain at failure is 1-2% less than the neat epoxy resin specimens in figure 5.1

Figure 5.15: Stress strain curves for the 5wt% GNP reinforced epoxy resin sample mixed using acetone as a solvent. The tensile strain at failure is also 1-2% less than the neat epoxy resin specimens in figure 5.1
5.2.3 The Effect of MWCNTs and EG on the Mechanical Properties of Epoxy Resin

In this study, MWCNTs and EG reinforced epoxy resin samples were made using a shear mixing technique. This was conducted to see how these nanoparticles compared in performance to GNP s. A 0.1 wt% loading was used and samples were mixed using a range of times (10 minutes, 1 hour and 2 hours) and different speeds (1000 rpm to 5000 rpm). The results from MWCNTs are presented first.

5.2.3.1 The Effect of MWCNTs

The tensile strength and Young’s modulus of the MWCNT reinforced epoxy resin samples are presented in figures 5.16 and 5.17.

![Figure 5.16: Tensile strength of MWCNT reinforced epoxy resin composites using 0.1 wt% MWCNTs shear mixed for different speeds and lengths of time. There is no clear pattern between speed or time and tensile properties.](image)

![Figure 5.17: Young’s modulus of MWCNT reinforced epoxy resin using 0.1 wt% MWCNTs shear mixed for different speeds and lengths of time. In general the addition of MWCNTs neither significantly improves or reduces the tensile strength of epoxy resin](image)
Much like the tensile results of the GNP reinforced epoxy resin composites the results for MWCNT reinforced epoxy resin composites also appear to be random. In terms of strength two samples (3000 rpm 2 hours and 2000 rpm 1 hour) are marginally better than neat epoxy resin with less than a 5% improvement. Other samples maintain the strength of pure epoxy resin (2000 rpm 1 hour and 4000 rpm 10 minutes). The remaining samples all reduce the strength of epoxy resin.

In terms of the Young’s modulus the biggest improvements come from the 1000 rpm 10 minute and the 4000 rpm 10 minute samples with the modulus exceeding 2.80 GPa (compared to 2.62 GPa for neat epoxy resin). All samples mixed for 2 hours come very close to the neat epoxy resin values and all samples mixed for 1 hour reduce the modulus of epoxy resin.

The optical microscope images in figure 5.18 show the dispersion for MWCNT reinforced epoxy resin samples. In general, the agglomerates are largest in the 10 minute samples and become reduced in size the longer the shear mixing time. The difference in size is quite obvious between the 10 minute and 1 hour sample but more subtle between the 1 hour and 2 hour samples.

Much like the GNP reinforced epoxy resin samples there does not appear to be a correlation between the size of the agglomerates and the mechanical properties. For example, the 2000 rpm 2 hour sample has the smallest agglomerates but it has a lower tensile strength than the 2000 rpm 1 hour sample. Also, the 1000 rpm 10 mins sample has significantly higher strength than the 1000 rpm 1 hour sample. Therefore although shear mixing does affect the size of agglomerates it appears as though this is not the critical factor in tensile properties. The adhesion of the MWCNTs to the epoxy resin could be a more important factor.

There does not appear to be much difference in performance between the MWCNT reinforced epoxy resin composites and the GNP reinforced epoxy resin composites. In both cases the majority of samples are reduced in strength by the addition of the filler and there is no pattern between time and speed of mixing and tensile properties.

![Figure 5.18: Comparison of microstructure of MWCNT reinforced epoxy resin composites shear mixed for different times. The micrographs show that the agglomerates become smaller and more spread out as the time increases. The differences in microstructure cannot be correlated to the tensile properties however. (scale bar is 100 μm)](image)
5.2.3.2 The Effect of Expanded Graphite

The tensile results are presented in figures 5.19 and 5.20. In terms of strength the addition of EG to epoxy resin yields the biggest reduction in strength of all the nanoparticles. None of the samples improve the tensile strength unlike the MWCNT reinforced epoxy resin and GNP reinforced epoxy resin samples. The tensile strength of all samples is below 65 MPa. The modulus appears to be less affected with no major reduction or improvement in any of the samples.

Figure 5.19: The effect of shear mixing speed and time on the tensile strength of EG reinforced epoxy resin composites. All samples result in a decrease in tensile strength compared to neat epoxy resin. The worst performing samples are those shear mixed for 10 minutes.

Figure 5.20: The effect of shear mixing speed and time on the Young’s modulus of EG reinforced epoxy resin composites. The addition of EG neither significantly improves or reduces the modulus of epoxy resin on average.
In the case of EG reinforced epoxy resin composites the size of the EG particles does appear to have a major influence on the properties. The EG particles can be quite large to begin with (on the order of 1 mm) and the particles are more difficult to shear mix because some particles float on the surface of the resin and avoid the rotating paddle of the shear mixer. This meant that even after shear mixing there were many EG particles which had not been exfoliated. All the 10 minute samples have much lower tensile strengths probably because 10 minutes was not enough time to significantly reduce the size of the EG particles meaning they acted as defects within the epoxy resin. This is visible in figure 5.21, where the 10 minute sample shows several agglomerates on the order of 200 µm which is much bigger than the agglomerates of MWCNTs and GNP s using the same speed and time of mixing. Overall EG performs the worst of all three nanofillers and this appears to be related to the size of the agglomerates. Even after mixing for one hour or two hours the agglomerates are larger compared to MWCNTs and GNP s. This could explain why the strength of the EG reinforced epoxy resin composites were lower than the GNP reinforced epoxy resin and MWCNT reinforced epoxy resin composites.

In terms of Young’s Modulus there appears to be no significant decrease or increase across all the samples or any correlation with the size of the agglomerates. The results appear within the natural scatter of the Young’s Modulus of pure epoxy resin which is 2.55-2.65GPa according to the manufacturer’s data sheet.

![Figure 5.21: Comparison of EG reinforced epoxy resin microstructures shear mixed at 1000 rpm for different times. The micrograph of the sample shear mixed for 10 mins shows much larger agglomerates than samples shear mixed for 1 hour and 2 hours. The agglomerates are also much larger than those of the MWCNT reinforced epoxy resin and GNP reinforced epoxy resin samples. Agglomerates of this size could act as defects rather than reinforcements and so damage the strength of the epoxy resin. (scale bar is 200µm)](image-url)
5.2.4 The Effect of Sonication Amplitude on GNP Reinforced Epoxy Resin

The third study used another method of dispersion called sonication in order to compare against the results from shear mixing. Sonication is cited in the literature as one way of exfoliating graphene from GNPs hence the motivation for carrying out this study. Three different sonication amplitudes were chosen: 20, 50 and 80%. The higher the amplitude the more energy is supplied to the system which could exfoliate more layers of graphene from GNPs. A loading of 0.5wt% GNPs was used. Results are presented in figures 5.22 and 5.23.

![Graph showing variation of tensile strength with sonication amplitude](image)

*Figure 5.22: The variation of tensile strength with sonication amplitude when 0.5 wt% GNPs were added to epoxy resin*

![Graph showing variation of modulus with sonication amplitude](image)

*Figure 5.23: Variation of modulus with sonication amplitude when 0.5 wt% GNPs were added to epoxy resin*
The tensile strength of all samples in figure 2.22 is lower compared to neat epoxy resin. However, the modulus remains at the same level as pure epoxy resin. Much like the shear mixing investigation there appears to be no trend between the sonication amplitude and the tensile strength. When the optical microscopy slides are examined across amplitudes there was no particular difference between them. Comparing the tensile strength of the shear mixed sample at 0.5 wt% with the sonication samples it can be seen that they have similar values of around 60 MPa. The agglomerates of the sonicated samples shown in figure 5.24 also appear bigger than the shear mixed samples. The fact that the agglomerates are much bigger in sonicated samples yet the difference in strength is negligible is evidence that agglomerate size is not the deciding factor in tensile strength performance. If it was a decisive factor dependent there should be a difference between the strength of sonicated and shear mixed samples. This leaves a poor matrix-reinforcement due to a lack of functionalisation as one possible reason for no improvement. Chemical functionalisation of GNPs will be investigated in the second investigation.

5.2.5 Concluding Remarks

This investigation was split into four separate studies. In the first study, it was shown that in general the shear mixing conditions have very little effect on the mechanical properties of GNP reinforced epoxy resin composites. A very important observation however, is that no re-agglomeration of GNPs occurs during curing.

The second study showed that increasing the weight of GNPs in the composite drastically reduces the tensile strength of epoxy resin but does not have significant effect on the modulus. The addition of acetone as a solvent to improve dispersion appears to improve the modulus of the composites but does not affect the strength. No reason has been established as to why the acetone appears to improve the young’s modulus of the composites. One theory is that the acetone could have functionalised the surface of the GNPs during shear mixing.
In the third study, the performance of GNP\textsubscript{s} was compared with MWCNT\textsubscript{s} and EG. The worst performer was EG as all of the samples reduced the strength of epoxy resin. MWCNT\textsubscript{s} and GNP\textsubscript{s} performed similarly to one another with no significant improvement in strength and modulus either way when low loadings were used.

In the final study, the effect of sonication amplitude was investigated and showed that there was no relationship between the sonication amplitude and mechanical properties. All samples had a lower strength than neat epoxy resin and there was no significant effect on the size of the agglomerates. In addition the agglomerates are much bigger in sonicated samples compared to shear mixed samples, but there is no difference in mechanical performance.

Overall it appears as though unfunctionalised GNP\textsubscript{s} tend to reduce the strength of epoxy resin regardless of the processing methods used. The results presented in this investigation were lower than anticipated and one possible reason for this could be because of a lack of functionalisation of the GNP\textsubscript{s} leading to a weak interface with the epoxy resin. Therefore, in the next investigation the surface chemistry of the graphene was modified in an effort to improve the interface and hopefully generate better mechanical results.
5.3 Functionalised GNP Reinforced Epoxy Resin Investigation

In the previous investigation epoxy resin was reinforced with unfunctionalised GNP s and the tensile properties were tested. The results show that in general there is little improvement in the tensile strength of epoxy resin and only moderate improvements for Young’s modulus. It is hypothesised that the lack of chemical functionalisation on the GNP s is a reason why results are lower than anticipated. Therefore in this investigation GNP s were chemically functionalised in an effort to enhance the interface with the epoxy resin and improve its reinforcing effect. Different functionalisations were used and three studies were carried out:

1. **The Effect of Silane Functionalised GNP s on the Mechanical Properties of Epoxy Resin.** Grade M25 GNP s from XG sciences were chemically modified with silane through an in-house process. This produced silane functionalised GNP s which were added to epoxy resin from 0.25 wt% to 1 wt% loading. The samples were processed using the shear mixer at a speed of 5000 rpm for 1 hour. This speed was chosen because it produced the highest tensile strength from the previous investigation and was economical time wise. Another processing method using sonication was also used to assess if sonication together with functionalised GNP s had a synergetic effect.

2. **The Effect of Oxygen Functionalised GNP s on the Mechanical Properties of Epoxy Resin.** In the second part of the study GNP s functionalised with three different concentrations of oxygen atoms were supplied by XG Sciences. GNP s were added to the epoxy resin using 0.1wt%, 0.25wt%, 0.5wt% and 1.0wt% loading. These samples were processed by shear mixing using a speed of 5000 rpm for 1 hour and cured in the normal way.

