Multiscale Carbon Fibre Composites with Epoxy-Graphite Nanoplatelet Matrices

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<td>A</td>
<td>Surface area</td>
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<td>B</td>
<td>Specimen thickness</td>
</tr>
<tr>
<td>d</td>
<td>Depth of beam</td>
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<tr>
<td>D</td>
<td>Maximum deflection</td>
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<td>$E'$</td>
<td>Dynamic storage modulus</td>
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<td>$K_{1C}$</td>
<td>Fracture toughness</td>
</tr>
<tr>
<td>$K_Q$</td>
<td>Stress intensity factor</td>
</tr>
<tr>
<td>L</td>
<td>Support span</td>
</tr>
<tr>
<td>$m$</td>
<td>Gradient from the compliance calibration curve</td>
</tr>
<tr>
<td>$M_f$</td>
<td>Final mass of the specimen after digestion</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Initial mass of the specimen</td>
</tr>
<tr>
<td>p</td>
<td>Particle loading</td>
</tr>
<tr>
<td>$p_c$</td>
<td>Critical percolation loading</td>
</tr>
<tr>
<td>$P_{GNPs}$</td>
<td>GNPs loading</td>
</tr>
<tr>
<td>$P_m$</td>
<td>Maximum load</td>
</tr>
</tbody>
</table>
\( P \)  
Load

\( p_m \)  
Density of the specimen

\( R \)  
Rate of crosshead motion

\( t \)  
Exponential constant

\( T_g \)  
Glass transition temperature

\( V \)  
Velocity

\( V_m \)  
Matrix volume fraction

\( V_v \)  
Void volume fraction

\( V_f \)  
Fibre volume fraction

\( W \)  
Specimen width

\( W_r \)  
Fibre content weight percentage

\( W_m \)  
Matrix content weight percentage

\( X_1 \)  
DGEBF content in a DGEBF/TGPAP blend

\( X_2 \)  
Stoichiometry of amine:epoxy

\( \Delta H \)  
Enthalpy of reaction

\( \eta \)  
Viscosity

\( \tau \)  
Shear stress

\( \gamma \)  
Shear strain

\( \omega \)  
Frequency

\( \delta \)  
Phase angle

\( Z \)  
Rate of straining of the outer fibre

\( \sigma_f \)  
Stress in the outer fibres

\( \varepsilon_f \)  
Strain in the outer surface

\( \sigma \)  
Specific conductivity

\( \phi \)  
Instrument’s work function
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>APTS</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>Graphite Nanoplatelets Modified APTS</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>Graphite Nanoplatelets As-received</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electrons</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon Fibres</td>
</tr>
<tr>
<td>CNFs</td>
<td>Carbon Nanofibres</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CAI</td>
<td>Compression after Impact</td>
</tr>
<tr>
<td>CCD</td>
<td>Central Composite Design</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>DCB</td>
<td>Double Cantilever Beam</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl Ether of Bisphenol A</td>
</tr>
<tr>
<td>DGEBF</td>
<td>Diglycidyl Ether of Bisphenol F</td>
</tr>
<tr>
<td>DDS</td>
<td>4, 4’-Diaminodiphenyl Sulfone</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic Mechanical Thermal Analysis</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of Experiments</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>ECT</td>
<td>Edge Crack Torsion</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray</td>
</tr>
<tr>
<td>ENF</td>
<td>End Notch Flexure</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic Deposition</td>
</tr>
<tr>
<td>GIC</td>
<td>Graphite-Intercalated-Compound</td>
</tr>
<tr>
<td>GF</td>
<td>Glass Fibre</td>
</tr>
<tr>
<td>GPS</td>
<td>3-glycidyloxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>GNPs</td>
<td>Graphite Nanoplatelets</td>
</tr>
<tr>
<td>ILFT</td>
<td>Interlaminar Fracture Toughness</td>
</tr>
<tr>
<td>ILSS</td>
<td>Interlaminar Shear Strength</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>LVR</td>
<td>Linear Viscoelastic Region</td>
</tr>
<tr>
<td>MARS</td>
<td>Modular Advanced Rheometer System</td>
</tr>
<tr>
<td>MDI</td>
<td>4, 4’-Methylene Diphenyl Diisocyanate</td>
</tr>
<tr>
<td>mGNPs</td>
<td>Modified GNPs</td>
</tr>
<tr>
<td>MTHPA</td>
<td>Methyl Tetrahydrophthalic Anhydride</td>
</tr>
<tr>
<td>NCs</td>
<td>Nanocomposites</td>
</tr>
<tr>
<td>NDT</td>
<td>Non-destructive Test</td>
</tr>
<tr>
<td>NMP</td>
<td>1-Methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PMCs</td>
<td>Polymer Matrix Composites</td>
</tr>
<tr>
<td>PP</td>
<td>Isotactic Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PW</td>
<td>Processing Window</td>
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<tr>
<td>RFI</td>
<td>Resin Film Infusion</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Methodology</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium Dodecylbenzene Sulfonate</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SENB</td>
<td>Single Edge Notch Bending</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TGPAP</td>
<td>Triglycidyl-(p)-Aminophenol</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Polyoxyethylene Octylphenylether</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>Graphite Nanoplatelets Modified Triton X-100</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>Graphite Nanoplatelets Unmodified</td>
</tr>
<tr>
<td>VARTM</td>
<td>Vacuum Assisted Resin Transfer Moulding</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>1D</td>
<td>1-Dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>2-Dimensional</td>
</tr>
<tr>
<td>4ENF</td>
<td>4 Point End Notch Flexur</td>
</tr>
</tbody>
</table>
Abstract

The University of Manchester
Ramli Junid
Doctor of Philosophy
Multiscale Carbon Fibre Composites with Epoxy-Graphite Nanoplatelet Matrices
September 2016

This thesis reports the effects of incorporating graphite nanoplatelets (GNPs) to epoxy-carbon fibre (CF) laminates to produce multiscale composites. A grade of epoxy resin typical for the application in aerospace engineering, triglycidyl-p-aminophenol (TGPAP), was used in this work cured with 4,4’-diaminodiphenyl sulfone (DDS). To improve the processability of TGPAP, a diluent, the diglycidyl ether of bisphenol F (DGEBF), was added to formulations. Compositions of TGPAP/DGEBF/DDS were optimised using response surface methodology (RSM) with the target response being to obtain high glass transition temperature ($T_g$) and low resin viscosity. From RSM, the optimum values were obtained at 55.6 wt. % of DGEBF and a stoichiometric ratio of 0.60. Before addition into epoxy, GNPs were treated either covalently using 3-aminopropyltriethoxysilane (APTS) or non-covalently using a commercial surfactant, Triton X-100 (abbreviated as A-GNPs and T-GNPs, respectively). After treatment, XPS analysis showed a new peak at 100 eV for A-GNPs indicating silicon and the C/O ratio increased from 11.0 to 26.2 for T-GNPs relative to unmodified GNPs (U-GNPs), suggesting attachment of the modifier molecules had occurred. Nanocomposites (NCs) were prepared by incorporate GNPs into epoxy using mechanical mixing. Rheological percolation threshold of GNP-epoxy suspensions were determined using oscillatory-shear rheometry as 3.9 wt. % for AR-GNPs, 3.6 wt. % for U-GNPs, 3.2 wt. % for A-GNPs and 3.5 wt. % for T-GNPs, suggesting surface treatment improved dispersion. At 4 wt. % of GNPs, flexural strain of NCs was decreased relative to neat epoxy by 46% for AR-GNPs, 48.6% for U-GNPs, 4.6% for A-GNPs and 30.8% for T-GNPs but flexural moduli showed small increases of 6.1-7.4%. Fracture toughness ($K_{IC}$) also improved. For example, the $K_{IC}$ increased from 0.80 ± 0.04 MPa.m$^{1/2}$ for neat epoxy to 1.32 ± 0.01 MPa.m$^{1/2}$ for NCs containing 6 wt. % of U-GNPs possibly due to the branching of cracks resulting from the embedded GNPs. Due to their mechanical performance, A-GNPs were used to fabricate epoxy/CF/A-GNPs multiscale composites. Multiscale composites showed inferior properties relative to a comparable conventional composite in flexural testing, interlaminar shear strength (ILSS) and interlaminar fracture toughness mode II ($G_{IIc}$) due to weaker bonding at the matrix-CF interface. However, multiscale composites showed ~40% higher capability than conventional composite to absorb energy during impact due to greater interfaces formed by the inclusion of A-GNPs into the system.
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Chapter 1  Introduction

1.1  Introduction

Polymer matrix composites are used widely in numerous applications since they can offer high strength combined with lower weight and often lower cost compared to other engineering materials [1]. In aerospace engineering, advanced polymer-fibre composites are now used to make many parts for structural applications, for example fuselage structures, wings, tails and doors as well as satellite structures and missile components [2], [3]. Typically, high-functionality epoxy resins with a high crosslinking capability, such as triglycidyl-p-aminophenol (TGPAP) cured with 4,4’-diaminodiphenyl Sulphone (DDS), are used as the composite matrices for aerospace engineering as this type of epoxy has a high glass transition temperature ($T_g$) and therefore may be used at relatively high temperatures. However, the viscosity of this type of resin is high and they are not easy to process. Therefore, mixing with other epoxy resins with lower viscosity is of current interest. Even though the most common epoxy resins, based on the diglycidyl ether of bisphenol A (DGEBA), are of low viscosity it is considered in the industry that resins based on the diglycidyl ether of bisphenol F (DGEBF) are a better choice to be mixed with TGPAP. This is because DGEBF has a lower viscosity than DGEBA but offers the same strength and forms a miscible epoxy blend with TGPAP [4].

The prime requirement of advanced polymer fibre composites for aerospace applications is for excellent mechanical and physical properties. However, this requirement is compromised by the delamination behaviour of these laminar composites and their inherent brittleness in matrix-dominated fracture due to the behaviour of the highly crosslinked matrices [5], [6]. In service, epoxy-fibre composites could experience loadings of varying modes in various directions [7]. In order to improve fracture behaviour, incorporating nanoscale-size fillers has been proposed since they have been shown to enhance mechanical properties of polymer for example, fracture toughness [8], [9]. In this respect, a nanomaterial based on carbon is an attractive prospect due to their low density and excellent mechanical
properties. Graphite nanoplatelets (GNPs) are to be used in this work. GNPs have high surface area and have been shown in polymer-GNP nanocomposites to improve properties compared to the unfilled polymer [10], [11]. The idea proposed is that GNPs will be added into conventional epoxy/carbon fibre composite to form a multiscale composite. Therefore, multiscale composite that will be developed in this work will consist of epoxy and two types of reinforcements, microscale carbon fibre and nanoscale GNPs.

In order to optimize the use of GNPs in composites, surface modification or functionalisation can be performed to introduce interactive groups onto the surface of GNPs. Surface-modified GNPs, with new adsorbed and/or bonded functional groups, were reported to strengthen interfacial adhesion between the nanofiller and the polymer matrix [12].