3. **The Effect of Carboxyl Functionalised GNP s on the Mechanical Properties of Epoxy Resin.** GNP s were purchased with carboxyl functionalisation from ACS Materials. The carboxyl functionalised GNP s were added to epoxy resin using a 0.1 wt% and 0.25 wt% loading and processed using the same method as the previous studies.

5.3.1 The Effect of Silane Functionalised GNP Reinforced Epoxy Resin

The reason for choosing to functionalise the GNP s with silane was to try and reproduce the improvements of another research group [14] who claimed a positive effect on the strength and modulus when they were added to the same epoxy resin system. The results for tensile strength and modulus of silane functionalised GNP reinforced epoxy resin are shown in Figures 5.25 and 5.26
respectively. The results show that the addition of the silane functionalised GNPs reduces the tensile strength of epoxy resin and the tensile modulus remains similar to that of the neat epoxy resin. There is also very little difference between the sonicated and non-sonicated samples. The only difference was for the 1 wt% sample where the modulus is on average ~0.4 GPa higher in the unsonicated sample compared to the sonicated sample. These results contradict the work of [14] where improvements in tensile strength and tensile modulus were seen with the addition of silane functionalised GNPs. Why is there a difference between the results of this study and [14]? One reason could be because functionalisation had not taken place. However, FTIR (figure 5.27) and XPS (figure 5.28) of the GNPs confirm that silane functionalization had taken place. Silicon peaks can be detected at binding energies of 150 eV and 99eV in the XPS spectrum. Characteristic Si-O-Si, Si-H, Si-O-CH₃, and Si-H₂ peaks can be detected in the FTIR spectrum in figure 5.27. Therefore lack of functionalisation can be discounted as a reason for the difference in results.

![Figure 5.25: Variation of tensile strength of epoxy resin with increasing weight fractions of silane functionalised GNPs. All samples reduced the strength of epoxy resin. There was no clear difference in performance between the sonicated and unsonicated samples.](image)
Figure 5.26: Variation of tensile modulus of epoxy resin with increasing weight fractions of silane functionalised GNP s. In general the modulus is maintained at the neat epoxy resin value apart from the 1 wt% sonicated sample.

Figure 5.27: FTIR of silane functionalised GNP s showing characteristic peaks (labelled on the spectrum) which confirm that proper functionalisation had taken place.
Figure 5.28: XPS of silane functionalised GNP{s}. The peaks at binding energies of 153 eV and 102 eV correspond to Silicon and would suggest successful functionalisation had taken place. Together with the evidence from the FTIR data this confirms that silane functionalisation was successful.

Another reason why the results could be different is because the curing cycle used in this study was different to [14]. In their work the curing cycle was 60 °C for 1 hour followed by 120 °C for 8 hours whereas in this study the curing cycle was 80 °C for 2 hours followed by 140 °C at 8 hours. Could this difference in curing cycle be the critical factor explaining the difference in results? In order to test this hypothesis samples were made using the same curing cycle as [14]. The results are presented in Figure 5.29. Stress strain curves for the specimens which make up the neat epoxy resin sample cured at a lower temperature are shown in figure 5.30. They appear to have a higher strain at failure by 1-2% compared to neat epoxy resin samples cured at 80 °C and 140 °C.
Figure 5.29: Comparison of tensile strength of samples cured using different cycles. Typically a lower curing temperature results in a lower tensile strength however in this case neat epoxy resin cured for 1 hour at 60 °C and 8 hours at 120 °C has a higher tensile strength than neat epoxy resin cured for 2 hours at 80 °C and 8 hours at 140 °C.

Figure 5.30: Stress strain response for epoxy resin cured at a lower temperature of 60 °C and 120 °C. The tensile strain at failure is 1-2% higher than neat epoxy resin specimens cured at 80 °C and 140 °C shown in figure 5.1.

The first significant observation is that pure epoxy resin cured at the lower temperature cycle used in [14] has a higher tensile strength (77 MPa) than the pure epoxy resin cured at the higher temperature cycle (73.23 MPa). The results are surprising because typically strength and modulus increase with a higher curing temperature as long as this temperature does not exceed the degradation temperature of the epoxy resin. In order to test that no degradation of the epoxy resin had taken place Thermal Gravimetric Analysis (TGA) was carried out. The TGA curve shows that the
epoxy resin only starts degrading at a temperature over 350 °C (Figure 5.31). Therefore this cannot be the reason for the difference in performance.

![TGA curve showing degradation onset](image)

**Figure 5.31**: TGA curve showing that decomposition of the epoxy resin begins to occur at ~350 °C as shown by a rapid loss of weight of the sample. Therefore decomposition of the sample cannot be a reason for reduced mechanical properties because it was cured at a maximum temperature of 140 °C which is well below the degradation temperature.

Work from [142] could shed some light on why higher temperature curing cycles do not necessarily result in higher tensile strengths. According to their research if the glass transition temperature of the infinitely cured network $T_{g,\infty}$, is exceeded during the cure cycle then this can reduce the strength of the epoxy resin. If however, the epoxy resin is cured below $T_{g,\infty}$, then tensile strength will improve up until the cure temperature is equal to $T_{g,\infty}$. This observation was also reported by [143, 144].

According to the manufacturers data sheet the $T_{g,\infty}$ should be 150-153°C. The cure temperature used in my investigation never exceeded 140 °C so it seems unlikely that the strength should be reduced for the reason proposed by [14]. What is also puzzling is that the neat epoxy resin results from my experiment cured using the lower temperature cycle do not concur with the results of [14]. Their neat epoxy resin reached a tensile strength of 50 MPa whereas in this study it reached 80 MPa. No reason has been established for this discrepancy in spite of contacting the authors of the paper.

Given that silane functionalisation was unsuccessful at improving tensile properties of epoxy resin, the next step was to see if other types of functionalised GNP's could yield improvements. In the next section the results for two other functionalised GNP's are discussed.
5.3.2 The Effect of Oxygen Functionalised GNPs on the Mechanical Properties of Epoxy Resin

Oxygen functionalised GNPs were purchased from XG Sciences as grades C300, C500 and C750 where the numbers represent the specific surface area in m$^2$ g$^{-1}$ of the GNPs. According to the manufacturer the concentration of oxygen bonded to the surface of the GNPs increases proportionally with the specific surface area of the GNPs. This was confirmed by XPS as shown in figures 5.32 and 5.33 which show the oxygen 1s peak and carbon 1s peak of the three grades respectively. For comparison the XPS of Grade M25 is also plotted. The oxygen concentration is highest in grade C750 (as shown by the tallest peak in figure 5.32) and lowest in M25 in accordance with the manufacturer. The oxygen concentration increases from grade C300 to grade C750.

The carbon peak decreases from C300 to C750 because oxygen takes up a greater proportion of the sample. The carbon 1s peak also shows the presence of C=O bonding as a small hump at 289eV which is further evidence of oxygen functionalisation. C750 has the most C=O bonds because it has the highest peak at 289 eV. The approximate ratios in atomic % of oxygen to carbon in the O1s and C1s peaks are shown in table 5.3. These values were calculating by integrating the area under the peaks.

![Figure 5.32: The oxygen 1s XPS spectra of the C grade GNPs and M25 grade from XG Sciences. The concentration of oxygen is highest in the C750 as shown by the tallest peak. The oxygen content is lowest in the M25 grade as it has the smallest peak. (CPS = Counts per second and is proportional to concentration)](image)
Figure 5.33: The XPS carbon 1s Spectra of the C grade GNPs from XG Sciences. The presence of a small peak at a binding energy of 289 eV is evidence of C=O bonding. This peak is highest in the C750 grade and lowest in M25. (CPS = Counts per second and is proportional to concentration)

Table 5.3: Atomic concentration of oxygen and carbon from O1s and C1s peaks in various types of GNPs

<table>
<thead>
<tr>
<th>Type of GNPs</th>
<th>O1s Oxygen %</th>
<th>C1s Carbon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M25 (unfunctionalised)</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>C300</td>
<td>11</td>
<td>89</td>
</tr>
<tr>
<td>C500</td>
<td>19</td>
<td>81</td>
</tr>
<tr>
<td>C750</td>
<td>27</td>
<td>73</td>
</tr>
</tbody>
</table>

The four types of GNPs in table 5.3 were added to epoxy resin and the tensile strength and tensile modulus was measured (see figures 5.34 and 5.35). The results show that the tensile strength of epoxy resin decreases when M25 grade is added. However, the addition of C300, C500 and C750 enhances or at least maintains the strength of neat epoxy resin. The improvement in performance of the C grade GNPs is maintained across higher loadings too and could be due to two factors: firstly the increase in specific surface area of C grades compared to M25 grade; or secondly the increase in oxygen concentration on the surface of the C grade GNPs compared to M25 GNPs. It is difficult to determine which factor is responsible for the improvement because the oxygen concentration is dependent on the surface area so the two increase simultaneously. Oxygen atoms bond to the free
bonds on the edges of the GNPs and more oxygen is capable of bonding to the GNPs, the higher the specific surface area of the GNPs. A high specific surface area means that there are fewer graphitic layers so C750 grade has fewer layers than the C500 and C300 grades. Previous experiments on carbon fibre composites could shed some light on which factor is responsible for the improvement. Carbon fibre is typically treated to change the surface chemistry of the fibre and provide higher interfacial shear strength with the matrix. It was discovered that fibre surface area was not the critical factor in promoting fibre surface adhesion [145-147]. It is more than likely therefore that this is the same case for GNPs and therefore the oxygen concentration appears to be the more critical factor.

In terms of the Young’s modulus there is no particular trend with increasing weight percentage or with the type of GNPs used. The majority of samples have a Young’s modulus slightly below the value of neat epoxy resin. Why does the tensile strength improve or is maintained and yet the modulus does not improve is an unanswered question. The stress strain responses follow the same shape as in all previous samples except there is around a 1% increase in strain at failure. Figure 5.36 shows representative stress strain curves for the C750 0.1 wt% specimens.

![Figure 5.34: Comparison of strength of different grades of GNP reinforced epoxy resin. Whilst the addition of M25 grade GNPs reduces the strength of epoxy resin, the addition of C grade (oxygen functionalised) GNPs enhance or maintain the strength of epoxy resin. This is evidence that oxygen functionalisation has an important effect on the adhesion between the GNPs and epoxy resin.](image-url)
Figure 5.35: Comparison of tensile modulus of different grades of GNP reinforced epoxy resin. There is no particular trend with all grades behaving similarly.

Figure 5.36: Stress strain responses for the specimens which make up the C750 0.1 wt% samples. The responses are the same shape as all other samples except that the strain at failure is around 1% higher than neat epoxy resin specimens.

5.3.2.1 Analysis of Microstructures

The results of the previous section support the theory that chemical functionalisation of the GNPs could be the deciding factor in the improvement in strength between C grade GNP reinforced epoxy resin and M25 grade GNP reinforced epoxy resin. However, in order to rule out that microstructural
differences are not responsible, micrographs were taken (figure 5.37) comparing the C grade and M25 grade epoxy resin composites. The micrographs were taken at 1 wt% loading and show the random nature of the microstructures. The sizes of the agglomerates in the C750 sample appear similar to the M25 sample however the performance of the C750 is superior. The sizes of the agglomerates in the C300 and C500 samples are not similar to the M25 sample and still the performance is much better. This is evidence suggests that the microstructure has very little effect on the mechanical properties of the composite.

![Micrographs](image)

*Figure 5.37: Comparison of microstructures of four different grades of GNPs at a 1wt% loading. The microstructures are varied with the M25 grade similar to the C750 but different to the C300 and C500 grades. The fact that the microstructures of C300, C500 and C750 are different to one another yet all three improve the tensile strength of epoxy resin is evidence to suggest it is the oxygen functionalisation which is responsible for the improved performance not dispersion.*

5.3.3 The Effect of Carboxyl Functionalised GNPs

Carboxyl functionalised GNPs were purchased from ACS materials and according to the manufacturer had a thickness of 0.8-1.2 nm and average lateral dimensions of 1-5 µm. Due to the small quantity of carboxyl functionalised graphene available it was not possible to verify the manufacturer’s claims since most of the GNPs were used to make tensile samples and conduct XPS analysis leaving an insufficient quantity for AFM analysis and SEM analysis.
The XPS analysis for the carbon 1s peak and oxygen 1s peak are shown in figure 5.38 and 5.39 respectively. Groups associated with carboxyl functionalisation (-C=O, -C-O, -C-C (sp²), -C-OH, O=C-OH, epoxy resin/ether groups) can be seen in the C1s peak in figure 5.38 indicating successful functionalisation. A clear peak at a binding energy of 531 eV is supporting evidence for functionalisation with oxygen atoms which would support carboxyl functionalisation are shown in figure 3.39.

Figure 5.38 The carbon 1s spectrum of the Carboxyl functionalised GNP from ACS materials. The peaks are characteristic of carboxyl functionalisation confirming that functionalisation was successful.

Figure 5.39: The XPS oxygen 1s spectrum of the carboxyl functionalised GNPs from ACS materials. The peak at 531 eV shows that oxygen atoms have successfully attached to the GNPs and would support the claim that successful carboxyl functionalisation has been achieved.
The tensile results from the carboxyl samples are shown in figure 5.40. The results show that the addition of carboxyl GNPs appear to improve the tensile strength of epoxy resin however it is impossible to tell whether this improvement continues at higher loadings. Further tests would be required to determine whether the improvements continue, which were not possible at the time with such a small quantity of carboxyl functionalised GNPs available.

![Figure 5.40: Tensile strength of carboxyl reinforced epoxy resin at 0.1 wt% and 0.25 wt%](image)

5.3.4 Concluding Remarks

This study aimed to improve the mechanical properties of GNP reinforced epoxy resin composites by functionalising the GNPs to enhance the interfacial adhesion of the GNPs with epoxy resin. GNPs were initially functionalised with silane to replicate the improvements recorded by [14] which used the same resin system and type of GNPs as in this investigation. Unfortunately, in spite of the successful functionalisation of the GNPs, similar improvements were not found. The reasons for this are not clear and in fact even the results for neat epoxy resin did not concur with the work of [14].

Functionalisation of GNPs with oxygen appears to have a positive effect on the mechanical properties of epoxy resin. The tensile strength of epoxy resin was enhanced or maintained at loadings up to 1 wt% whereas with the addition of unfunctionalised GNPs the tensile strength reduced when more GNPs were added. Evidence from research on carbon fibre epoxy resin composites would suggest that the oxygen functionalisation is the key factor in the improvement of properties and not the increase in specific surface area of the GNPs that occurs simultaneously with the increase in oxygen functionalisation.

No significant conclusions can be drawn regarding the carboxyl functionalised GNPs due to the small sample size.
5.4 Surfactant Assisted Dispersion Investigation

In the final investigation, GNP s were dispersed in a surfactant called Triton X-100 before being shear mixed in epoxy resin and cured. Surfactants have been used to improve the dispersion of nanoparticles and prevent agglomeration which formed the motivation for carrying out this study.

The brief method for carrying out this investigation was as follows. GNP s were sonicated in acetone for 30 minutes and then mixed with surfactant and shear mixed for 2 hours at 3000 rpm. (This speed and time was chosen because it produced the most improvement in Young’s Modulus from the second investigation and there were less time constraints at this stage of the project). The acetone was evaporated off during the heat generated during shear mixing but to make sure all of it was removed the beaker and its contents were heated at 100 °C until they reached a constant mass. The investigation was split into three studies:

1. **Experimentally determining the best ratio of GNP s to Surfactant.** The first part of the study was to determine what weight ratio of GNP s to surfactant worked best. Too much surfactant may have degraded the properties of epoxy resin, whereas too little surfactant may not have produced a noticeable improvement in dispersion. It was therefore important to experimentally determine the optimum amount which should be used for the second part of the investigation.

2. **The Effect of GNP Loading using the Best Ratio of GNP s to Surfactant.** In the second study, the loading weight of GNP s was increased using the best ratio of surfactant determined experimentally from part 1. This was carried out to see if better properties could be sustained at higher loading weights of GNP s.

3. **The Effect of Surfactant Addition Only on the Mechanical Properties of Epoxy Resin.** In the final part of the investigation, only surfactant was added to epoxy resin. This experiment acted as a control in order to determine whether it was the GNP s or the surfactant or the two together which were responsible for changes in the mechanical properties of epoxy resin.

5.4.1 Experimentally Determining the Best Ratio of GNP s to Surfactant

Different weight ratios of GNP s to surfactant were tried to see what the optimum ratio was. The ratios were calculated by weight and ranged from 1:5 to 1:30. A 0.5 wt% loading of GNP s in epoxy resin was used in each case. The results are shown in figures 5.41 and 5.42.

The results show that increasing the ratio of surfactant to GNP s improves the strength of epoxy resin. The 1:20 and 1:30 ratios slightly improve the tensile strength compared to neat epoxy resin whereas
1:5 and 1:10 ratio reduce the strength compared to neat epoxy resin. The 1:15 ratio roughly maintains the strength of the neat epoxy resin.

Regarding the tensile modulus, there are also improvements up to 1:15, however when the ratio increases further, the tensile modulus declines. The addition of surfactant with GNP improves the tensile modulus from 2.67 GPa (neat epoxy resin) to 3.13 GPa. The ratio 1:15 appears to be the best to produce improvements in both modulus whilst not damaging strength and was therefore chosen to be used in the next part of the study on surfactants.

Figure 5.41: Variation of strength when 0.5 wt% GNP were added to epoxy resin using different ratios of surfactant. Ratios 1:15 and 1:20 improve the strength compared to neat epoxy resin whereas 1:5 and 1:10 reduce the strength. A 1:15 ratio maintains the strength.

Figure 5.42: Variation of modulus when 0.5 wt% GNP were added to epoxy resin with different ratios of surfactant. The modulus improves relative to neat epoxy resin in all cases. The ratio 1:15 produces the greatest improvement in modulus.
5.4.2 The Effect of GNP Loading Using the Best Ratio of GNP to Surfactant

Having experimentally determined that the best ratio of GNP to surfactant was 1:15 by weight, the next stage was to increase the loading of GNP and to compare them against nanocomposites made without surfactant. The results are presented in Figures 5.43 and 5.44.

Figure 5.43: Effect of GNPs and surfactant on the strength of epoxy resin using a GNP to surfactant ratio of 1:15. The strength is maintained up until 0.5 wt% and then declines thereafter.

Figure 5.44: Effect of GNPs and surfactant on the Young’s modulus of epoxy resin using a GNP to surfactant ratio of 1:15.
In terms of strength, adding up to 0.5 wt% GNP with surfactant roughly maintains the strength at the value of the neat epoxy resin sample (71.84 MPa compared to 73.23 MPa for neat epoxy resin). At 1 wt% the strength decreases below the neat epoxy resin value and continues decreasing in a linear way up to 5 wt%. The total reduction in strength is 14% of its original value. In terms of modulus improvements are seen up to 1 wt%. The modulus peaks at 0.5 wt% GNPs reaching 3.13 GPa and declines thereafter but at 1 wt% the value is still higher than the neat epoxy resin value.

The values can be compared to the results of GNPs added to epoxy resin without surfactant shown in figures 5.45 and 5.46. The two lines are fairly similar up to 1 wt% but then deviate from one another particularly at higher weight percentages. The addition of 5 wt% of GNPs with surfactant has a value almost 5 times less than the value without surfactant.

In the next section, surfactant only was added to epoxy resin, and the mechanical properties were tested. This is because it was unknown whether the surfactant was responsible for the changes, or the GNPs were responsible, or whether the combination of the GNPs and surfactant was responsible.

![Figure 5.45: Comparison of strength of samples made with GNPs and surfactant and samples made with GNPs only. Both samples deteriorate in strength with the addition of GNPs.](image-url)
Figure 5.46: Comparison of Young’s modulus of samples made with GNP
ts and surfactant and samples made with GNP
ts only. The modulus increases at first for the sample with GNP
ts and surfactant but then rapidly decreases after 0.5 wt%

5.4.3 The Effect of Surfactant Addition only on Tensile Properties

This part of the study attempted to explain why there were differences between the samples using GNP
ts with surfactant, and the samples using GNP
ts without surfactant. Was it the surfactant, or the GNP
ts or the combination of the surfactant and GNP
ts which was responsible for the differences? In order to discuss this question a control experiment was conducted whereby surfactant only was added to epoxy resin in increasing amounts. The same amounts of surfactant were used in the previous study but without the addition of GNP
ts. The results of this experiment are illustrated in figures 5.47 and 5.48. The exact quantities of surfactant used are shown in the table 5.4. The same processing was used as per the surfactant and GNP
ts samples.

Table 5.4: Quantities of resin and surfactant used in the effect of surfactant only investigation

<table>
<thead>
<tr>
<th>Surfactant only sample</th>
<th>Quantity of Resin</th>
<th>Quantity of Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
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<td>3</td>
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<td>5</td>
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</table>
The data shows that the addition of small amounts of surfactant can improve the tensile strength of epoxy resin. The tensile strength reaches as high as 80 MPa when 2.1 g of surfactant is added which demonstrates that it is the surfactant which is improving the properties of the epoxy resin and not the GNPs. However, the properties of epoxy resin decline from their neat value when 21 g of surfactant or more is added. At 63 g and 105g of surfactant, the strength of the epoxy resin drops significantly. Comparatively, the samples using GNPs without surfactant perform better as more GNPs are added, but their strength is still lower than neat epoxy resin. Therefore in conclusion the addition of GNPs in small amounts with surfactant can maintain the strength of neat epoxy resin. However, the addition of small amount of surfactant by itself improves the tensile strength of epoxy resin.