1.2 Aims and Objectives

The aim of this study is to introduce GNPs into conventional epoxy/carbon fibre composites to form a multiscale composite and study their effect on physical and mechanical properties. To achieve this aim, the objectives of this work are:

i. Optimise an epoxy blend using response surface methodology (RSM) by varying DGEBF content in TGPAP/DGEBF mixtures and the stoichiometric ratio of amine to epoxy to achieve high $T_g$ and low viscous epoxy.

ii. Modify the surface structure of the GNP by covalent and noncovalent methods and characterise these GNPs to observe the effects of treatment.

iii. Incorporate unmodified and modified GNPs into the epoxy resin blends and investigate the effects of treatment on the rheological behaviour of their suspensions.

iv. Study the processing and properties of cured epoxy/GNP nanocomposites reinforced with unmodified and modified GNPs.

v. Use selected epoxy/GNPs nanocomposites as matrices with carbon fibre (CF) to manufacture multiscale laminated composites.
vi. Investigate the effects of GNP addition on the properties of multiscale epoxy/CF/GNP composites.

1.3 Thesis Structure

This thesis consists of 7 chapters. Chapter 2 is a literature review of the subject and matter of this research work. These previous studies provide the basis for processing choices, analysis and discussion in this work.

Chapter 3 describes the materials, equipment and methodology used to prepare samples and to carry out characterisations. This chapter includes the techniques used to modify the GNPs, mixing of epoxy/GNPs, characterisation techniques and processing techniques used to manufacture multiscale composites.

Chapter 4 reports the effects of formulation variables (DGEBF content in the epoxy blend and the stoichiometric ratio of amine hardener to epoxy) on the properties of cured epoxy resins in terms of glass transition temperature, rheological processing window and curing heat of reaction. An optimised epoxy formulation was determined and carried forward into the next stage of work.

Chapter 5 presents the characteristics of treated GNPs and the properties of epoxy/GNPs nanocomposites. This includes changes in elemental composition of GNPs after treatment, rheological behaviour of epoxy/GNP suspensions and properties of cured nanocomposites as a potential matrix for carbon fibre composites.

Chapter 6 reports the manufacturing technique to fabricate epoxy/GNPs carbon fibre multiscale composites. The quality of the manufactured multiscale composites was assessed, their properties were characterised and compared with conventional epoxy/carbon fibre composites by means of mechanical testing.

Chapter 7 contains the conclusions of this study and recommendations for future work.
1.4 Description of the Study

This research therefore combines the studies to optimise TGPAP/DGEBF/DDS blend to achieve high $T_g$ of epoxy resin with low viscosity, characterisation on the effects of GNPs to the properties of nanocomposites and to develop and characterise multiscale composite which consists of epoxy/GNPs/CF.

The novelty of the work in this study was also identified. To the best of our knowledge, blending of DGEBF and TGPAP to form a new type of epoxy resin have not been reported in the literature so far. Most previous studies in the area of epoxy-based composites have used DGEBA as the matrix resin. In addition, response surface methodology (RSM) was used as the method to optimise the epoxy blend. In order to improve interfacial interaction between epoxy and GNPs, other researchers also presented similar method to modify the GNPs using chemical agents. For example, similar methods were reported by Zaman et al. [12] and Meng et al. [13] who applied surface treatment to GNPs and characterised the epoxy nanocomposite by mechanical testing. However, the types of surfactants and modifiers that they have used for the treatment of GNPs are different to those from this work.

Most previous studies in the area of multiscale composites used prepreg moulding [14]–[16], hand lay-up [17]–[19] or vacuum assisted resin transfer moulding (VARTM) [20]–[22] as the method of composite manufacturing. Due to high viscosity of epoxy resin, these methods cannot be applied in this work. Therefore, vacuum assisted resin film infusion (VARFI) was used, in which to the best of our knowledge has not been reported to date. Furthermore, the use of nanoparticles especially GNPs, as additional reinforcement to produce multiscale composite is still relatively new. Previous groups who have used similar systems (epoxy/GNPs/CF) to the system used in this work includes Park et al. [23], Qin et al. [24], Hadden et al. [25] and Cho et al. [5]. However, they did not characterise the multiscale composite by four point end-notched flexure (4ENF) fracture toughness and damage tolerance using compression after impact (CAI) which has been used in this study.
2.1 Epoxy Resins

In polymer matrix composites, thermosetting polymer resins are commonly used as matrices to bind the reinforcements as well as to transfer load during service [26]. In this work, an epoxy resin was used as the matrix. These thermosetting polymers exhibit excellent chemical and corrosion resistance as well as good mechanical strength and thermal properties [27] and consequently are used in many diverse applications including in the automotive industries, electronics (printed circuit boards and semiconductor encapsulants) and as adhesives and composite matrices in aerospace industries [28].

![Epoxy functional group](image)

**Figure 2.1: Epoxy functional group** [29].

Epoxy resins are characterized by the epoxy functional group, a three-membered ring [29] as shown in Figure 2.1. This is a very versatile chemistry and many types of epoxy resins are available in the market suitable for a wide range of applications. Common epoxy resins are typically derived from epichlorohydrin (a highly reactive compound) and these are termed glycidyl-based resin [28]. In this work, two types of epoxy resins were used, the diglycidyl ether of bisphenol F (DGEBF) and triglycidyl-\(p\)-aminophenol (TGPAP).

2.1.1 Diglycidyl Ether of Bisphenol F (DGEBF)

Traditionally, the diglycidyl ether of bisphenol A (DGEBA) is the most commonly used epoxy resin [30], [31]. DGEBA is a bifunctional resin, in that it has two functional epoxy groups attached to its molecular structure (Figure 2.2a). The diglycidyl ether of bisphenol F (DGEBF) used in this study is another type of bifunctional epoxy resin (Figure 2.2b). DGEBF is a more flexible molecule than
DGEBA, therefore it is reported that the viscosity of DGEBF and the Young’s modulus of cured resins are lower than equivalent DGEBA resin systems [32], [33] but they have greater solvent resistance [34].

![Chemical structure of DGEBA](a) DGEBA

![Chemical structure of DGEBF](b) DGEBF

Figure 2.2: Chemical structure of (a) DGEBA and (b) DGEBF [34], [35].

Epoxies based on bisphenol F are normally used as a diluent to reduce the viscosity of other epoxy resins, especially in systems containing epoxy resins of higher functionality (i.e. >2) [28]. As a diluent, DGEBF can aid processing, for instance allowing for faster degassing (bubble release) with a lower resin viscosity.

2.1.2 Triglycidyl-p-Aminophenol (TGPAP)

TGPAP (Figure 2.3) is a tri-functional epoxy resin with much higher viscosity than DGEBF (typically > 3500 vs. ≈ 1400 mPa s) [36]. Due to its higher functionality compared to DGEBF, reaction between TGPAP and a curing agent [34] forms a highly-crosslinked network with a higher $T_g$ [28]. As a consequence, this cured system is normally brittle [37]. Typically, the inherent brittleness of epoxy resins is improved by adding toughening modifiers, which include thermoplastics and nanomaterials [38]–[40].

![Chemical structure of triglycidyl-p-aminophenol (TGPAP)](Figure 2.3: Chemical structure of triglycidyl-p-aminophenol (TGPAP) [28].)
2.1.3 Crosslinking

Figure 2.4: Chemical structure of 4, 4'-diaminodiphenyl sulfone (DDS) [28].

Epoxy resins cure by crosslinking via chemical reaction to form three dimensional networks. In order to crosslink, epoxy resins typically need to react with a curing agent, most commonly a diamine [28]. Figure 2.4 shows the chemical structure of the 4, 4'-diaminodiphenyl sulfone (DDS) curing agent, the curing agent used in this work. Figure 2.5 shows the reaction scheme between the epoxy groups of the resin and the amine groups of the hardener. The main chemical reactions (a-b) will take place where firstly, a primary amine will react with an epoxy to form a secondary amine and a hydroxyl group. After that, further non-linear (branching) reactions can occur with the secondary amine reacting with an epoxy group [41] to form a tertiary amine. The reaction occurs through the opening of the oxirane ring to form a longer and linear C-O bond [28]. The hydroxyl group produced also may react with the oxirane ring of the epoxy in a branching reaction as shown in Figure 2.5c.

**Figure 2.5:** Amine-epoxy reactions (a-b) and hydroxyl-epoxy reaction (c) [41]. R and R’ are alkyl groups where both need not to be identical [42].
2.2 Nanocomposites

A nanocomposite is a multiphase material where one of the constituents has at least one of its dimensions in the nanoscale (< 100 nm) [44]. In polymer matrix nanocomposites, the reinforcements are nanomaterials (also known as nanofillers). Typically, they exist in several forms such as (Figure 2.6) particles (e.g carbon black), fibrous (e.g. carbon nanotubes) or layered (e.g. layered silicates or graphene) [45], [46]. It has been reported that nanocomposites show distinctive properties compared to neat polymers due to the high surface area of the nanomaterial reinforcements [47]. Typically, the surface area of a nanomaterial is related to the aspect ratio, which defined as the ratio of the length to the diameter (or thickness) of the constituent [48]. Many types of nanofillers have been studied and often the properties of the resulting nanocomposite was found to be significantly improved [49], [50]. To achieve this, researchers have extensively studied processing methods in order to optimize the utilization of the nanomaterials embedded in the polymer matrix. Amongst the critical factors for a nanocomposite is the dispersion of the nanofiller and the interfacial interaction between the filler and the matrix where both have received great attention from researchers. The role of a nanofiller as a reinforcement has been optimised and synergy with another type of nanofiller in

Figure 2.6: Nanofiller reinforcement geometries and formula for surface area/volume [43].
polymer nanocomposites were also studied [51]. In comparison, investigation of carbon fillers has increased dramatically in the last few years. This is true especially for carbonaceous nanomaterials within the graphene family, such as graphite nanoplatelets (GNPs), due to their unique characteristics of high conductivity and strength. In this work, graphite nanoplatelets (GNPs) were used as the nanofiller. Therefore, further discussion in this thesis will emphasize and focus on GNPs as nanoreinforcement.

### 2.2.1 Graphite Nanoplatelets (GNPs)

GNPs are carbon nanoparticles that recently have been used extensively to form polymer nanocomposites. GNPs are also known as graphene nanoplatelets, graphite nanosheets, graphene nanosheets (GNs) and graphite nanoflakes (GNFs).

![Figure 2.7](image-url)

**Figure 2.7:** (a) Acid intercalated graphite (b) expanded graphite by thermal shock (c) pulverized expanded graphite to form GNPs of specific dimensions [52].

Young et al. [53] in their review stated that some popular approaches to producing graphene nanomaterials include mechanical exfoliation, liquid-phase exfoliation, thermal exfoliation and chemical vapour deposition (CVD). The method of thermal exfoliation was however typically used since it is capable of producing grapheme-based nanoparticles in bulk quantities. Preparation by this method was first initiated in 1859 by Brodie [54], who treated graphite with an oxidising mixture of potassium chlorate and fuming nitric acid. Since this work, many similar attempts have followed to form graphitic oxides by using strong oxidation agents containing one or
more concentrated acids. For example, Hummers and Offeman [55] in 1957 used concentrated sulphuric and nitric acids with potassium chlorate to obtain a graphitic oxide. Their method was reported to require less than two hours and was done at temperatures below 45 °C, which was considered much safer than other methods. Nowadays, many studies report similar procedures to that of Hummers and Offeman to obtain GNPs. The steps of the procedure are explained as follows and Figure 2.7 shows the transformation of graphite in each step. Firstly, graphite flakes or powder are intercalated with sulphuric and nitric acids. Some researchers have reported the ratio between those acids is 4:1 [56]. At this point, the intercalated graphite is normally known as a graphite-intercalated-compound (GIC) or acid intercalated graphite (Figure 2.7a). Subsequently, the GIC is exposed to heat in order to expand the intercalated graphene layers. Several methods have been used to thermally expand the GIC which include microwave heating, electric current and thermal shocking (for example placing the GIC in an oven preheated to up to 600 °C-1050 °C) [56]–[58]. This treatment causes the intercalated graphite to decompose and force the graphite layers to separate randomly (Figure 2.7b). This process allows the GIC to expand since it causes both destruction of graphite crystal structure together with an enormous increase in volume in the c direction of the graphite GIC. Some researchers have termed this product as expanded graphite in their published work. Finally, the expanded graphite is pulverized to form GNPs of specific dimensions using an ultrasonic processor or mechanical milling (Figure 2.7c).

![Figure 2.8: Structure of modified GNPs [59].](image-url)
Categorised in the graphene family, GNPs are layered materials of high aspect ratio, which is of benefit in transferring load across the interface within a polymer nanocomposite [12]. GNPs consist of stacks of two-dimensional graphene layers, weakly bonded by van der Waals forces [60]. Figure 2.8 shows the graphene structure which consists of carbon atoms connected in a hexagonal lattice. Other molecules on the surface indicate functional groups that could be attached by treatment, usually to enhance bonding strength between polymer-GNPs interface [47]. For example, amine groups such as -NH\(_2\) and -NH- (Figure 2.8) could be introduced by chemical functionalisation using ethylenediamine and \(p\)-phenylenediamine [61].

Since the discovery of monolayer graphene in 2004, tremendous efforts have been applied to the study of graphene-based nanomaterials [62]. The Young’s modulus of a single graphene layer, as measured by nanoindentation, is ~1 TPa [63] with specific surface area reported to be 2630 m\(^2\)/g [64]. This is coupled with high thermal conductivity (~3080–5150 W m\(^{-1}\) K\(^{-1}\)) [65] and a high electron mobility on its surface (15000 cm\(^2\)/V s) [66]. Due to these excellent mechanical, thermal and electrical properties, carbonaceous nanomaterials within graphene family like GNPs have attracted much interest and are the best candidate to be used as cost-effective carbon nanofillers [67]–[69]. For example, GNPs are reported to be less expensive than CNTs [70], respectively $1.40/kg for GNPs and $1000/kg for CNTs [71]. Their potential for outstanding properties makes GNPs highly suitable for the development of polymer nanocomposites for structural and functional applications.

### 2.2.2 Surface Modification of GNPs

The performance of polymer nanocomposites is determined by three factors: the matrix type, dispersion of the nanofiller and the matrix-filler interface [72]. The polymer-filler interface has attracted extensive research due to its critical effects on both the dispersion of the filler and on the load transfer between the filler and the matrix [73]–[75]. In addition to poor dispersion, the interface interactions between nanofillers and polymer matrices have often been reported as weak [58], [76].
Hence, typically there is a need to improve the polymer-filler interface bonding as well as to improve the dispersion of the nanofillers in the matrix. For example, a study by Li et al. [75] indicated that the presence of functional groups in graphene oxide promoted uniform dispersion and good interfacial stress transfer, giving improvement in mechanical properties of epoxy nanocomposites. To do this, typically a process known as functionalization or surface modification of nanomaterials by chemical or physical methods [77] is often used. In some cases, chemical functionalization was termed as covalent functionalization while physical functionalization was termed as noncovalent functionalization. In this work, both the covalent and non-covalent approaches have been used. Figure 2.9 shows the various interactions which can be formed between carbon nanofiller with polymer matrices including covalent and non-covalent functionalization.

![Figure 2.9: Different interaction of carbon nanofiller with polymer matrices which includes covalent and non-covalent functionalization.](image)

### 2.2.2.1 Covalent Methods

Covalent functionalization treatments have been carried out with the aim to introduce functional groups onto a nanofiller, for instance through oxidation [79], [80] or
amino functionalization [81]. This treatment could give better interfacial interaction between polymer-nanomaterials by improving the wettability of carbon-based particles like GNP s [82]. Covalent functionalization by acid intercalation could be carried out on graphite as one of the methods to produce GNP s. Therefore, GNP s could experience an oxidation process if strong sulphuric and nitric acid were used [83], [84]. In addition, nano-reinforcements in polymer nanocomposites also could be treated covalently by using a coupling agent to improve interfacial compatibility [26]. The silanization process, for instance, is a commonly used method to modify carbon-based nanomaterials [85], using a silane coupling agent such as 3 aminopropyltriethoxysilane (APTS). APTS molecules can be attached covalently on the GNP s surface via a silanization reaction during treatment (Figure 2.10) [84], [86], [87], which ultimately converts the GNP s surface/edges from hydrophobic to hydrophilic allowing dispersion of GNP s more uniformly. Ma et al. [87], for example, grafted CNTs with APTS and the resultant epoxy-CNT nanocomposites showed a significant improvement in mechanical and thermal properties. They reasoned that the improvement was due to grafting of the silane molecules onto the CNTs producing better dispersion of the nanotubes in the epoxy matrix as well as enhancing interfacial interactions. Li et al. [88] also observed an enhancement in Young’s modulus and fracture toughness of epoxy-graphene oxide (GO) nanocomposites modified with APTS. Generally, nanofillers functionalised by covalent method gives stronger interfacial bonds with polymers compared to noncovalent functionalization which results in better composites properties [77], [89].

![Figure 2.10: Schematic of reaction for APTS treatment on nanofiller](image.png)
Even though functionalization by the covalent method is promising in offering improvement in properties for nanocomposites, it has some drawbacks that need to be considered. In particular, the techniques using strong acids are not environmentally friendly and may cause damage to the nanofiller. In some cases, it may fragment the nanofiller into smaller particles which may reduce the performance of nanocomposites due to a reduced aspect ratio [77]. In addition, covalent functionalization may also disrupt the π electrons of carbon atoms and cause weaker transportation of electrons, reducing conductivity.

2.2.2.2 Noncovalent Methods

Noncovalent (or physical adsorption) functionalization is an approach in which the interface between the filler and a polymer matrix can be altered in a safer way as typically, no hazardous chemicals or strong corrosive acids are required. Generally, this technique involves weak forces (π–π interactions) without changing the plane structure of nanofillers [90] (Figure 2.9). Normally, a surfactant will be employed in order to tune the surface of a nanofiller [91], which was reported to impart better mechanical properties to the resultant nanocomposites through improvement in dispersion of GNPs [92]. In addition, GNP aggregates can also be prevented with surface modification using surfactant. Studies related to GNP modification by surfactants were reported by many groups, for instance the use of polyeoxyethylene octylphenylether (Triton X-100) [93], sodium dodecylbenzene sulfonate (SDBS) [94] and polyoxyalkyleneamine [95]. Previously, it has been reported that Triton X-100 is effective in dispersing both CNTs and GNPs [96]. The non-covalent treatment of GNP in this study is based on these studies. For GNPs treated with surfactant, the hydrophobic side of the surfactant can interact with GNPs by adsorption while its hydrophilic side can attach to the epoxy through hydrogen bonding [97]. The adsorption of surfactant on the GNPs surface may lower surface tension, reducing reaggregation. In addition, van der Waals attraction in carbon based nanofillers could be overcome by electrostatic or steric repulsive forces from the surfactant [98]. Figure 2.11 shows the schematic representation of possible mechanisms for the attachment of surfactant on the nanofiller structure [99].
Figure 2.11: Schematic representation of possible mechanism for the adsorption of surfactant on GNP: (a) GNP encapsulated by micelle surfactant (b) hemimicellar adsorption of surfactant and (c) random adsorption of surfactant on GNP [99].

2.3 Epoxy/GNP Nanocomposites

As mentioned previously, GNP are suggested to be used as an additional reinforcement for conventional epoxy/carbon fibre composites. Therefore, it is important to understand the characteristics of epoxy/GNP nanocomposites prior to using them as a matrix for epoxy/carbon fibre/GNP multiscale composites.

2.3.1 Dispersion of GNP in Polymer Resins

According to Thostenson et al. [100], the difference between surface energy and van der Waals forces between a polymer matrix and a nanofiller will cause affinity between the particles, resulting in aggregation of the filler which is undesirable in composite fabrication. In the case of layered nanomaterials, like layered silicates and GNP, dispersion of aggregates (of stacks of the platelets) and exfoliation of the stacks into smaller stacks/individual layers is essential. In order to optimize the performance of the resultant nanocomposite, the particles must also be separated and
distributed throughout the matrix phase. Figure 2.12 shows the dispersion stages of layered nanomaterials in a matrix polymer.

Based on Figure 2.12, the phase separated stage occurs when the stacks of graphite platelets are not penetrated by polymer molecules, resulting in properties in the same range as traditional micro-scale particulate composites [46]. If the polymer molecules penetrate in-between the platelets in the stacks, the term intercalated is applied to the structure. When the platelets are fully delaminated, it is termed as exfoliated [46]. At this stage of separation, the effectiveness of layered nanomaterials as a filler is optimised, as surface-to-volume ratio and aspect ratio are maximised.

Depending on the application of the resultant nanocomposites, the state of dispersion and distribution of nanofiller within a polymer matrix is important in order to meet the final property requirements. For example, in order to improve the electrical conductivity of a polymer matrix, good dispersion accompanied with reasonably good distribution of nanofiller is required. This condition is schematically illustrated

Figure 2.12: Illustration of dispersion stages for layered nanomaterials in a polymer matrix composite [101].
in Figure 2.13c [102], [103]. On the other hand, it is well known that an improvement in mechanical properties requires both good dispersion and distribution as represented in Figure 2.13d.

<table>
<thead>
<tr>
<th>Schematic of Nanofillers Dispersion</th>
<th>State of Dispersion and Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Nanofiller and Matrix</td>
<td>Poor distribution and poor dispersion</td>
</tr>
<tr>
<td>(b) Nanofiller and Matrix</td>
<td>Good distribution but poor dispersion</td>
</tr>
<tr>
<td>(c) Nanofiller and Matrix</td>
<td>Poor distribution but good dispersion</td>
</tr>
<tr>
<td>(d) Nanofiller and Matrix</td>
<td>Good distribution and good dispersion</td>
</tr>
</tbody>
</table>

**Figure 2.13:** Possible states for dispersion and distribution of nanofillers within a nanocomposite matrix [102].

Processing methods have been developed to improve the degree of dispersion and exfoliation of nanomaterials within graphene family including in thermoplastic material [104] and thermosetting resin [58]. In thermosetting resin like epoxy, numerous methods were reported. This includes the use of solvents to reduce the viscosity of the resin for easier processing and dispersion of nanomaterials. Excess solvent is typically evaporated by degassing procedure before cure of the resin. However, use of a solvent during processing followed by drying afterwards is costly,
time-consuming and gives environmental/safety concerns [105]. Melt mixing or melt blending of filler in an epoxy resin is considered more advantageous since no solvent is used. In order to obtain a stable suspension of GNPs, shear mixing and/or sonication are normally applied to disperse and distribute the GNPs [106], [107]. Water bath sonication also can be used for graphene dispersion and it is suitable for low viscosity of resin. It was observed that, as a function of sonication time, the dispersion and stability of suspension containing graphene nanoparticles, improved [108]. In addition, it has been reported that, dispersion technique by mechanical mixing is one of the suitable technique that can be used to disperse nanomaterials within graphene family [108].