In terms of the Young’s modulus the addition of small amounts of surfactant (2.1 g) initially maintains the modulus at the neat epoxy resin value. However, when larger amounts of surfactant are added the modulus declines rapidly and reaches 0.23 GPa at 105 g of surfactant. The best improvement comes when 0.5 wt% of GNPs and surfactant is used and the modulus reaches 3.13 GPa. It therefore appears as though GNPs and surfactant are working together to improve the modulus.

In order to understand if the use of surfactant had an effect on the dispersion of GNPs optical microscope samples were produced which is discussed next.

![Graph showing the variation of strength of epoxy resin with the addition of surfactant. A small amount of surfactant (2.1g) increases the strength of epoxy resin to 80 MPa but with the addition of more surfactant the strength rapidly decreases in a linear fashion.](image)
5.4.3.1 The Effect of Surfactant on the Microstructure

Micrographs of GNP reinforced epoxy resin with and without surfactant are shown in figure 5.49. There are clear differences between the micrographs. At loadings of 0.1wt% the micrographs appear similar. However, at higher loadings of 3wt% and 5wt% the differences become apparent. Samples with surfactant are much more evenly dispersed than those without. The black agglomerates are finer and spread evenly whereas without surfactant the agglomerates are much larger and form large clumps.

Relating the microstructure to the tensile strength and modulus is difficult. Although the dispersion is better with surfactant its presence also disrupts the curing of epoxy resin and alters its properties. The higher the loading of GNP the more surfactant is required to disperse it and therefore the more the mechanical properties of epoxy resin are altered.

In terms of affecting the curing of the epoxy resin, the surfactant molecules may get in the way of a normal reaction occurring which could reduce mechanical properties. Typically the epoxide group of the resin reacts with the amine group of the hardener. If however, the concentration of surfactant molecules increases, they will physically prevent epoxide groups coming into close contact with the amine groups and so inhibit the reaction. This could explain why when higher quantities of surfactant were used the strength and modulus drop significantly. On the other hand Triton X-100 does have one OH group which could take part in a reaction with the epoxide of the resin once all of the amine
groups from the hardener have been consumed. In this case the Triton X-100 would act like a secondary hardener. According to [148] Triton X-100 does not decompose until \( \sim 230 \, ^\circ C \), therefore it is unlikely to decompose into other reactants which could chemically react with the resin. In short the addition of small amounts of surfactant could enhance the mechanical properties by providing extra OH groups to react with excess epoxide groups from the resin which could explain the improvement seen in the results at low concentrations. Using higher concentrations of surfactant adversely affects the curing reaction. For example adding more than 105 g of surfactant to 140 g of resin meant that the resin did not fully cure after being heated through the standard cycle.

Figure 5.49: Comparison of microstructure of GNP reinforced epoxy resin with and without surfactant at different loadings of GNPs. The surfactant has a positive effect on the dispersion as there is a much more even coverage of GNPs in micrographs d) and f) compared to c) and e). Scale bar is 500 µm.
5.4.4 Concluding Remarks

The use of surfactant Triton X-100 can enhance the tensile strength and Young’s modulus of epoxy resin when used in moderation and in conjunction with GNPs. The addition of 0.5 wt% of GNPs with surfactant resulted in a tensile strength of 71.98 MPa and a Young’s modulus of 3.13 MPa (~15% increase). This result is the best compromise of strength and stiffness out of all the results in this chapter. Adding more surfactant does not improve the properties, however. Another important result is that the micrographs clearly show that using surfactant produces a more even dispersion of GNPs in epoxy resin.

5.5 Summary of Results

This chapter consisted of four separate investigations. The main findings across the four investigations are as follows:

- The addition of unfunctionalised GNPs to epoxy resin in general reduces the tensile strength of epoxy resin regardless of the method of dispersion whether it is sonication or shear mixing. The addition of higher loadings of GNPs decrease the strength even more.
- The addition of unfunctionalised GNPs to epoxy resin had no effect on the Young’s modulus unless acetone was used as a solvent in which case improvements were seen although improvements were not consistent.
- Oxygen functionalisation of GNPs appears to be a critical factor for effective reinforcement.
- No reagglomeration of GNPs occurs during curing.
- EG was the worst nanofiller in terms of reinforcement and reduced the tensile strength more than GNPs or CNTs.
- The addition of a small quantity of surfactant to help disperse GNPs can improve the strength and modulus of epoxy resin.

In total, 16 samples of unfunctionalised GNP reinforced epoxy resin samples were tested and of those 16 samples only one sample (the 500rpm 1 hour sample) produced a minor improvement in strength. The improvement of this sample was less than 5% and so cannot be considered statistically significant. It is clear from figure 5.8 that adding higher weight fractions of unfunctionalised GNPs reduce the tensile strength of epoxy resin.

The biggest improvement in tensile strength occurred when 0.1 wt% of C750 GNPs were added to epoxy resin resulting in a tensile strength of 80.21 MPa (~14% increase) which is statistically
significant because it is greater than the standard deviation of \(\sim 3.76\) MPa for pure epoxy resin samples. In fact, all samples of C grade GNP reinforced epoxy resin (12 samples in total) outperform the M25 grade GNP reinforced epoxy resin which statistically significant evidence that oxygen functionalisation has a key impact on improving mechanical properties.

Regarding the Young’s modulus results, the addition of both acetone and GNPs to epoxy resin did improve the Young’s modulus, however the improvements are not consistent enough to be statistically significant and should therefore be treated with caution. The biggest improvement in Young’s modulus occurred using 0.5 wt\% of GNPs with surfactant resulted in a Young’s modulus of 3.13 MPa (\(\sim 15\%\) increase)

5.5.1 Comparison of Results with the Literature

Comparing the results of this study to those of the literature is difficult since most literature only presents positive results and any negative results remain unpublished. The results of one investigation [141], match well with the results from this study. A decrease in tensile strength was reported when unfunctionalised GNPs were added to epoxy resin, and a small increase in tensile strength when oxygen functionalised GNPs were added to epoxy resin.

However, the best results of this study fall short of the best results from the literature. For example [128] reported a 37% improvement in Young’s modulus and 38% improvement in tensile strength using a 0.46 vol\% of GNPs. In [109] a 40% improvement in tensile strength was reported using a 0.1wt\% loading of GNPs. Both [109] and [128] report superior improvements to the maximum reported increase in tensile strength and Young’s modulus in this study of \(\sim 14\%\) and \(\sim 15\%\) respectively.

What are the possible reasons why [109] reported a superior tensile strength, and [128] reported a superior Young’s modulus to the results of this study?

One possible reason why [109] achieved a higher tensile strength than this study is because [109] used a higher concentration of oxygen functionalised GNPs. When examining the materials used in [109] it is apparent that the GNPs had been intentionally oxidised using a modified Hummer’s method. As has been shown by investigation 5.3.2, oxygen functionalisation appears crucial to tensile strength enhancement of epoxy resin. Therefore a plausible reason why [109] achieved better results than this study is because [109] used GNPs functionalised with a higher percentage of oxygen atoms. In this study, the maximum oxygen functionalisation of GNPs was determined to be on the C750 grade GNPs with oxygen atoms making up approximately 8\% of the total number of atoms on the GNPs. It is highly possible that [109] achieved a much higher oxygen functionalisation than 8\%
due to the Hummer’s process. Unfortunately no XPS data is included with [109] so it is impossible to
tell how much oxygen functionalisation was achieved after the Hummer’s method was applied to the
GNPs. However, [149] has shown that the percentage of oxygen functionalisation can be as high as
40% using the Hummer’s method, which is far greater than the 8% oxygen functionalisation of the
C750 GNPs used in this investigation. Accordingly, a higher oxygen functionalisation has been shown
to improve the tensile strength of epoxy resin.

Regarding the reason why [128] achieved a higher Young’s modulus than this investigation, one
possible explanation could be because of the solvent which was used in the manufacture of their
specimens, namely DMF. In [128] unfunctionalised GNPs were dispersed in DMF before being mixed
into epoxy resin. The DMF was then evaporated and the epoxy resin was cured. It was claimed that
DMF improves the dispersion of GNPs which leads to a higher Young’s modulus. However, no control
experiment was conducted to determine whether the DMF alone was responsible for the
improvement. It could therefore be plausible that DMF improved the modulus as shown in [159] and
not the GNPs. Even though the DMF was evaporated from the epoxy resin before curing there may
have been some residual solvent in the cured epoxy resin which enhanced the Young’s modulus.

This chapter has focused on tensile properties of nanocomposites. The next chapter will explore the
fracture toughness of nanocomposites.
6 Fracture Properties

Results and Discussion

One of the drawbacks of carbon fibre composites (described in chapter 1) is their low resistance to delamination which is attributed to the low fracture toughness of epoxy resin compared to metals. In chapter 5 it was shown that the addition of GNPs functionalised with oxygen improved the tensile strength of epoxy resin and maintained the Young’s modulus even at loadings up to 1 wt%. By contrast the addition of unfunctionalised GNPs to epoxy resin reduced its strength. In this chapter, epoxy resin was reinforced with GNPs in an attempt to improve its fracture toughness. In the first part, the fracture toughness of pure epoxy resin was tested to represent a baseline on which to measure future results. In the second part epoxy resin was reinforced with different grades of GNPs and different loadings.
6.1 Pure Epoxy Resin Investigation

The first part of the investigation measured the fracture toughness of unreinforced pure epoxy resin in accordance with ASTM D5545. These results were used as a benchmark to measure improvements against in future investigations. The results are presented in figure 6.1.

The mean fracture toughness of the 7 specimens tested was $0.21 \text{ MPa m}^{1/2}$ with a standard deviation of 0.03. This did not fall within the values from the manufacturer’s data sheet of $0.69-0.76 \text{ MPa m}^{1/2}$. One reason for this could be that the dimensions of the specimens did not exactly confirm to the standard. For example the specimen should have a thickness which is half the width. Practically this was hard to achieve because the specimens needed to be smoothed off to remove defects which reduced the thickness to less half the width. In most cases the width was more like one third of the width. Specimen dimensions are normalised when calculating the fracture toughness but they did not conform to the standard so they could have had an effect on the results, although typically fracture toughness increases as the thickness of the specimen decreased. Therefore a more probable reason why the results did not agree with the manufacturer’s values was because creating a crack with uniform depth was extremely tricky. The crack was created using a drop weight which caused a razor blade to be pushed down into the V shaped notch in the specimen. Upon examining the fracture surfaces of the failed specimens, it was obvious that the crack was not initiated uniformly across the thickness of the notch. Instead cracks initiated preferentially at the corners of the notch see figure 6.2 and figure 6.3. An average value for the depth of the crack had to be used in calculation which could have reduced the reliability of the results.

Figure 6.1: fracture toughness results for the 7 specimens tested of pure epoxy resin. The average fracture toughness was $0.21 \text{ MPa m}^{1/2}$ with a standard deviation of 0.03
Figure 6.2 a) two-dimensional diagram of fracture toughness specimen shape b) fracture toughness specimen after crack has been initiated c) three dimensional representation of the fracture surface of the specimen after failure. The red area depicts that the crack does not have the same depth across the thickness of the specimen. Instead the depth is greater around one edge of the specimen compared to the other (see figure 6.3 for real image). This is one of the limitations of this test and could be why the value of fracture toughness from this experiment does not match the value given on the data sheet by the manufacturer.