2.3.2 Percolation Theory

Percolation theory describes the phenomenon of connected clusters in a random behaviour [109]. To illustrate percolation, often a square lattice as shown in Figure 2.14 is presented with each site of the lattice is occupied randomly by black circles (particles) with probability $p$. On the other hand, the empty site is unoccupied with probability $1 - p$.

![Figure 2.14: Square lattices with two different concentrations of occupied sites with probability, $p$.](image)

If the empty or unoccupied sites are assumed to be insulator and the occupied sites are assumed as electrical conductors, electrical current will be able to flow between
nearest neighbour conductors. At low concentration of $p$ (Figure 2.14a), a small cluster is formed by the conductor sites. The lattice is dominated by the unoccupied sites to give a nonconductive path. At higher concentration of $p$ (Figure 2.14b), a larger cluster of conductor sites was formed. Top and bottom, left and right sides of the lattice are connected with the nearest neighbour conductor sites. Such a cluster is called percolated network [110]. Before the formation of a percolated network, there exists a threshold probability known as the critical loading ($p_c$) where the transition from insulator to conductor occurs. The connectivity of the clusters at this percolation threshold as derived in percolation theory is given as [111]:

$$\sigma = \sigma_c (p - p_c)^t$$

Where $\sigma$ is the electrical conductivity of the composite, $\sigma_c$ is the proportionality constant, $p_c$ is the critical loading, $p$ is particle loading and $t$ is the power law constant which describes the dimensionality of the clusters.

Similarly, in order to be effective as reinforcement in mechanical performance, the amount of particles within a composite needs to reach the critical loading. Typically, interaction between particles and determination of critical loading within suspensions was studied by oscillatory-shear rheometry [112]–[114]. The critical loading or percolation threshold can be predicted to indicate the transition where particles started to connect and form a continuous cluster within a suspension which can be expressed in the following equation:

$$G' = G'_c (p - p_c)^t$$

Where $G'$ is the storage modulus, $G'_c$ is the proportionality constant, $p$ is the GNPs loading, $p_c$ is the critical GNPs loading, and $t$ is the elasticity exponent which is related to stress-bearing mechanisms [113], [114]. The percolation threshold in rheology can be identified as when storage modulus ($G'$) exhibits a plateau at low frequencies [115].
Published work on the rheological behaviour of epoxy/GNPs suspension is rare at the time of this thesis writing. Therefore, other types of system will be used as a reference. For example, Abdel-Goad et al. [116] characterized the rheological behaviour of GNPs nanocomposites using various types of polymers which include polycarbonate (PC), low-density polyethylene (LDPE), isotactic polypropylene (PP), and polystyrene (PS). They studied the rheological behaviour at the mixing temperature during compounding of GNPs and polymer, which was 280 °C for PC while for PP, PS and PE it was 220 °C. They observed that the addition of GNPs into the polymer increased the modulus and viscosity of the mixture. Up to a certain concentration of GNPs, they observed viscous (liquid-like) behaviour which then changed to elastic (solid-like) behaviour as indicated by the formation of a plateau of modulus at lower frequencies. This phenomenon was identified as being due to percolation, the threshold for which was determined to be around 4 wt. % for PC/GNPs, 9 wt. % (PP/GNPs and PS/GNPs) and 12 wt. % for PE/GNPs. The authors stated that the reason for the different values of the percolation threshold for PP, PS and PE is because of variations in the network structure due to different interaction between individual polymers and GNPs. Valles et al. [117] have studied the viscoelastic behaviour of PMMA/GNPs of 5 μm and 20 μm flake size. They found that the 20 μm lateral dimension of the flake significantly increased the viscosity of the system whilst the 5 μm flake did not affect the viscosity significantly. They also determined that the rheological percolation in the system occurred at around 2-5 wt. % of GNPs. Previously, a similar result was reported by Macosko and Kim [118] who showed the dependence of rheological behaviour on the aspect ratio of GNPs for polymer nanocomposites.

2.3.3 Properties of Cured Epoxy Nanocomposites

In regard to improvements in the behaviour of epoxy/GNP nanocomposites (E/G NCs), many researchers have reported improvements in their mechanical, thermal and electrical properties. Therefore discussion of the properties of epoxy nanocomposites (NCs) is focussed on these three areas.
2.3.3.1 Mechanical Properties

Asma and Daniel [57] in 2004 probably were among the earliest who have used GNPs as nanofiller to investigate the mechanical properties of E/G NCs. They used epoxy system based on an anhydride-cured system of diglycidyl ether of bisphenol A (DGEBA) and methyl tetrahydrophthalic anhydride (MTHPA). The advantage of GNPs with layered nanostructure which was known to have high aspect ratio similar to silicate clay (montmorillonite) that can give great improvement to polymer [119] was studied. Tensile tests showed 10% and 25% increases in Young’s modulus for 2.5 wt. % and 5 wt. % of GNPs addition, respectively (Figure 2.15). The authors attributed the improvement due to high aspect ratio and high strength of the GNP. In addition, they also stated that the distribution and good interfacial adhesion between the epoxy/GNPs also contributed to give improved tensile properties of the nanocomposites due to enhanced load transfer between the phases. However, the stress-strain curve in their result shows that the nanocomposites failed at lower strain which indicates more brittle behaviour than the neat epoxy.

![Figure 2.15: Elastic modulus of epoxy/GNP nanocomposites (E/G NCs) as a function of GNPs concentration from past work.](image-url)
A similar trend for modulus in E/G NCs was reported by Zaman et al. [12] who compared NCs containing unmodified GNP (U-GNPs) and NCs containing modified GNP (mGNPs) using 4,4’-methylene diphenyl diisocyanate (MDI). Even though both nanocomposites (NCs) showed increase in modulus, the NCs containing mGNPs (Figure 2.15) exhibited superior properties than NCs containing U-GNPs. Miller et al. [120] also reported similar levels of mechanical performance to compare mGNPs with U-GNPs nanocomposite. They reasoned that the mGNPs resulted in bridging between nanoparticles with matrix molecules which led to stronger adhesion and interface strength. In addition, Zaman et al. [12] also stated that the mGNPs were exfoliated during modification process, increasing the effectiveness of load transfer. However, their results (Figure 2.15) show that the effectiveness of mGNPs was observed to diminish beyond 4 wt. % of loading presumably due to the formation of higher numbers of aggregates which reduces the efficiency of reinforcement. Optimal loading was also reported by Valles et al. [121], in which after a certain amount filler loadings within the matrix properties of the nanocomposites deteriorated due to aggregation of graphene. Similar enhancement of elastic modulus for epoxy/GNP nanocomposites relative to neat epoxy was also reported by King et al. [122].

The effect of GNP on flexural modulus has also been reported for E/G NCs. For example, Wang et al. [123] varied the size of the GNP to fabricate the NCs, using 5 μm and 1 μm grades with similar thicknesses. NCs fabricated using 5 μm GNPs showed higher flexural modulus at equivalent loadings. For instance, at 5 wt. % loadings, NCs fabricated using the 5 μm GNPs showed a 25.7% increase in modulus over neat epoxy compared to only a 3.9% increase for the 1 μm GNPs. The author stated that the reason for this is the higher aspect ratio of the 5 μm GNPs, which facilitated load transfer from the matrix to the filler. Similar results was also reported by King et al. [69] who studied the effect of different size GNP on the properties of epoxy resin. They found that, epoxy nanocomposites containing 5 μm GNP gave superior mechanical properties compared to 2 μm GNPs. Improvement in flexural modulus for E/G NCs was also reported by Jana and Zhong [124] with a 13% increase observed at 5 wt. % of GNPs and by Shen et al. [125] with a 19%
increase at 1.50 wt. % of GNPs. Shen et al. [125] reported a decrease in flexural strength of up to 9% at 1.50 wt.% of filler and gave two reasons for this. First, GNPs aggregation which reduced the surface area, and second the formation of voids as a result of restricted polymer flow into the aggregates.

Nanoscale materials have been reported to improve the fracture toughness of thermosetting polymers such as epoxy resins. For example, Jana and Zhong [124] reported a consistent increase in fracture toughness as a function of GNPs concentration for an epoxy resin matrix. The highest improvement (27.8%) for fracture toughness in their work was reported at 5 wt. % of GNP (Figure 2.16), and the authors stated that the improvement in fracture toughness was due to the rigidity of the GNPs which enhances resistance to crack propagation. Meng et al. [13] modified the GNPs (mGNPs) using a long chain surfactant, Jeffamine D 2000. As a result, at 0.25 vol. % of filler loading, mGNPs/epoxy had an increased fracture energy release rate $G_{IC}$ by 59.7% compared to 39.5% for unmodified GNPs NCs relative to neat epoxy. They stated that the reason for this was that the long chain molecules of D2000 bridged the interface between the GNP and epoxy, promoting

Figure 2.16: Fracture toughness of E/G NCs as a function of GNPs loading from past work.
stronger adhesion. In addition, this greater interaction also helps to improve the dispersion and distribution of GNPs in the epoxy matrix. Similar behaviour for the fracture toughness of E/G NCs containing GNPs was also reported by Chandrasekaran et al. [126] and Moghadam and Taheri [127] (Figure 2.16).

A few reasons have been proposed to explain the mechanism of reinforcement for E/G NCs. Chandrasekaran et al. [126] explained the reinforcing mechanism of GNPs in epoxy nanocomposites by two failure modes. Firstly, crack bifurcation where crack growth is inhibited by the embedded GNPs but continues to propagate along the interface between the particles and the epoxy (Figure 2.17a). Secondly, from their observations of SEM images of fracture surface, failure of the composite structure could also occur by the separation of GNPs layers (Figure 2.17b). Crack propagation will progress and pass through the region between GNP layers to cause breakage.

![Figure 2.17: Schematic of toughening mechanism by GNPs in composites (a) Crack bifurcation and (b) Failure between layers [126].](image)

Pearson and Yee [128] also proposed the toughening mechanisms for epoxy resins as illustrated in Figure 2.18. First is particle bridging, where it was often cited as the most probable toughening mechanism for polymer [128]. By particle bridging, a reinforcement particle spans the two crack edges to effectively delay crack propagation. Second is crack pinning where particle reinforcement behaves as an impenetrable object resulting in the crack bowing out, which requires extra energy for the crack to propagate. Third is crack path deflection where the particle plays a
role in deviating crack path to another direction, delaying propagation. Fourth and
fifth are particle yielding and particle yielding-induced shear banding. Here,
particles of different modulus to the matrix create significant stress concentration that
can trigger shear banding in the matrix [128]. Last, is microcracking, a situation
where more strain is allowed to be imparted to the structure before the microcracks
coalesce and the specimen breaks.

![Toughening mechanisms of epoxy resins](image)

**Figure 2.18:** Toughening mechanisms of epoxy resins: (1) particle bridging, (2)
crack pinning, (3) crack path deflection, (4) particle yielding-induced shear
banding, (5) particle yielding, and (6) microcracking [128].

### 2.3.3.2 Thermomechanical Properties

Asma and Daniel in their work [57] also characterised the viscoelastic properties of
their E/G NCs. They found that in dynamic mechanical analysis (DMA), with 2.5
and 5 wt. % of GNPs the NCs at 30 °C showed 8% and 18% higher storage modulus
compared to neat epoxy. Storage modulus was also measured at 150 °C where 34 %
and 53 % increases were observed compared to neat epoxy. \( T_g \) was measured as 143,
145 and 146 °C for 0, 2.5 wt. % and 5 wt. % of GNPs respectively. The same trends
for storage modulus were also found by other researchers as they increased the GNPs
concentration [129], [130]. This behaviour was reported to be due to two reasons. Firstly, good interaction between the matrix and GNP nanofiller [131]. Secondly, good dispersion and distribution of fillers, with smaller particle size and higher degree of exfoliation of GNPs [64].

Chandrasekaran et al. [132] reported the thermomechanical properties of E/G NCs produced by dispersing GNPs using a three-roll mill. Data from their work is presented in Table 2.1 with GNPs loading range from 0.1 to 2.0 wt. %. Higher storage moduli in both the glassy and rubbery regions were observed which correlate to stronger interface bonding between epoxy/GNPs which enhance the effectiveness of load transfer [133]. Based on their data, no significant changes can be observed in storage modulus after GNPs concentration exceed 0.5 wt. %. They also mentioned that for nanocomposites containing 0.5 wt. % of GNPs, the tan δ peak intensity is lower compared to neat epoxy and other samples and speculated that at 0.5 wt. % of GNPs, the nanocomposites reached the rheological percolation limit. The network formation at this loading reduces the mobility of polymer chains and decreased the height of the tan δ peak. No significant change in \( T_g \) was observed for the NCs relative to neat epoxy.

<table>
<thead>
<tr>
<th>Epoxy/GNPs (wt. %)</th>
<th>Storage modulus at 25 °C (GPa)</th>
<th>Rubbery modulus at 180 °C (GPa)</th>
<th>Loss factor (Tan δ)</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy/0 wt.% GNPs</td>
<td>2.75 ± 0.05</td>
<td>19.9 ± 1.0</td>
<td>1.12 ± 0.02</td>
<td>148</td>
</tr>
<tr>
<td>Epoxy/0.1 wt.% GNPs</td>
<td>2.89 ± 0.05</td>
<td>27.10 ± 0.19</td>
<td>1.07 ± 0.03</td>
<td>149</td>
</tr>
<tr>
<td>Epoxy/0.3 wt.% GNPs</td>
<td>2.94 ±0.01</td>
<td>29.11 ± 0.31</td>
<td>1.18 ± 0.03</td>
<td>148</td>
</tr>
<tr>
<td>Epoxy/0.5 wt.% GNPs</td>
<td>3.18 ± 0.04</td>
<td>23.43 ± 1.9</td>
<td>0.92 ± 0.03</td>
<td>149</td>
</tr>
<tr>
<td>Epoxy/1.0 wt.% GNPs</td>
<td>3.01 ± 0.04</td>
<td>32.35 ± 0.08</td>
<td>1.15 ± 0.01</td>
<td>151</td>
</tr>
<tr>
<td>Epoxy/2.0 wt.% GNPs</td>
<td>3.14 ± 0.07</td>
<td>34.37 ± 0.4</td>
<td>1.14 ± 0.02</td>
<td>148</td>
</tr>
</tbody>
</table>

Enhancements in thermomechanical properties have also been reported for grafting of GNPs with chemical agents or surfactants to improve interfacial bonding with
matrix polymers. As an example, GNP modification reported by Zaman et al. [12], using 4,4’-methylene diphenyl diisocyanate (MDI), produced an enhancement in the $T_g$ of epoxy matrix from 94.7 to 108.6 °C by inclusion of 2.5 wt. % treated GNPs compared to pristine GNPs. Ganguli et al. [84] prepared E/G NCs by modifying GNP using 3-aminopropoxy triethoxy silane coupling agent to increase interfacial bonding. As a result, the rubbery-region storage modulus of cured NCs was enhanced from ~100 MPa to ~240 MPa for untreated and modified GNPs, respectively.

2.3.3.3 Electrical Properties

Epoxy resins are insulating polymers with electrical conductivity reported to be approximately $\sim 10^{-14}$ S/cm [134], [135]. In contrast, carbon nanomaterials like GNPs are known to be capable of allowing the flow of an electric current [136]. Therefore, incorporating GNPs into an epoxy resin can cause the cured NCs to be electrically conductive if a sufficient amount of GNPs was added to reach the electrical percolation threshold. The amount of GNPs required to reach the percolation threshold is usually known as the critical filler loading, $p_c$ [137].

Several studies have been reported aiming to improve the electrical properties of epoxy resins using GNPs. Wang et al. [135] measured the electrical properties of E/G NCs prepared using shear mixing. It was observed that the electrical conductivity increased slowly between 0 – 2 wt. % of GNPs loading. At this stage, the electrical conductivity shows a frequency-dependent behaviour which indicates an insulating characteristic (Figure 2.19). The reason for this being that the amount of GNPs is still insufficient to cause network formation between particles. After this, for 3 wt. % of GNPs electrical conductivity increased about six orders of magnitude from $1.68 \times 10^{-14}$ for neat epoxy to $5.79 \times 10^{-8}$ S/cm for the NCs. At $\geq 4.0$ wt. % of GNPs, the conductivity is essentially constant as a function of frequency, indicating that a percolated network had formed. Particle-particle interaction is strong enough to form a conductive path for the NCs to exhibit conducting behaviour. The percolation threshold of electrical conductivity in this work was concluded to be
between 3 – 4 wt. % of GNPs where a sudden increase by a few orders of magnitude was observed [138]. The use of GNPs in an epoxy matrix to study electrical conductivity was also reported by Jovic et al. [139], who observed that conductivity was increased by 11 orders of magnitude for the transition between 0 – 8 wt. % of GNPs. Similar to previous group, they also determined that the electrical percolation threshold for their NCs occurred at around 3 wt. % of GNPs.

![Figure 2.19: Frequency dependence of conductivity of E/G NCs from past work [135].](image)

Ganguli et al. [84] modified GNPs (mGNPs) using a coupling agent, 3-aminopropoxyl triethoxysilane (APTS). Electrical conductivity measurements for NCs containing mGNPs were compared to NCs containing unmodified GNPs (U-GNPs). As expected, resistivity of the epoxy resin decreased significantly with the inclusion of GNPs but levelled off at higher concentration as percolation occurs. The results show that the NCs containing mGNPs exhibit inferior properties compared to those containing U-GNPs. For example, in their work, at 2 wt. % of GNPs, the epoxy/mGNPs NC shows 88.9% higher resistivity than the equivalent epoxy/U-GNPs. Previously, similar behaviour in electrical properties of nanocomposite has been reported by Ma et al. where APTS has been used as surface modifier [87]. This
could be attributed to the attachment of APTS molecules on the surface of the mGNPs which restrict electron mobility.

Zaman et al. [95] investigated the electrical properties of E/G NCs using a long-chain surfactant, polyoxyalkyleneamine, to modify the GNPs surface structure. They observed electrical resistivity to decrease by six orders of magnitude and the formation of a GNP network for electrical conductivity was occurred at 0.244 vol. %. However, the electrical conductivity of E/G NCs containing unmodified GNPs was not presented in their paper to compare with modified GNPs.

Other types of polymers have been used to study the electrical conductivity with graphite-based materials as nanofiller, including poly(phenylene sulphide) (PPS) [140], poly(methyl methacrylate) PMMA [79], polyurethane [141] and polypropylene [142] where all of which have showed improved electrical conductivity.

2.4 Multiscale Composites

As explained previously, multiscale composites are composites which contain reinforcements at varying size-scales [20]. Typically, a multiscale composite is formed by adding nanoscale materials into a conventional fibre-reinforced composite. Examples of nanoscale materials used to manufacture multiscale composites include CNTs [20], [143], CB [144], nanoclays [145] and CNFs [146]. In this work, a multiscale epoxy/CF/GNPs composite was manufactured using E/G NCs as the matrix for a carbon fibre composite. As the study of the properties of multiscale composites containing GNPs is still new, other types of system will also be referred to for discussion.

2.4.1 Carbon Fibre Reinforcement

The reinforcement phase in a composite will determine its strength and stiffness. In polymer matrix composites, carbon fibres (CF) are considered as the best
reinforcements due to their excellent mechanical properties and their amenability to large-scale production techniques [147]. Since CF offer high strength-to-weight ratio they are used in a wide range of applications which includes aerospace, automotive, sporting equipment and military [148].

**Table 2.2: Tensile properties of carbon fibres [149].**

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Tensile strength (GPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>2.5-7.0</td>
<td>250-400</td>
<td>0.6-2.5</td>
</tr>
<tr>
<td>Pitch (Mesophase)</td>
<td>1.5-3.5</td>
<td>200-800</td>
<td>0.3-0.9</td>
</tr>
<tr>
<td>Rayon</td>
<td>~1.0</td>
<td>~50</td>
<td>~2.5</td>
</tr>
</tbody>
</table>

The interest in CF production started in the late 1950s with textile form of rayon (fibres made from cellulose) carbonized into CF for missile applications [150]. However, it has been reported that commercial CF production commenced only in the late 1960s after the introduction of the polyacrylonitrile (PAN) precursor that gave fibres with a higher yield [151]. Subsequently, CF was also produced from a pitch precursor which is known to be cheaper [149] but which produces fibres with generally inferior strength compared to a PAN precursor. Table 2.2 shows typical values of tensile properties produced by different precursors.

Fibre architecture can significantly affect the processability and properties of the resultant composites due to the complexity of the spaces left between the fibres. Thus, resin flow can be influenced by fibre arrangement in a textile, such as orientation, crimp and interlace. As a result of fibre architecture, manufactured composites can have defects such as voids and invariant fibre wetting. Continuous CF are produced as a fibre tow, with each tow consisting of several thousand individual fibres [152]. The geometry of the fibre is defined by the spatial arrangement of the fibres tows, which can be 1-dimensional, 2-dimensional or 3-dimensional. For example, in the 1-dimensional case, CF tows are oriented in a single direction, often referred to as the 0° direction. Whereas in 2-dimensions, CF tows are often arranged in two directions by interlacing the tows to form a
bidirectional fabric. CF tows oriented at $0^\circ$ are known as the warp tows while tows oriented at angles $>0^\circ < 90^\circ$ are the weft tows. Examples of 1D and 2D products of CF are shown in Figure 2.20.

![Figure 2.20: Carbon fibres geometry of (a) 1D (the fine weft fibres are not CF) and (b) 2D [153].](image)

### 2.4.2 Manufacturing of Composites

A number of methods have been used in industry to manufacture and fabricate CF composites. These include hand lay-up, vacuum bagging, filament winding, resin transfer moulding, resin film infusion (RFI), vacuum assisted resin transfer moulding (VARTM), etc. [154]. To the best of our knowledge, no work related to the manufacturing of multiscale composite was reported by the industry to date. In this work, a manufacturing technique based on liquid infusion moulding is applied. Therefore, manufacturing of composites by this method is discussed in the next subsection.

#### 2.4.2.1 Resin Film Infusion (RFI)

Since the inclusion of GNPs into epoxy resin is expected to increase the viscosity of the system, processing and manufacturing of the multiscale composite will be difficult. Due to this drawback, manufacturing methods such as vacuum assisted resin film infusion (RFI) was developed (Figure 2.21). In RFI, films of semi-solid matrix material are placed in between dry reinforcement fabrics. Vacuum bagging is
used to remove air trapped during infusion so that porosity can be reduced during the flow of the matrix. To infuse the resin throughout the reinforcement fabrics, heat is applied to melt the semi solid matrix materials. During melting, the polymer will flow due to the vacuum-only pressure created by the vacuum pump and infuse the dry fabrics in all directions including $z$ axis [155] and finally will cure after a certain period of time.