Figure 6.3: Optical microscope image of the fracture surface of an epoxy resin sample showing the initial crack depth highlighted in dashed red line. The crack depth is not uniform across the thickness of the specimen. It has a depth of 0.659 mm in the middle but towards the left edge the depth is zero. This highlights the difficulty of making specimens with carefully controlled crack depths. An uneven crack depth will affect the fracture toughness results. A better specimen is shown in figure 6.4
6.2 The Effect of GNPs on the Fracture Toughness of Epoxy Resin

In the second part of this investigation different grades of GNPs (M25, C300, C500 and C750) were added to epoxy resin at 0.1 wt% and 0.5 wt% and the fracture toughness was tested. The results are presented in figure 6.5. Load versus flexural extension responses for the C750 0.5 wt% specimens are shown in figure 6.6 as an example of the typical response shown by all samples.

At a 0.1 wt% loading the fracture toughness is slightly lower compared to neat epoxy resin, although they are all within the standard deviation of one another. There is an improvement with the C750 grade of GNPs at 0.1 wt% but the improvement does not continue when 0.5 wt% of C750 is added.

Due to the unreliable nature of this test I do not believe that the results of this experiment are a true reflection of the effect of GNPs on fracture toughness. One would have thought that an improved tensile performance of the epoxy resin reinforced with C grade GNPs could translate to improved fracture toughness but this is not obvious. There were no differences in the fracture surfaces of the specimens reinforced with different types of GNPs.

Figure 6.4: An epoxy resin specimen with a more uniform crack depth. The depth of the crack in the middle of the specimen is 0.553 mm and this depth remains fairly constant across the thickness of the specimen. This specimen would have given more reliable results.
6.2.1 Concluding Remarks

It is difficult to make any solid conclusions from these results given the lack of reliability of the tests. In general however it appears as though adding different types of GNPs to epoxy resin does not drastically affect its fracture toughness either way. In order to get more reliable data the test method must be developed to ensure crack is created of uniform and controlled depth so that the fracture toughness can be accurately calculated.
Another drawback of carbon fibre composites summarised in chapter 1 is their low through thickness conductivity which makes non-destructive testing techniques and structural health monitoring difficult. The epoxy resin which binds the carbon fibres together is an insulating barrier to electrical charge. Therefore, in this chapter the epoxy resin was reinforced using graphene nanoplatelets, carbon nanotubes and expanded graphite in an effort to enhance its conductivity. The chapter begins by explaining the technique used to measure electrical conductivity and assessing its reliability. Secondly, the electrical conductivity of pure epoxy resin is presented which represent a baseline to measure improvements against. Following this, the effect of shear mixing speed and time on the electrical conductivity of EG reinforced epoxy resin, MWCNT reinforced epoxy resin and GNP reinforced epoxy resin composites is investigated in that order. The results are compared against mathematical models from other research groups.
7.1 Reliability of Measurement Technique

The AC Impedance technique as discussed in section 3.5.3 was used to measure conductivity. There were two benefits to using this technique over traditional DC conductivity measurements. Firstly, it enabled the user to determine if a percolated network had been formed and secondly it was capable of detecting lower conductivities than conventional the DC measurement that existed in our laboratory. It was important to test that the AC Impedance analyser was accurate to ensure results of future experiments would be reliable, so three standard resistors with a resistance of 27 kΩ, 8.2 MΩ and 10 MΩ were placed in the circuit and their resistance was measured. The resistors were coated with the same conductive silver epoxy resin that was used to make conductive contacts on the nanocomposite samples, to make sure that the silver epoxy resin did not alter the resistance of the samples. The results from the AC Impedance technique are presented in Figure 7.1 and demonstrate that the resistance matches the values of the standard resistors which provided confidence for future measurements. The resistance is constant across the entire frequency range (1-10⁴ Hz) because the capacitative component of impedance (which is a function of frequency in insulating materials) is negligible at this frequency range. Only at higher frequencies would the resistance become dependent on frequency, when the capacitative component of impedance becomes more dominant.

Figure 7.1: Resistance of three standard resistors of known resistance. The value of resistance is independent of frequency and is exactly the same value as the resistance quoted on the three resistors. Therefore this AC impedance technique is an accurate and reliable method of measurement for future samples.
7.2 Pure Epoxy Resin Investigation

Having confirmed that the measurement technique was accurate the first part of the study was to measure the conductivity of pure epoxy resin which would represent a benchmark to measure improvements against in later experiments. Three epoxy resin specimens were tested in total and the results are presented in figure 7.2. The graph shows that none of the epoxy resin specimens reached percolation illustrated by the fact that none of the curves reach a plateau at lower frequency. This is to be expected because epoxy resin is purely insulating and there are no conductive phases which could create a percolating network. Below 100 Hz no results are recorded because the conductivity of the specimens is below the limit of the machine. However, it is expected that the conductivity would continue decreasing as the frequency decreases, with the gradient becoming steeper at lower frequencies. Above 100 Hz the conductivity of the specimens increases as the frequency of the current increases which is typical of the universal dielectric response [127]. The three specimens show reasonable similarity to one another indicating homogeneous specimens were prepared. These results could then be compared against samples reinforced with nanoparticles.

![Graph showing conductivity of three epoxy resin specimens](image_url)

*Figure 7.2: Conductivity of three epoxy resin specimens in order to compare scatter in the sample. The three specimens show reasonable similarity to one another and confirm there is no percolating network due to an absence in a plateau in the conductivity. No data is recorded below 100 Hz because the conductivity was too small to measure and beyond the machine's capability.*
7.3 Expanded Graphite Reinforced Epoxy Resin Investigation

The first nanoparticle to be tested was expanded graphite. A loading of 0.1 wt% of EG was shear mixed into epoxy resin for different lengths of time (10 minutes, 1 hour and 2 hours). Five different shear mixing speeds were used (1000 rpm to 5000 rpm at intervals of 1000 rpm) for each mixing time. Therefore 15 samples were made in total with each sample consisting of a minimum of three specimens. The results are plotted in figures 7.3, 7.4 and 7.5 corresponding to 10 minutes, 1 hour and 2 hours mixing time respectively. The curves plotted are the average conductivity across the three specimens in each sample.

Only three samples reach percolation (a) ‘EG, 0.1 wt%, 5000 rpm, 10 min’, (b) ‘EG, 0.1 wt%, 2000 rpm, 2 hours’ and (c) ‘EG, 0.1 wt%, 4000 rpm, 2 hours’. These three curves are the only curves which reach a plateau which intercept the y axis. The DC conductivity is equivalent plateau value on each graph. Samples which do not have a plateau value do not have a defined DC conductivity. The most conductive sample is the 4000 rpm 2 hour sample at $1.08 \times 10^{-5}$ S m$^{-1}$. The other two conductive samples are on the order of $10^{-6}$ S m$^{-1}$. No samples achieve percolation which are shear mixed for 1 hour.

![Graph showing conductivity vs frequency for different shear mixing conditions](image-url)

*Figure 7.3: Conductivity of epoxy resin reinforced with 0.1 wt% EG shear mixed for 10 minutes at different speeds. Only the sample mixed at 5000 rpm achieves percolation and a DC conductivity $\sim 2.5 \times 10^{-5}$ S m$^{-1}$ as shown by the plateau region.*
Figure 7.4: Conductivity of the 0.1 wt% EG reinforced epoxy resin samples shear mixed for 1 hour at different speeds. None of the samples achieve percolation illustrated by the fact none of the curves become independent of frequency.

Figure 7.5: Conductivity of 0.1 wt% EG reinforced epoxy resin samples shear mixed for 2 hours at different speeds. The 2000 rpm and the 4000 rpm samples reach percolation with DC conductivities of $10^{-6}$ S m$^{-1}$ and $10^{-5}$ S m$^{-1}$ respectively. The 3000 rpm and 2000 rpm samples come close to reaching percolation. The 5000 rpm sample is the furthest from reaching percolation.
In general, samples mixed for 2 hours appear closer to reaching percolation than samples mixed for shorter times. Two of the samples achieve percolation from the figure 7.5 (2000 rpm and 4000 rpm) and other samples (1000 rpm and 3000 rpm) appear closer to becoming independent of frequency. A possible reason why shear mixing for 2 hours seems better than shear mixing for shorter times could be related to the initial size of the EG particles. EG particles are quite large (1-5 mm in length) and in order to break them down and exfoliate graphitic layers the shear mixing time would need to be longer. It was observed that after shear mixing for 10 minutes and 1 hour, there were still large EG particles of up to 1 mm in length which clearly had not been broken up by the shear mixer, whereas after 2 hours they had been broken up as shown in figure 7.6 a) and b). Large EG particles would reduce the chance of percolation because they would act as isolated agglomerates whereas exfoliated EG particles would have a greater chance of creating a connected network leading to percolation as shown in figure 7.6 c) and d).

![Figure 7.6 a) Photograph of a dispersion droplet taken from the ‘EG 0.1 wt% 3000 rpm 10 mins’ sample showing the presence of a large unexfoliated EG particle; b) photograph of a dispersion droplet taken from the ‘EG 0.1 wt% 4000 rpm 2 hour’ sample showing the presence of fine black particles where EG has become exfoliated. This microstructure is better from a conductivity perspective because there is more chance of the exfoliated flakes touching one another to form a network; c) graphical representation of an unexfoliated EG particle; d) graphical representation of an exfoliated EG particle. Exfoliation leads to more chance of a percolated network being formed.](image-url)
Regarding the samples shear mixed for 2 hours, there does not appear to be a clear trend between shear mixing speed and conductivity or the percolation. For example, one might expect a trend between percolation and mixing speed. However, the 2000 rpm sample has the highest conductivity and similarly, the 4000 rpm sample reaches percolation whereas the 5000 rpm one does not. It appears that there is still a degree of randomness to the results. One reason for this is that the shear mixer does not appear capable of controlling the size of the agglomerates on the nanoscale between finite values. By examining the microstructure of the samples there is a large variation in agglomerate size. This randomness could be because more time is required to make sure all particles are shear mixed down to the same size. The randomness can be illustrated by showing the scatter that exists between four specimens used to calculate the average value of each sample. In Figure 7.7 the 4 specimens from the ‘EG 2000rpm 2hrs’ sample are shown. It is obvious that there is a large scatter between all four specimens. Specimens 1 and 4 reach percolation, but their DC conductivity is an order of magnitude apart whereas specimens 2 and 3 do not reach percolation. This graph is the worst in terms of scatter and does not represent all the other samples some of which are consistent. However, it is evidence that there is a random element to the conductivity results.

The random element is also apparent among the 10 minute mixed samples. Earlier it was hypothesised that longer shear mixing times lead to a greater chance of forming a percolated network. If this is the case then why does the 5000 rpm 10 minute sample conduct and none of the 1 hour mixed samples conduct? The inconsistency could be because there was such a huge variation in the as supplied particle sizes of the EG to begin with. The size of the EG particles was on average around 1 mm in length but there were also much larger particles measuring up to 5 mm. If these smaller particles were used to make the 5000 rpm 10 mins sample then they would have had a head start and would not need to be shear mixed as long as other samples in order to reach the same size. Therefore it appears as though the 5000 rpm 10 minute sample is an anomalous result. In general however, it appears as though longer shear mixing times do lead to better conductivity. In addition there should be better consistency between individual specimens as the particle size should be more homogenous.