![Figure 2.21: Schematic illustration of RFI [156].](image)

### 2.4.2.2 Resin Infusion (RI)

In resin infusion (RI), vacuum pressure is used to draw degassed resin throughout the dry reinforcement stack in the fabric lay-up (Figure 2.22). Typically, resin will be degassed using vacuum oven before infusion to remove air trapped. This process could help to minimise air bubble and void within composites structure [157].

![Figure 2.22: Schematic illustration of RI [158].](image)
2.4.2.3 Resin Transfer Moulding (RTM)

Similar to RI, the RTM technique also uses vacuum assistance in its application. The dry reinforcement material is placed in the mould (Figure 2.23). After the mould is closed and clamped, resin will be injected using external pressure to encapsulate the reinforcement preform until the mould is full [159]. The part is then cured within the mould to produce an accurate component with smooth surfaces on both sides [160].

![Figure 2.23: Schematic illustration of RTM](image)

2.4.3 Effects of Nanoparticles on the Properties of Multiscale Composites

Typically, multiscale composites are manufactured for structural applications which require excellent mechanical properties. Therefore, most of the published work on multiscale composites reports on the effects of nanoparticles on the mechanical properties of the composite structure [15], [162], [163]. Similarly, in this work characterisations for the manufactured composites are based on structural applications. As mentioned previously, the use of GNPs as additional reinforcement to form multiscale composite is still rare. Therefore, other types of nanoparticles will also be used as reference to discuss their effects on the mechanical properties of multiscale composite.

2.4.3.1 Flexural Properties

Avila et al. [18] studied the effect of GNPs on bending stiffness and strength of epoxy/CF/GNP composites. They have dispersed the GNPs by sonication and shear
mixing following the method as explained by their group for nanocomposites [164].

Addition of GNPs into the epoxy/CF composite produced a significant increase in modulus at 0.5 wt. %, but the changes are fluctuated at higher GNPs concentration (Figure 2.24). However, flexural strength showed an average improvement of 102 % for 0.5 wt. % of GNPs addition (Figure 2.26). Changes in failure modes were speculated to be the reason with the control sample (epoxy/CF) showing intralaminar failure (Figure 2.25a) while the multiscale composites showed “zigzag” pattern due to combined inter and intralaminar failure modes (Figure 2.25b) due to the presence of GNPs’ near the fibres, which improved the energy dissipation. Hence, higher peak loads were obtained in bending for epoxy/CF/GNP compared to epoxy/CF composites.

![Figure 2.24: Flexural modulus of multiscale composites from past work.](image)

![Figure 2.25: SEM image indicating failure specimen for epoxy/CF composites containing GNPs at (a) 0 wt. % and (b) 1.0 wt. % [18].](image)
In another study, Qin et al. [24] reported increases in both flexural modulus (Figure 2.24) and flexural strength (Figure 2.26) for an epoxy/CF/GNP system. They prepared the multiscale composites by immersing the CF in an epoxy/GNPs suspension followed by prepreg and lay-up. As reported, the increase for both modulus and strength in flexural properties for the multiscale composite compared to the epoxy/CF composite is 7%. They identified stronger interfacial adhesion between matrices-CF was achieved in the case of multiscale composites compared to the epoxy/CF composites. SEM image at the fractured surface indicated a clear interfacial rupture for epoxy/CF composite compared to multiscale composite which was also reported by Siddiqui et al. [165] previously. Green et al. [166] also reported a similar trend of behaviour for their multiscale composites of epoxy/E-glass/CNFs. Two reasons were given for the improvement. Firstly, a stronger matrix with the CNFs inclusion in the resin and secondly, the CNFs in the matrix enhanced matrix-fibre interfacial interactions.

Chen et al. [167] reported increases in flexural strength and flexural modulus of 15% and 16% respectively with an addition of 0.5 wt. % of graphene oxide (GO) to an epoxy/CF composite. They reasoned that the superior properties of the multiscale
composite (relative to a conventional composite) were due to greater matrix-fibre interfacial strength. However, further addition of GO above 0.5 wt. % decreased the performance of the multiscale composites which, according to their report, is attributed to two reasons. Firstly, higher amounts of GO particles resulted in aggregation creating stress concentrations that affect the properties. Secondly, higher amounts of GO lead to ineffective adhesion to the CF and hence weaker interfaces, which consequently affect the mechanical properties. Flexural properties of multiscale composites with GO as additional reinforcement was also reported by Ashori et al. [61], in which maximum improvement was obtained at 0.3 wt. % of GO. They reported 76% and 10% increases relative to neat epoxy for flexural strength and modulus at 0.3 wt. % of GO. Further increase of GO in the structure decreased the properties of the composites due to aggregation of GO which gave weaker interfacial adhesion of CF/matrix.

2.4.3.2 Interlaminar Shear Strength (ILSS)

Table 2.3: Flexural properties of epoxy/GNPs/CF composites at different applied voltage [23].

<table>
<thead>
<tr>
<th>Applied voltage</th>
<th>GNPs content</th>
<th>Fibre volume fraction ($V_f$, %)</th>
<th>Interlaminar shear strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>GNP deposited on CF</td>
<td>21.5</td>
<td>50.9 ± 10.7</td>
</tr>
<tr>
<td>10 V</td>
<td>GNP increase as a function of applied voltage</td>
<td>29.8</td>
<td>38.4 ± 4.6</td>
</tr>
<tr>
<td>20 V</td>
<td>GNP increase as a function of applied voltage</td>
<td>27.5</td>
<td>34.1 ± 9.8</td>
</tr>
<tr>
<td>30 V</td>
<td>GNP increase as a function of applied voltage</td>
<td>25.9</td>
<td>20.7 ± 4.6</td>
</tr>
<tr>
<td>40 V</td>
<td>GNP increase as a function of applied voltage</td>
<td>36.3</td>
<td>38.9 ± 6.0</td>
</tr>
<tr>
<td>50 V</td>
<td>GNP increase as a function of applied voltage</td>
<td>34.2</td>
<td>55.5 ± 7.4</td>
</tr>
</tbody>
</table>

Park et al. [23] aimed to manufacture epoxy/CF/GNP multiscale composites using GNPs coated on CF by electrophoretic deposition (EPD) technique using different applied voltages. They found that the amount of GNPs deposited on CF surface increased as a function of the applied voltage (Table 2.3). As a result of GNP deposition, the ILSS value was found to decrease as a function of applied voltage. The authors speculated that a weak interface between fibre and matrix was created.
due to the presence of copper on the CF surface during EPD coating. An interfacial crack was initiated along the copper layer that allowed the crack to propagate easily. In the case of the composite with deposition at 50 V, the ILSS is slightly higher than the control sample. The authors stated that if the voltage is high enough, the adhesion between fibre and matrix is stronger.

Green et al. [166] also characterised their multiscale epoxy/E-glass/CNFs composites by means of ILSS testing. The results showed that ILSS increased by 23% and 8% for 0.1 and 1.0 wt. % of CNFs relative to neat epoxy as a matrix (Figure 2.27). According to the authors, the smaller increase for 1 wt. % of CNFs was due to inhomogeneous dispersion of CNF or non-uniform wetting of glass fibres within the polymer matrix. They added that the CNFs could possibly have been filtered during their vacuum resin infusion technique, leading to non-uniform distribution of CNF within the system hence smaller increase is exhibited. The filtering effect is apparent especially for multiscale composite manufactured using nanoparticles with high aspect ratios [168].

![Figure 2.27: Interlaminar shear strength of multiscale composite from past work.](image-url)
Seyhan et al. [169] compounded 0.1 wt.% of amino-functionalized CNTs (CNTs-NH\textsubscript{2}) to enhance dispersion ability [170] into an epoxy matrix for an E-glass composite using a three-roll mill in an attempt to improve structural properties. After which multiscale composites were manufactured by vacuum-assisted resin transfer moulding. ILSS testing indicated that 11% improvement was achieved for the multiscale composites relative to epoxy/E-glass composite which is the controlled sample (Figure 2.27). They stated that the reason could possibly due to the accumulation of CNTs near to the glass fibres which forms a strengthened region. This strengthen region is resulted from the CNTs-NH\textsubscript{2} bundle and aggregates which is smaller than the size of fibres tow that improves the interfacial strength between matrix and glass fibres.

Zhang et al. [171] manufactured epoxy/CF multiscale composites by coat the CF with graphene oxide (GO). As a result, they observed an improvement in ILSS of the composites with the highest enhancement (~12.7 %) correspond to 5 wt. % of GO. However, further increase of GO of up to 10 wt. % reduced the ILSS. Author reasoned that the enhancement in ILSS was due to homogenously dispersed of GO at lower loadings which reduced interlaminar stress concentration. Beyond 5 wt. % of loading, excess and aggregation of GO occurred hence influenced the stress distribution, weakened the interface and affect the ILSS. Similar effects was also reported by Chen et al. [167] where GO aggregation beyond 0.5 wt. % of loadings was observed and resulted to inferior properties in ILSS compared to lower loading of GO.

**2.4.3.3 Mode II Interlaminar Fracture Toughness (ILFT)**

ILFT can be carried out in three different modes of loadings. Mode I is commonly performed by double cantilever beam (DCB) testing. The end notch flexure (ENF) method is commonly used to carry out the Mode II test. Mode III is suggested to be conducted by the edge crack torsion test (ECT) [172]. Schematic illustration of these modes is shown as in Figure 2.28.
Many works are reported related to fracture toughness of epoxy/GNPs nanocomposites. However, no studies of fracture toughness were found for multiscale composites of the system used in this research, which is epoxy/GNPs/CF. Therefore other multiscale composite systems are used for discussion in this section. Seyhan et al. [118] reported no significant changes in mode I ILFT for multiscale composites of epoxy/CNTs/E-glass, concluding the root cause was due to the presence of CNT which hinder fibre bridging in the specimens. However, they also reported an 8% increase in mode II (ENF) for composite containing 0.1 wt.% CNT-NH₂ relative to the unfilled epoxy/E-glass composite. The mechanism they proposed is that the presence of CNTs in the system act as obstacles to crack propagation which resulted to higher energy absorption compared to the control sample. For the mode II test, they stated that the ENF specimen showed a discontinuous crack growth evidenced by micro crack coalescence at the fracture surface which indicates the CNTs trapped the crack and delayed the crack extension. Therefore, higher energy absorption was obtained for mode II ILFT.

Zhu et al. [15] used mode II ILFT testing to evaluate the effects of functionalized CNTs and CNFs incorporated into epoxy/glass fibre (GF) multiscale composites. They functionalized both of the carbon nanofillers using a coupling agent 3-glycidyloxypropyl trimethoxysilane (GPS) realised that surface modification to nanofillers can also improve the properties of matrix [174]. Firstly, a comparison was made for epoxy/glass fibre containing 0.5 wt.% of unmodified CNF (UF-CNФ),
GPS-CNF and short GPS-CNT (aspect ratio 25-200). The result indicated that the short GPS-CNT gave the highest improvement (74 %) in mode II fracture toughness relative to conventional composites (without nanofiller) (Table 2.4). After that, composites containing 0.25 wt. % of functionalized long CNTs (aspect ratio 660-6250) treated with GPS (long GPS-CNT) was also characterised and a further increase in mode II fracture toughness was recorded (91 %) relative to conventional composites (Table 2.4). The authors stated that the CNF was tightly packed near to the glass fibres which obstructed pull-out of glass fibres during crack propagation (Figure 2.29a). In addition, CNT serve as obstacles and many pull-outs were observed suggesting crack bridging of the matrix (Figure 2.29b). The high aspect ratios of both fillers was also said to be the reason for improvement in mode II fracture toughness, as the long GPS-CNTs were proposed to bridge the narrow gaps between the glass fibre and hence contribute to higher crack resistance.