This section has considered the electrical properties of expanded graphite epoxy resin composites. In the next section these results will be compared against MWCNTs.
Figure 7.7: Conductivity of the four specimens which make up the EG 2000 rpm 2 hours sample. There is a large degree of scatter. Specimens 1 and 4 reach percolation although their DC conductivities are an order of magnitude apart. Specimens 2 and 3 do not reach percolation. This is evidence that there is a random element to conductivity because the shear mixer is not capable of controlling the size of the particles within a tight range.
7.4 MWCNT Reinforced Epoxy Resin Composites

A loading of 0.1 wt% of MWCNTs was shear mixed into epoxy resin for different lengths of time (10 minutes, 1 hour and 2 hours). Five different shear mixing speeds were used (1000 rpm to 5000 rpm at intervals of 1000 rpm) for each mixing time. Therefore 15 samples were made in total with each sample consisting of a minimum of three specimens. The results are plotted in figures 7.8, 7.9 and 7.10 corresponding to 10 minutes, 1 hour and 2 hours mixing time respectively. The curves plotted are the average conductivity across the specimens in each sample.

MWCNTs appear to be the best nanoparticle to improve the conductivity of epoxy resin. In total nine samples reach percolation. The 5000 rpm 1 hour sample achieves the highest DC conductivity (3.52 x 10⁻⁵ S m⁻¹) and the entire batch of samples shear mixed for 1 hour achieved percolation. Three out of five samples from the 10 minutes batch and four out of five from the 2 hour batch achieve percolation. Therefore, from the perspective of MWCNTs composites, shear mixing for 1 hour seems to be the optimum time. Shear mixing for either 10 minutes or 2 hours either results in lower conductivity or no percolating network. A possible reason for this is as follows: shear mixing for short times such as 10 minutes does not break up agglomerates to release individual nanotubes; shear mixing for too long such as 2 hours separates the nanotubes too far away from one another such that they do not touch one another and could introduce defects into the structure.

![Figure 7.8: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 10 minutes at different speeds. Three samples reach percolation the 1000 rpm, 3000 rpm and 4000 rpm. The highest conductivity recorded was 1.05 x 10⁻⁵ S m⁻¹ by the 1000 rpm sample.](image-url)
Figure 7.9: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 1 hour. The samples here all reach percolation suggesting 1 hour is the optimum time for electrical conductivity enhancement. The highest conductivity achieved was $3.52 \times 10^{-5}$ S m$^{-1}$.

Figure 7.10: Conductivity of MWCNT reinforced epoxy resin samples, shear mixed for 2 hours at different speeds. All samples except the 1000 rpm sample reach percolation. The highest conductivity was $1.13 \times 10^{-5}$ S m$^{-1}$. 
Why are MWCNTs much better than EG at enhancing the conductivity of epoxy resin? The answer could be because of the much higher aspect ratio of MWCNTs compared to EG. The MWCNTs used in this investigation had a diameter of 30-50 nm and a length of 10-20 µm. In comparison, EG particles had a length of ~1 mm and a width of ~0.1-0.5 mm. When SEM images of the MWCNTs are examined, agglomerates are clearly visible as shown in figure 7.11 a). However, on closer inspection thin individual tubes can be seen protruding from the agglomerates. The individual tubes can span long distances because of their high aspect ratio and can connect neighbouring agglomerates allowing the passage of charge from one agglomerate to another as shown in figure 7.11 b)

![SEM image of MWCNT agglomerates showing individual tubes protruding from them](image1)

![Graphical representation of MWCNTs in epoxy resin showing how agglomerates could connect via protruding tubes to form a percolating network](image2)

*Figure 7.11: a) SEM image of MWCNT agglomerates showing individual tubes protruding from them b) graphical representation of MWCNTs in epoxy resin showing how agglomerates could connect via protruding tubes to form a percolating network. This is a consequence of their high aspect ratio.*
With EG, this kind of connection is harder, because the aspect ratio is lower. The SEM image shown in figure 7.12 a) shows that EG particles can have a length of ~1 mm and a width of ~0.1-0.5 mm. There are no high aspect ratio protrusions like in MWCNTs and this means that it is harder to connect individual EG particles to transfer charge as shown in figure 7.12 b). In order to make the EG particles connect they must be brought closer to one another either by increasing the concentration or by manipulating their orientation which is difficult to achieve.

Figure 7.12: a) SEM image of EG particles with one highlighted showing they are much bigger than MWCNTs b) Graphical representation EG particles after exfoliation in epoxy resin. Due to the lower aspect ratio of EG compared to MWCNTs there are less likely to be connections made between individual particles leading to lower conductivity.
7.4.1 Effect of Shear Mixing Speed and Time on Consistency of Results

Another observation from the results of MWCNT reinforced epoxy resin composites is that in general the specimens become more consistent as the time of shear mixing increases. For example the ‘CNT 0.1wt% 4000 rpm 2hours’ sample has a much lower scatter than the ‘CNT 0.1wt% 1000rpm 10mins’ sample shown in figures 7.13 and 7.14 respectively. In total four specimens were tested per sample. In the samples mixed for 10 minutes (figure 7.13) specimen 3 is an order of magnitude lower than specimens 2 and 4 and specimen 1 does not reach percolation at all. In contrast the specimens from the 2 hour sample (figure 7.14) all reach percolation and are all of the same order of magnitude.

![Figure 7.13](image1.png)

*Figure 7.13: Conductivity of the four samples which make up the ‘CNT 0.1wt% 1000rpm 10 mins’ sample. There is a much higher degree of scatter than in Figure 7.14 which uses a 2 hour mixing time. Specimen 1 does not reach percolation and specimen 3 has conductivity an order of magnitude lower than specimens 2 and 4.*

![Figure 7.14](image2.png)

*Figure 7.14: Conductivity of the four specimens which make up the 4000 rpm 2 hours sample. There is a small scatter and all of the specimens are on the same order of magnitude. The maximum conductivity is $1.69 \times 10^{-5} \text{ S m}^{-1}$ and the minimum is $1.03 \times 10^{-5} \text{ S m}^{-1}$. The scatter is much smaller than in figure 7.13 which uses a 10 minute shear mixing time.*
7.4.2 Effect of MWCNT Loading on the Conductivity of Epoxy Resin

The weight percentage of MWCNTs was increased to see how it affected the conductivity. Three samples were made at 0.1 wt%, 0.5 wt% and 1 wt% and shear mixed at 5000 rpm for 1 hour and the results are plotted in figure 7.15. The DC conductivity increases from $\sim 10^{-6}$ S m$^{-1}$ (at 0.1 wt%) to $\sim 2 \times 10^{-4}$ S m$^{-1}$ (at 1 wt%). This would be expected because at higher loadings there are more MWCNTs per unit volume of epoxy resin and therefore more chance of connections between individual nanotubes. Beyond 1 wt% the MWCNT epoxy resin mixture becomes much harder to process due to a rapid increase in viscosity. This was therefore chosen as the limit of this particular study. Heating the mixture could have reduced the viscosity to enable easier processing up to 2 wt%.

![Figure 7.15](image-url)

*Figure 7.15: Influence of MWCNT loading weight on the electrical conductivity of epoxy resin. The more MWCNTs are added to epoxy resin, the higher the conductivity*
7.5 Modelling of MWCNT Reinforced Epoxy Resin Composites

The dispersion of MWCNTs has been modelled by [150]. In their model they considered three scenarios. The first scenario is when MWCNTs are perfectly dispersed and exist as individual tubes. The second scenario is when MWCNTs exist as spherical agglomerates consisting of many entangled nanotubes as shown and the third scenario occurs when there is a mixture of individual tubes and agglomerates (See figure 7.16) The composite is divided into cubes of length \( L \), each of which contains either one nanotube or one agglomerate.

![Figure 7.16: a) First scenario where MWCNTs are dispersed as individual tubes; b) Second scenario when MWCNTs exist as entangled spherical agglomerates; c) Third scenario where there are a mixture of individual tubes and agglomerates.](image)

If the nanotubes are perfectly dispersed (figure 7.16 a)) the percolation threshold \( P \), can be calculated using equation 7.1

\[
P = \frac{V_{\text{filler}}}{V_{\text{total}}} = \frac{V_{\text{CNT}}}{L^3} = \frac{\pi d^2 l}{4 \left(\cos^2 \theta \cdot (l + IPD)\right)}
\]

(7.1)

\( V_{\text{total}} \) is the total volume of the composite, \( L^3 \) is the volume of one element, \( V_{\text{filler}} \) is the total volume of the filler, \( V_{\text{CNT}} \) is the volume of an individual MWCNT, IPD is the Interparticle distance required for conduction by tunnelling, \( l \) is the length of one nanotube and \( d \) is the diameter of one nanotube.
\( \cos^2 \theta \) represents the angle between MWCNTs and a fixed direction and the brackets represent the average value. For a 3D random distribution, it has been shown that \( \langle \cos^2 \theta \rangle = 1/3 \).

The IPD required for conduction to take place via quantum mechanical tunnelling is 10 nm. This value has been shown to be constant regardless of the polymer separating the particles. Since the length of the nanotube \( l \) is much greater than 10nm (\( l \gg \text{IPD} \)) equation 7.1 can be simplified to equation 7.2

\[
P_c = \frac{4 \pi l^2}{3} \left( \frac{1}{\text{IPD}} \right)^3 = \frac{27 \pi l^2}{4l^2} = 21.195 \frac{1}{\alpha^2}
\]

(7.2)

In reality however, the nanotubes exist as agglomerates and individual tubes (figure 7.16 c)). The equation must be modified using the parameter \( n \), which is the number of individual nanotubes in each agglomerate as shown in equation 7.3.

\[
P_c = \frac{V_{\text{filler}}}{V_{\text{total}}} = \frac{n V_{\text{CNT}}}{L^3}
\]

(7.3)

Two parameters are then introduced which demonstrate the role of dispersion state and aspect ratio on the percolation threshold of the composite in agglomerated MWCNT composites. The two parameters are \( \varepsilon \) (equation 7.4), which represents the local volume fraction of MWCNTs and \( \xi \) (equation 7.5), which is the volume fraction of agglomerated MWCNTs.

\[
\varepsilon = \frac{n V_{\text{CNT}}}{\pi D^2} \left( \frac{6}{\pi D^2} \right)
\]

(7.4)

\[
\xi = \frac{\frac{V_{\text{sol}}}{L} \sum_{i} n_i V_{\text{CNT}}}{V_{\text{filler}}}
\]

(7.5)

\( P < \varepsilon < 1 \) and \( 0 < \xi < 1 \) when \( n \geq 2 \)

The higher the value of \( \varepsilon \), the more closely packed the nanotubes are in an agglomerate. When \( \varepsilon \) is 1 then the agglomerate is so closely packed that no polymer can penetrate it. When \( \xi \) is 1 this means that all of the nanotubes exist as agglomerates whereas if \( \xi \) is 0 then all of the nanotubes exist as individually dispersed nanotubes. For ultra-low percolation levels \( \xi \) should be as close as possible to 0 and \( \varepsilon \) should be as close as possible to \( P \).
In real composites there is a mixture of perfectly dispersed nanotubes and nanotubes in the form of spherical agglomerates. In this case the equation for percolation can be simplified to equation 7.6:

$$P_c = \frac{\xi \pi}{6} + \frac{(1-\xi)21.195}{\alpha^2}$$

(7.6)

This equation can be used to predict the percolation threshold of CNT composites when there is a mixture of agglomerates and individual CNTs, if the aspect ratio of the nanotubes is known.

The model proposed from [150] was backed up by experimental work of their own and from other research groups [129, 131, 151-153]. They related the percolation threshold of a composite to the aspect ratio of the nanotubes using different values of $\xi$ and $\alpha$ as shown in figure 7.17.

For simplicity the two parameters $\xi$ and $\alpha$ can be taken as equal. For a shear mixing process such as the one used in this study the parameters were considered to be between 0.05 and 0.1 from experimental findings. From the manufacturers data sheet the MWCNTs used in this study were a maximum of 50 nm in diameter and 20 $\mu$m in length the aspect ratio would be 400. Reading off from the graph at an aspect ratio of 400 (and following the curves for $\xi$ =0.1 and $\alpha$ and $\xi$ =0.05) the percolation threshold should be between ~0.05 vol% and ~0.2 vol%. This is equivalent to ~0.08 wt% and ~0.32 wt% respectively. This seems reasonable since a percolation threshold is reached using 0.1wt% MWCNTs in this study.

Figure 7.17: The relationship between percolation threshold and aspect ratio of MWCNTs adapted from [150]. Different methods of dispersion will alter the values of $\xi$ and $\alpha$. For a shear mixing process used in my investigation the parameters should have values of 0.05-0.1 according to [150]. The aspect ratio of the MWCNTs used in this study was ~400. Reading off from the curve the percolation threshold should be between 0.05 and 0.2 vol% for MWCNTs with an aspect ratio of 400 when $0.05<\xi, \alpha<0.1$. 
7.6 GNP Reinforced Epoxy Resin Composites

A loading of 0.1 wt% of GNPs was shear mixed into epoxy resin for different lengths of time (1 hour and 2 hours). Five different shear mixing speeds were used (1000 rpm to 5000 rpm at intervals of 1000 rpm) for each mixing time. Therefore 10 samples were made in total with each sample consisting of a minimum of three specimens. An additional mixing speed of 9000 rpm was added later to see if this had a significant impact on results. The results are plotted in figures 7.18, 7.19 corresponding to 1 hour and 2 hours mixing time respectively. Note that a 10 minute mixing time was not used for GNPs because previous experiments on MWCNTs and EG had shown 10 minutes to be the least effective mixing time for both mechanical and electrical properties. The curves plotted are the average conductivity across the minimum three specimens in each sample.

None of the GNP reinforced epoxy resin samples reach percolation as illustrated by the fact none of the curves become independent of frequency. Therefore it would appear that 0.1 wt% is well below the percolation threshold for these samples. In order to determine the percolation threshold of the GNP reinforced epoxy resin samples, the loading of GNPs was increased from 0.1 wt% to 5 wt%. The results are plotted in figure 7.20 and demonstrate that even at a loading of 5 wt% no percolation is achieved. An additional sample was made using 10 wt% GNPs (figure 7.21) and at this loading percolation is achieved in one of the specimens from the sample (‘10wt% GNP Specimen 4’). None of specimens 1-3 achieved percolation however.

Figure 7.18: Conductivity of GNP reinforced epoxy resin shear mixed for 1 hour at different speeds. None of the samples reach percolation.
Conductivity of GNP reinforced epoxy resin shear mixed for 2 hours. None of the samples reach percolation and the curves appear very similar to neat epoxy resin. Thus GNP appears ineffective at transferring conductivity to epoxy resin at 0.1wt% loading regardless of shear mixing time.

Figure 7.19: Conductivity of GNP reinforced epoxy resin shear mixed for 2 hours. None of the samples reach percolation and the curves appear very similar to neat epoxy resin. Thus GNP appears ineffective at transferring conductivity to epoxy resin at 0.1wt% loading regardless of shear mixing time.

Figure 7.20: Variation of conductivity with loading weight of GNP. Even samples with 5 wt% GNP did not reach percolation. GNP appears the least effective nanofiller for electrical conductivity enhancement.
Figure 7.21: Conductivity of the four specimens which make up the 10 wt% GNP reinforced epoxy resin samples. Only Specimen 4 reached percolation. This shows there is a large scatter in results between individual specimens of the same sample. The shear mixing speed was 5000 rpm and mixing time was 1 hour.

It is clear that GNPs are the worst performer of the three nanoparticles when it comes to improving the conductivity of epoxy resin. But why is this so? In the next section this question will be discussed by using a theoretical model [154] which has successfully predicted percolation thresholds in GNP reinforced polymer composites.

7.7 Modelling of GNP Reinforced Epoxy Resin Composites

The model proposed by [154] which will be used in this analysis has successfully predicted the percolation threshold of several experiments [42, 64, 155-157]. The model assumes that GNPs take the form of discs of diameter $D$, and thickness $t$. The percolation threshold (in terms of volume fraction) is given by equation 7.7:

$$P_c = \frac{27\pi D^2 t}{4(D + IPD)^3} \quad (7.7)$$

The interparticle distance (IPD) required for conduction to take place via quantum mechanical tunnelling is 10 nm. Therefore, since $D >> IPD$ the formula can be simplified to equation 7.8:
\( p_c = \frac{27\pi}{4D} = \frac{21.195}{\alpha} \)  \hspace{1cm} (7.8)

\( \alpha \) is the aspect ratio of the GNPs and is calculated using equation 7.9

\[ \alpha = \frac{D}{t} \]  \hspace{1cm} (7.9)

If we take the value of D and t as claimed by the manufacture as 25 \( \mu \text{m} \) and 6 nm respectively, then the aspect ratio \( \alpha \), is:

\[ \alpha = \frac{D}{t} = \frac{25000}{6} = 4167 \]

The percolation threshold \( p_c \) (as a volume fraction) can then be calculated using equation 7.8

\[ p_c = \frac{21.195}{4167} = 0.005 \]

The percolation threshold here is given as a volume fraction of 0.005. In order to convert a volume fraction to a weight fraction equation 7.10 is used:

\[ \text{wt\%}_f = \frac{\rho_{\text{GNP}} \times V_f}{\rho_E + (\rho_{\text{GNP}} - \rho_E) \times V_f} \times 100 \]  \hspace{1cm} (7.10)

\( \rho_{\text{GNP}} \) is the density of GNPs taken as 0.54 g cm\(^{-3}\) (please see appendix for calculation of density)

\( \rho_E \) is the density of epoxy resin taken as 1.10 g cm\(^{-3}\)

\( V_f \) is the volume fraction of GNPs in epoxy resin

Using equation 7.10 a volume fraction of 0.005 is equivalent to 0.25 wt\% of GNPs. However, from these results percolation is only achieved at 10 wt\% which using equation 7.10 is equivalent to a volume fraction of 0.037 (3.70 volume \%). Why is there this discrepancy? According to equation 7.8 the aspect ratio of the GNPs which results in a percolation threshold of 3.70 volume\% should be:

\[ \alpha = \frac{21.195}{0.037} = 573 \]

The manufacturer’s estimated aspect ratio of 4167 is in fact an order of magnitude bigger than the aspect ratio of 573 predicted by the model. In order to satisfy an aspect ratio of 573 it would mean that the dimensions of the GNPs are not the same as those provide by the manufacturer. For example if the initial lateral size of the GNPs is 25 \( \mu \text{m} \) as claimed by the manufacturer then the thickness of the GNPs must be equal to 0.044 \( \mu \text{m} \) to satisfy an aspect ratio of 573. However, the manufacturer claims that the thickness of the GNPs is 6-8 nm. Again why is there a discrepancy between the model and the manufacturer’s claims? One reason could be that the manufacturer’s
measurements are incorrect or agglomeration has occurred which has reduced the aspect ratio of the GNPs. Another reason could be that shear mixer has reduced the lateral size of the GNPs. The final possibility is that the model is incorrect.

In order to discuss this, the thickness of the agglomerates was measured to see if they matched the manufacturer’s claim of 6-8 nm. AFM was employed to measure the thickness of the agglomerates. An AFM image of a dispersion of GNPs on a silicon wafer is presented in figure 7.22. The image shows the topology of one agglomerate labelled at the centre of the image. The height profile of the agglomerate is measured along the x and y axis of the image and shows that the thickness of the agglomerate is \(~0.17\) \(\mu\)m. The maximum lateral dimension of the agglomerate was measured using the software as 19 \(\mu\)m.

**Figure 7.21:** AFM image of a GNP agglomerate on a silicon wafer substrate after being shear mixed at 5000 rpm for 1 hour in epoxy resin. The agglomerate is number 16 from table 7.1. The height profile of the flake in the x and y profiles below the AFM image shows the flake is approximately 0.17 \(\mu\)m.
A total of 17 agglomerates were measured the results of which are recorded in table 7.1. The aspect ratio of each agglomerate was calculated. The average lateral dimension across the 17 agglomerates is 26 µm which is close to the manufacturer’s claim of 25 µm. However, the average thickness is 0.32 µm (320 nm) which is well above the 6-8 nm claimed by the manufacturer. Therefore the true aspect ratio is not 4167 as predicted by the manufacturer but two orders of magnitude less than this. The average aspect ratio is 96 when calculated using the AFM images.

**Table 7.1: Dimensions of 17 agglomerates measured using AFM and their aspect ratios**

<table>
<thead>
<tr>
<th>Agglomerate number</th>
<th>Maximum thickness of agglomerate (µm)</th>
<th>Maximum lateral dimension of agglomerate (µm)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.19</td>
<td>65</td>
<td>342</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>17</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>0.33</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>0.70</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>0.19</td>
<td>19</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>0.19</td>
<td>19</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>0.25</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>10</td>
<td>0.31</td>
<td>9</td>
<td>29</td>
</tr>
<tr>
<td>11</td>
<td>0.30</td>
<td>18</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>0.16</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>0.30</td>
<td>21</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>0.32</td>
<td>75</td>
<td>234</td>
</tr>
<tr>
<td>15</td>
<td>0.63</td>
<td>29</td>
<td>46</td>
</tr>
<tr>
<td>16</td>
<td>0.17</td>
<td>19</td>
<td>112</td>
</tr>
<tr>
<td>17</td>
<td>0.80</td>
<td>38</td>
<td>48</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.32</strong></td>
<td><strong>26</strong></td>
<td><strong>96</strong></td>
</tr>
</tbody>
</table>

The Percolation threshold using the new aspect ratio of 96 can be calculated:

\[ P = \frac{21.195}{96} = 0.22 \]

A percolation volume fraction of 0.22 is expected which is equivalent to 22% volume percentage. Converting volume % to weight percentage using equation 7.10 gives an estimated percolation
threshold of 12 wt% which is reasonable considering the experimentally determined percolation threshold of GNP reinforced epoxy resin composites was determined to be 10 wt%.