**Table 2.4: Mode II fracture toughness of composites containing CNF and short and long CNT (aspect ratio 25-200 and 660-6250 respectively) functionalised 3-glycidyloxypropyl trimethoxysilane (GPS) from past work [15].**

<table>
<thead>
<tr>
<th>Epoxy/glass fibre (fillers)</th>
<th>Mode II toughness (J/m²)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No nanofiller</td>
<td>565</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt. % UF-CNФ</td>
<td>783</td>
<td>+39</td>
</tr>
<tr>
<td>0.5 wt. % GPS-CNФ</td>
<td>843</td>
<td>+49</td>
</tr>
<tr>
<td>0.5 wt. % short GPS-CNT</td>
<td>981</td>
<td>+74</td>
</tr>
<tr>
<td>0.5 wt. % long GPS-CNT</td>
<td>1078</td>
<td>+91</td>
</tr>
</tbody>
</table>

*Figure 2.29: SEM images of Mode II fracture surfaces (a) dense CNFs wrapped around glass fiber and (b) ENF specimen showing GPS-CNTs bridging the local matrix crack [15].*
Wichmann et al. [175] conducted a study of the mechanical properties of epoxy/glass fibre multiscale composites by using CNT and CNT-NH$_2$. No changes were observed for both modes I and II ILFT for the composites containing nanoparticles compared to that without nanoparticles. They did not provide a thorough explanation as to why the result indicated no significant changes in both mode I and II relative to control sample, except they stated that it is due to the influence of fibre-matrix debonding.

### 2.4.3.4 Impact Resistance and Damage Tolerance

Damage tolerance can be defined as the load-carrying capability of a structure once it has been damaged by service loads [176]. The damage tolerance of a polymer matrix composite (PMC) should be considered [177], as they may experience damage during manufacturing, assembly or during service life as a result of mishandling or misuse [178]. In laminate PMCs, the main failure mechanism is delamination (interlaminar failure) [173] which has a significant effect on their compressive strength as shown in Figure 2.30 which compares the effect of compression loading to a damaged specimen compared to tension. Therefore, compression after impact (CAI) is an important test to characterise the damage tolerance of laminate PMCs.

![Figure 2.30](image-url): (a) Tension after impact and (b) compression after impact [176].
According to Oterkus et al. [173], there are three main steps to carry out a CAI test. Firstly, the specimen is inspected by an ultrasonic scan aimed to check manufacturing defects within the composites structure. Secondly, it is placed between two plates and impacted by a load at the centre of the specimen. Finally, the CAI test is carried out on the impacted specimen, placed in a slot to prevent buckling during compression.

![Figure 2.31: Typical energy-time curve in impact testing [179].](image)

Energy changes during the impact event can be presented as an energy-time curve as shown in Figure 2.31. From the graph, I represent the applied impact energy, II represents the energy absorbed by the specimen and III shows the amount of energy returned to the impactor [180]. The percentage of energy absorption can be calculated using equation (2.3).

\[
E \ (\%) = \left( \frac{E_{II}}{E_I} \right) \times 100
\]  

(2.3)

Inam et al. [181] studied the effect of amino-functionalized CNT (CNT-NH$_2$) on the properties of epoxy/CF composites. They dispersed the CNT-NH$_2$ at 0.025, 0.05 and
0.1 wt. % using a high power ultrasonication and the composites were manufactured using vacuum infusion. As a result, increases in absorbed energy of 3% and 6% were observed for the multiscale composites containing 0.025 and 0.05 wt. % of CNT-NH$_2$ relative to epoxy/CF composites. The level of absorbed energy dropped for the sample containing 0.1 wt. % CNT-NH$_2$. However, authors did not discuss the reason for the increased in absorbed energy at the first two loadings and decrease at the maximum loading applied. Despite higher energy was absorbed for composite added with CNT-NH$_2$ (at 0.025 and 0.05 wt. %), no significant effect was observed on the damage area for that specimen relative to the epoxy/CF specimen. Images taken by ultrasonic C scanning showed similar damage area on the impacted surface between epoxy/CF and epoxy/CF/CNT-NH$_2$ (0.1 wt. %).

Kamar et al. [182] studied the effect of GNPs on the properties of epoxy/S2-glass composites. The multiscale composites were prepared with GNPs added at 0.1, 0.25, 0.5 and 1.0 wt. % by dispersing the nanoparticle into the epoxy resin using tip sonication. For impact testing, only data with GNPs at 0.25 and 1.0 wt. % was compared with the conventional composite (epoxy/S2-glass). They presented the impact test data, including the peak load-deflection graph in which the peak load refers to the amount of force the composite can withstand before significant damage occurs. They found that for 20 and 40 J impacts, energy absorbed increased as a function of GNPs content. However, for a 60 J impact, the control specimen shows the highest absorbed energy. They stated that the reason could be due to many parameters, which include thickness variation between tested specimens, variation on sample surface which resulted to boundary condition within the sample.

The effects of nanomaterials within the graphene family on the mechanical properties of composites was also reported by Jiang et al. [183] who studied the effect of GO on impact resistance. Enhancement in impact resistance with the inclusion of GO at all loadings (0.2 – 2.0 wt. %) relative to neat epoxy was attributed to chemical interaction and mechanical interlocking between fibre/matrix. However, the authors stated that at the highest loading applied (2.0 wt. %), GO sheets aggregate and show inferior properties than multiscale composites containing lower loadings of GO.
Table 2.5: CAI Strength from past work.

<table>
<thead>
<tr>
<th>References</th>
<th>System</th>
<th>Impact energy (J)</th>
<th>CAI Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yokozeki et al.</td>
<td>Epoxy/CF</td>
<td>6.67</td>
<td>175 176 188</td>
</tr>
<tr>
<td></td>
<td>Epoxy/CF/CNF 5 wt.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Epoxy/CF/CNF 10 wt.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kostopoulos et al.</td>
<td>Epoxy/CF/CNT 0.5 wt.%</td>
<td>8</td>
<td>237 265</td>
</tr>
<tr>
<td>Iqbal et al.</td>
<td>Epoxy/CF/nanoclay 3 wt. %</td>
<td>15</td>
<td>105 122 128</td>
</tr>
<tr>
<td></td>
<td>Epoxy/CF/nanoclay 5 wt. %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Very few studies related to the effect of nanoparticles addition on the residual properties after impact of PMCs have been reported to date. Table 2.5 shows CAI data for different systems from work reported by several groups. It has been reported that no detailed study on the mechanism of failure in CAI strength has been reported [185]. However, the CAI strength is known to depend on the severity of damage created during impact testing [19]. Iqbal et al. [19] only mentioned that the increase in CAI strength of multiscale composite relative to conventional composite is due to increases in shear strength and modulus of the NC matrices which improved the buckling resistance under compression [19]. Yokozeki et al. [184] did not discuss the reason behind the CAI results that they presented. Whereas, Kostopoulos et al. [16] gave a general reason for the improved in CAI strength. They stated that the excellent mechanical behaviour of CNT, their large surface area and the failure mechanism that occurred were responsible for the superior behaviour of epoxy/CF/CNT relative to epoxy/CF. They did not explain in detail the mechanism of how the nanoparticles affect the CAI strength.

As carbon based nanomaterial like GNPs are known to be thermally conductive, the thermal properties of multiscale composites have also been studied, for example by Noh and Kim [186]. They reported enhancements in thermal conductivity of composite for a combination of GNPs and CF. However, as this work is focussed on the mechanical properties of multiscale composites, characterisation of the functionality of multiscale composites will not be discussed here.
2.5 Summary

This chapter gives an overview of the effects of GNP s as reinforcement in nanocomposites and multiscale composites. Good dispersion and distribution of GNP s within a matrix material is known to be crucial to improving properties in polymer nanocomposites. In order to optimize the benefits of using GNP s as reinforcement, both covalent and noncovalent functionalisation of GNP s can be carried out prior to mixing them with a polymer. This process is reported to improve the dispersion of GNP s in a polymer matrix, enhancing interfacial interaction between epoxy/GNP s [187] and imparting superior mechanical properties to the nanocomposites. However the functionality of nanocomposites produced using functionalised GNP s, for instance electrical conductivity, can show inferior properties than for nanocomposites manufactured using unmodified GNP s.

The use of nanoparticles as an additional reinforcement to be incorporated into polymer matrix laminate composites is a fairly new research topic. This is true especially for the case of GNP s. Previously, other types of nanoparticles have been used to manufacture multiscale composites such as CNTs and CNFs. The effects of nanoparticle reinforcement in multiscale composites was reported to improve mechanical properties, which includes flexural strength [188] and flexural modulus [18], interlaminar shear strength [166] and mode II interlaminar fracture toughness [15].

This study attempts to manufacture multiscale composites of epoxy/CF/GNP s. Coupled with the use of high viscosity TGPAP epoxy resin, it is expected that the inclusion of GNP s will result in high resin viscosity. Therefore, processing and fabrication of multiscale composites in this work will be challenging since the epoxy/GNP suspension needs to be spread over the whole area of CF to ensure good wetting of the CF. Hence, the manufacturing process of the multiscale composite is expected to be technically different from the methods that have been reported elsewhere.
Chapter 3  Experimental

This chapter presents materials, processes and methods used to carry out this study. It has three main sections. Firstly, materials and techniques used to study blending of two types of epoxy resin using response surface methodology (RSM) are reported. At the end of this stage, a selected epoxy blend was determined and brought forward to the next stage of experimental work. The second section describes materials and techniques used to prepare epoxy/GNPs matrix which involves treatment and modification of the GNPs, characterisation of modified GNPs as well as mixing and dispersing of GNPs into the selected epoxy formulation. Finally, these mixtures were cured (to form nanocomposites) and their structure and properties were characterised. From the second section, one epoxy/GNP system was chosen to be used to form epoxy/GNPs/carbon fibre multiscale composites. The third section describes the techniques used to study the preparation and properties of these multiscale composites.

3.1  Epoxy Blending by Response Surface Methodology

In this section of study, two types of common epoxy resins were blended to produce a new type of epoxy resin system. Optimisation of variables were determined through response surface methodology (RSM) assisted by the use of Design Expert software.

3.1.1  Materials

Bisphenol F diglycidyl ether (DGEBF) (2-[[2-[[2-(oxiran-2-ylmethoxy)phenyl]methyl]phenoxy)methyl]oxirane) and triglycidyl-p-aminophenol (TGPAP) (4-(oxiran-2-ylmethoxy)-N,N-bis(oxiran-2-ylmethyl)aniline) were used in this work. 4,4’-diaminophenyl sulfone (DDS) (4-(4-aminophenyl)sulfonylaniline) was used as the curing agent. Throughout this thesis, epoxy blend refers to the mixture of DGEBF and TGPAP. Details of each material are given in Table 3.1. DGEBF was supplied as a transparent liquid of low viscosity, whereas TGPAP (a
trifunctional epoxy resin) was a high viscosity liquid with a yellow-orange colour. DDS was supplied in a powder form for easy incorporation into epoxy resins. In this thesis, TGPAP is also defined as trifunctional epoxy (Tri) while DGEBF is the bisphenol F epoxy (BPF).