Therefore the reason for the high percolation threshold of GNPs is because their aspect ratio is much lower than claimed by the manufacturer. The model is in reasonable agreement with the experimental results.

7.8 Summary

This chapter compared the electrical conductivity of three different nanoparticles dispersed into epoxy resin.

- MWCNTs were most effective at improving the electrical conductivity of epoxy resin. Using a shear mixing process percolation was achieved using 0.1 wt% of MWCNTs whereas GNPs performed poorly in comparison and did not reach percolation until 10 wt% was used.
- Shear mixing as a process does not produce agglomerates of consistent sizes. Agglomerates range from less than 10 µm to over 100 µm regardless of the speed and time of shear mixing. The large spread in agglomerate size means it is difficult to see any pattern between the speed and time of shear mixing and the conductivity of the MWCNT and EG composites.
- GNPs were the poorest performer when it came to enhancing conductivity of epoxy resin. The main reason for this is because of the poor physical connectivity between individual flakes.
- AFM results appear to show that GNPs are poorly exfoliated and have an average thickness of 320 nm instead of the 6-8 nm claimed by the manufactured.

7.8.1 Comparison of Results with the Literature

Referring back to table 3.2, it is clear that the percolation thresholds of much of the literature [128] [38] [39] [37], are much lower that the percolation threshold achieved in this study for GNP reinforced epoxy resin. In addition the maximum DC conductivity of the same cited literature is superior to the maximum DC conductivity achieved in this study which was ~4 x 10^{-6} S m^{-1} at 10 wt% loading.

One of the reasons suggested why the results of this study are much lower than the results of the literature, is because inefficient exfoliation of the GNPs had taken place during shear mixing. In this study only unfunctionalised GNPs were tested, whereas in investigations [38] [39] and [128] GNPs had been functionalised which could have aided the exfoliation process. Other investigations [158]
and [37] appear to show that the three roll mill technique is a good method of exfoliation without reducing the lateral sizes of the GNPs. However, this technique was not used in this study because the epoxy resin used was not viscous enough to be processed as it kept falling in between the rollers.

It would be useful to have tested the electrical conductivity of the C750 grade GNPs which had been functionalised with oxygen. It is known that adding oxygen functionality to graphene reduces the conductivity of the individual platelets. However, oxygen functionality could help in the exfoliation process leading to a better exfoliation of GNPs and therefore improving the chance of percolation. Therefore comparing the results of the literature with this study is difficult since in the majority of the literature the GNPs were functionalised, whereas in this study the GNPs were unfunctionalised.
8 Conclusions

In this chapter the main findings of the project and recommendations for further work are summarised. The conclusions are split into mechanical and electrical findings.
8.1 Overall Summary

In chapter 1 the aims and objectives of the project were set out. The first objective of the project was to improve the fracture toughness and tensile strength of epoxy resin in order to enhance the through thickness damage tolerance of composites. The second objective of the project was to improve the conductivity of epoxy resin to help with damage detection in the through thickness direction of composites.

With regards to the first aim, the results show that small improvements were made to the tensile strength of epoxy resin; however they are not significant enough to replace existing engineering materials. In spite of these modest improvements the experiments have provided a basis to carry out future research and there is a better understanding of why the improvements have been lower than expected which will help future researchers make a more significant impact. Therefore the project has not been fruitless and we are a step closer to understanding how to harness the potential of graphene from a composites perspective.

In terms of the fracture toughness of epoxy resin it is very difficult to make a conclusion because of difficulties in carrying out the test to the standard (ASTM D5045-99). Making a crack of a consistent size was a tricky process and further trials are required to ensure reliability of data.

The main findings from a mechanical perspective are summarised below.

- The addition of unfunctionalised GNP s to epoxy resin reduces its tensile strength. The tensile strength dropped by ~50% with the addition of 5 wt% GNP s. Evidence suggests this was due to the lack of chemical bonding between the GNP s and the epoxy resin.
- Changing shear mixing processing conditions had very little impact on the mechanical properties of the GNP reinforced epoxy resin composites. There was no clear relationship between the speed of shear mixing and duration of shear mixing on the mechanical properties.
- No agglomeration of GNP s occurs during curing. This is important because if GNP s can be exfoliated during processing they will not restack during curing.
- The use of acetone as a solvent during mixing of the GNP s in epoxy resin appears to improve the Young’s modulus of the nanocomposites by ~17% when 5 wt% GNP s is added. However, no explanation has been established why this occurs. One suggested reason is that the acetone functionalises the GNP s during shear mixing which improves the adhesion of the GNP s with epoxy resin.
• Using surfactant to improve dispersion of GNP can improve the tensile strength of the epoxy resin. However, the improvements are small (<5%) and only occurs when small amounts of GNP are used <0.1wt%.

With regards to the second aim of the project, the addition of GNP to epoxy resin made very little improvement to the conductivity of epoxy resin. A maximum conductivity of $4 \times 10^{-6} \text{ S m}^{-1}$ was achieved when 10 wt% GNP were added. Much better results were obtained when MWCNTs were added to epoxy resin. A maximum conductivity of $2 \times 10^{-4} \text{ S m}^{-1}$ was measured at a 1 wt% loading of MWCNTs.

The effect of shear mixing speed and time had no effect on GNP reinforced epoxy resin composites, but for the MWCNT reinforced epoxy resin composites, shear mixing for 1 hour or 2 hours produced better conductivities than shear mixing for 10 minutes. In addition, as the time of mixing increased so too did the consistency in results between individual specimens in a sample. There was less scatter between specimens in 2 hour mixed samples compared to specimens in 10 minute mixed samples.

EG samples performed better than GNP but not as well as MWCNTs. The shear mixer was not able to break own the EG particles to a uniform size.

8.2 Recommendations for Further work

This study has highlighted several areas which should be investigated in order to make future improvements in performance of GNP reinforced epoxy resin composites.

• Calculation of wetting angle of epoxy resin (before curing) on GNP and functionalised GNP. The wetting angle, explained in section 3.2, is an important factor controlling the interface and performance of reinforcements in epoxy resin. Improving the wetting of GNP with epoxy resin is crucial to improving their performance and understanding the factors which enhance the wetting should be studied.

• Calculation of Hildebrand and Hansen solubility parameters of epoxy resin. The importance of these parameters for stable dispersions was outlined in section 3.1.3. There is no published data on the numerical values of solubility parameters of epoxy resin so it would be useful to have these to determine how stable epoxy resin is to carry out exfoliation. In this investigation stability of GNP in epoxy resin was carried out by eye but it would be better to have numerical values to compare them against other solvents.
• Understanding the effect of three roll milling on dispersion. This study used shear mixing and sonication as the methods of dispersing GNP s into epoxy resin but it did not use the three roll mill. It would be useful to compare the three roll mill technique with the other mixing techniques to see which is more effective. A higher viscosity resin (> 10 Pa s) would be required for this investigation because low viscosity resins slip through the gaps in the rollers.

• Investigation of plasma functionalisation of GNP s to tailor the interface to improve its compatibility with epoxy resin. Plasma functionalisation has been used to modify surfaces and provide protective coatings in many industries. The same technique could be used to modify the surface of GNP s in a controlled manner without damaging the GNP s. Different chemical groups could be attached to the surface of GNP using this method which could translate to an improved interface with epoxy resin and better mechanical properties.

• Improving the method of crack initiation for fracture toughness specimens to make the test more reliable. Fracture toughness results were presented in this investigation but the results did not match the manufacturer’s data sheet. Crack initiation was hard to standardise and cracks that were created were not of a uniform depth. A machined crack would be a better way of making standardised specimens.

• Investigation into the effect of processing on the thickness of GNP s when they are embedded in epoxy resin. The key to improving the electrical conductivity of GNP s epoxy resin composites is to reduce the thickness of the flakes whilst maintaining the lateral dimensions. An investigation into the effects of shear mixing sonication and three roll milling on the thickness of the GNP s should be undertaken.
8.3 Appendix

8.3.1 Calculation of density of M25 grade GNPs

The density of M25 grade GNPs was calculated using a volume displacement technique. In short a fixed weight of NMP (44.46 g) was added to 100 ml measuring cylinder (NMP was chosen because the GNPs become evenly distributed in the NMP and also because the NMP has a boiling point of 205°C so would not evaporate or vaporise during measurement). M25 grade GNPs were weighed in a plastic boat (1.3511g). The GNPs were transferred to the measuring cylinder. Some of the GNPs stuck to the sides of the wall of the measuring cylinder rather than mixing into the NMP. Therefore extra NMP (20.10g) was added to wash down the GNPs from the sides of the walls.

Total mass of NMP added = 44.46 + 20.10 = 64.56 g

Volume of NMP added = mass x density of NMP = 64.56 x 1.03 = 66.4968 ml

Volume of NMP and GNPs read off by eye on the measuring cylinder = 69 ml

Therefore volume of 1.3511g of GNPs = 69 − 66.4968 = 2.5032 ml

\[
\text{Density of GNPs} = \frac{\text{mass}}{\text{volume}} = \frac{1.3511}{2.5032} = 0.54 \text{ g cm}^{-3}
\]

8.3.2 AFM Measurements for the calculation of the aspect ratio of GNPs

The images below were used to calculate the average aspect ratio of M25 grade GNP shown in table 7.1. The agglomerates which were measured are labelled 1 to 17 and the maximum thickness and lateral dimension was recorded.
X Profile: $\Delta X = 3480.6714 \text{ } \mu\text{m}; \Delta Z = -0.6742 \text{ } \mu\text{m}$

Y Profile: $\Delta X = 2590.7773 \text{ } \mu\text{m}; \Delta Z = -0.7196 \text{ } \mu\text{m}$
**X Profile:** $\Delta X = 3480.6714 \ \mu m; \ \Delta Z = -0.6905 \ \mu m$

**Y Profile:** $\Delta X = 2590.7773 \ \mu m; \ \Delta Z = -0.7279 \ \mu m$
X Profile: $\Delta X = 3480.6714 \, \mu m$, $\Delta Z = -0.6751 \, \mu m$

Y Profile: $\Delta X = 2330.9787 \, \mu m$, $\Delta Z = -0.7012 \, \mu m$
X Profile: \( \Delta X = 3480.6714 \mu m; \Delta Z = -0.6861 \mu m \)

Y Profile: \( \Delta X = 2330.9787 \mu m; \Delta Z = -0.7288 \mu m \)
X Profile: $\Delta X = 3480.6714 \, \mu m; \Delta Z = -0.6968 \, \mu m$

Y Profile: $\Delta X = 2360.3310 \, \mu m; \Delta Z = -0.7273 \, \mu m$
X Profile: \( \Delta X = 3475.2117 \, \mu m; \Delta Z = -0.6779 \, \mu m \)

Y Profile: \( \Delta X = 2379.6909 \, \mu m; \Delta Z = -0.7010 \, \mu m \)
8.4 References


191


J. B. Bai and A. Allaoui, "Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites—