Table 3.1: Materials used in epoxy resin formulation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Trade name</th>
<th>Equivalent weight (g/eq)</th>
<th>Density (g/cm³)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycidyl p-aminophenol (TGPAP)</td>
<td>Araldite MY0500</td>
<td>101</td>
<td>1.21 – 1.22</td>
<td>Huntsman</td>
</tr>
<tr>
<td>Diglycidyl ether of bisphenol F (DGEBF)</td>
<td>DER 354</td>
<td>164</td>
<td>1.19</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>4,4’-diaminodiphenyl sulfone</td>
<td>DDS</td>
<td>62.08</td>
<td>1.36</td>
<td>Huntsman</td>
</tr>
</tbody>
</table>

3.1.2 Design of Experiment

A design of experiments (DOE) approach was carried out by Response Surface Methodology (RSM) assisted by the use of Design Expert software. An efficient design tool known as a Central Composite Design (CCD) was chosen for this study.

In this work, the number of variables (or factors), \( k \), was equal to 2, namely the DGEBF content in epoxy blend (X1) and the stoichiometric ratio of amine to epoxy groups (X2). The CCD used has a core 2-level factorial design in which one level is referred to as low level (lower bound of actual value, coded as -1) and the other as the high level (upper bound of actual value, coded as +1) of each variable. The number of experiments required for this CCD was calculated as \( 2^k \) for the 2-level factorial cube points, \( 2^k \) for axial or star points (which extends the measured experimental volume beyond that of the 2-level factorial) and several replication samples at the centre of the 2-level experimental volume to allow estimation of curvature of standard error. It is recommended to have 3 or 5 replicates at the centre of experimental region [189], and in this work, 3 were used. Hence, the total number of experiments was \( 2^2 + 2^2 + 3 = 11 \). Figure 3.1 shows the CCD design with coded values (low level, -1 and high level, +1) which consists of 4 axial points, 4 cube
points and 3 replicate points (denoted as 0, 0) at the centre. Determination of each point for the construction of CCD is explained in the next subsection.

Figure 3.1: The CCD design used in this study (a) 4 axial points, (b) 4 cube points and (c) summation of all points from (a) and (b) with 3 replications at the centre.

3.1.2.1 Centre Points

Figure 3.2: Actual formulation values in the CCD.
As mentioned previously, two variables were studied in this work. The first variable (DGEBF in weight %) X1 was investigated in the range between 0 – 100% from the total weight of epoxy blend. The main area of interest for the second variable (stoichiometry), X2 was from 0.5 – 1.0 of amine:epoxy (g/g). However, in order to obtain a better perspective of the effect of stoichiometry at 0.5, a lower value of 0.42 was chosen as the lower bound of X2. The crossing point between lower and upper bound for both variables (X1 and X2) will be the centre of the CCD design located at (0, 0) for coded value (Figure 3.1a) or at (50, 0.71) for actual values (Figure 3.2).

3.1.2.2 Axial Points

The actual lower and upper bounds for both variables will be the values of the axial (or star) points in the CCD. In this case, the lower and upper actual value for X1 will be 0 and 100 with coded values -1.414 (low level) and +1.414 (high level). Similarly, the lower and upper actual values for X2 will be 0.42 and 1.0 and with coded values of -1.414 and +1.414, respectively. Maps are shown in Figure 3.1a, for coded values and in Figure 3.2 for actual values. These coded values for both low and high level of axial/cube points can be determined through trigonometric calculation (depending on what value has been set as low and high level in cube/axial points). An example of a calculation is shown in the next subsection to obtain the actual value.

3.1.2.3 Cube Points

The 4 cube points were determined through calculation. The position of a cube point divides the area between two adjacent axial using two 45° (angles as shown in Figure 3.3). The determination of the points was calculated to ensure that the radial distance of the cube points is the same as the distance of the axial points from the centre point. This will ensure that all points for both axial and cubes points are rotatable from the centre point as shown by dashed circle in Figure 3.2. Rotatability of these points will ensure uniformity of error prediction. Through calculation, the actual values for cube points were determined to be (14.6, 0.5), (14.6, 0.92), (85.4, 0.5) and
(85.4, 0.92) as indicated in Figure 3.2. Respectively, their coded values were (-1, -1), (-1, +1), (+1, -1) and (+1, +1). An example for the calculation to determine the actual value of cube point with coded value at (-1, -1) is as follows.

![Figure 3.3: Cube point (-1, -1) to determine actual value for (a) X1 and (b) X2.](image)

From Figure 3.3a, X1:

\[
\sin 45^\circ = \frac{50 - X1}{50}
\]

50 \(- X1 = 50 \sin 45
\]

50 \(- X1 = 35.4
\]

\[
X1 = 50 - 35.4
\]

\[
X1 = 14.6
\]

From Figure 3.3b, X2:

\[
\sin 45^\circ = \frac{0.71 - X2}{0.29}
\]

0.71 \(- X2 = 0.29 \sin 45
\]

0.71 \(- X2 = 0.21
\]

\[
X2 = 0.71 - 0.21
\]

\[
X2 = 0.50
\]

Hence, the actual value for point (-1, -1) is (14.6, 0.50), and values for other cube points were determined using the same method. The amount of DDS or amine was obtained through calculation using equation (3.5). An example of this calculation is also shown where [ ] refers to concentration, EEW is epoxy equivalent weight, \( \text{wt}_{\text{TGPAP}} \) is the weight percent of TGPAP and \( \text{wt}_{\text{BPF}} \) is the weight percent of DGEBF. As an example, for the actual value at point (14.6, 0.50) the calculation to determine the amount of DDS or amine is as follows.
Table 3.2: Experimental design in coded and actual values.

<table>
<thead>
<tr>
<th>Run</th>
<th>Coded value</th>
<th>Actual value (weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X1</td>
<td>X2</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>-1.414</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1.414</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>-1.414</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>1.414</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(3.1) \[ \text{Stoichiometry, } X2 = \frac{[\text{Amine}]}{[\text{Epoxy}]} \]

Where,

(3.2) \[ [\text{Epoxy}] = \frac{\text{wt}_{\text{TGPAP}}}{\text{EEW}_{\text{TGPAP}}} + \frac{\text{wt}_{\text{DGEbf}}}{\text{EEW}_{\text{DGEbf}}} \]

Hence,

(3.3) \[ [\text{amine}] = \text{stoichiometry} \times \left( \frac{\text{wt}_{\text{TGPAP}}}{\text{EEW}_{\text{TGPAP}}} + \frac{\text{wt}_{\text{DGEbf}}}{\text{EEW}_{\text{DGEbf}}} \right) \]

\[ [\text{amine}] = 0.50 \times \left( \frac{14.64}{110} + \frac{85.36}{164} \right) \]

\[ [\text{amine}] = 0.335 \]

\[ [\text{amine}] = 0.335 \times 62.08 \]

\[ \text{amine} = 20.3 \text{ g} \]
Samples of the epoxy blends were characterised to determine, processing time (t), heat of reaction during cure (ΔH) and glass transition temperature of the cured resin (T_g).

3.1.3 Blending Procedure

Blending of epoxy (Figure 3.4) was carried out by mechanical mixing using a Heidolph overhead stirrer, model RZR 2020. The blend (DGEBF, TGPAP and DDS) was first weighed into a glass jar and then placed in a preheated (100 °C) silicone oil bath. The blend was stirred at 2000 rpm for 30 minutes and the blended epoxies formed a miscible transparent mixture with a light yellow colour.

![Epoxy blend setup](image)

Figure 3.4: Epoxy blend setup, reproduced from [190].

3.1.4 Responses of Epoxy Blend

This subsection describes the characterisation techniques used to determine the responses (Y_i) as the effects of changing the variables X1 and X2.
3.1.4.1 Glass Transition Temperature

The glass transition temperature \( T_g \) is an important property of cured epoxy resins as it is the temperature at which the material changes from hard and glassy to soft and rubbery accompanied by a significant drop in modulus, and therefore \( T_g \) dictates the maximum temperature the epoxy can experience before mechanical properties start to decrease. The effects of both variables as well as their interaction on the \( T_g \) of cured resins were studied. Values of \( T_g \) were measured by dynamic mechanical thermal analyser (DMTA) using a Perkin Elmer DMA 8000. Details about DMTA are explained in the section on characterisation of nanocomposites (3.2.7.1).

For curing, blended epoxy was poured into a flexible mould made from polytetrafluoroethylene (PTFE)-coated fabric and degassed in a vacuum oven to eliminate trapped air at 100 °C for about 30 minutes. The degassed epoxy was then put into a circulating-air oven and heated following a cure cycle developed within our group for similar epoxy system [153]. The cure cycle is 2 hours at 130 °C, 2 hours at 160 °C and 2 hours at 200 °C, followed by a post cure for 5 hours at 200 °C. Cured samples were then cut into specimens of 40 mm x 10 mm x 3 mm using a diamond saw. DMTA was carried out in dual cantilever mode at a frequency of 1 Hz from 30 °C to 320 °C at a heating rate of 5 °C/min. Peak tan \( \delta \) was taken as the \( T_g \) in this work. To ensure reproducibility, at least 3 specimens were tested for each sample.

3.1.4.2 Processing Window

The processing window of the epoxy blends is defined as the length of time at which the epoxy can retain a viscosity low enough for it to be processed. In this work, the processing window was determined as the time for the epoxy blend to reach a viscosity of 100 Pa s, as stated in ASTM D 4473-95 [191].

The rheometer used was a Thermo Scientific Haake MARS (Modular Advanced Rheometer System). Viscosity measurements in oscillatory shear mode were carried
out by placing the epoxy between two parallel plates of diameter 35 mm fitted to the upper measuring head and the fixed lower mount. The distance between the plates was then closed to give a 0.5 mm gap and the furnace was closed around the plates. For curing, the specimen was first heated to 80 °C at which point measurements began at an oscillation of 1 Hz frequency with a controlled stress at 2.0 Pa. The temperature was increased further by 10 °C/min until 130 °C and then remained constant during cure of the specimen and viscosity increased to 100 Pa.s. At least 3 repetitions were done for every run in the CCD. More detail about rheometry is given in the subsection on characterisation of epoxy/GNPs suspensions (3.2.5.1).

3.1.4.3 Enthalpy of Reaction

Enthalpy or heat of reaction for the epoxy blends was measured using differential scanning calorimetry (DSC). The DSC measures the difference in energy input or heat capacity between a sample and a reference which subjected to dynamic (heated or cooled) or isothermal temperature scanning. There are two types of DSC: heat flux and power compensated DSC. Work reported at this stage used a heat flux DSC 8500 Perkin Elmer. Upon heating of both pans at a programmed rate, energy is calculated from the temperature difference between the sample and the reference (empty pan) due to exothermic or endothermic changes in the sample [192]. A schematic of a heat flux DSC technique is shown in Figure 3.5.

![Figure 3.5: Schematic illustration of heat flux DSC [193].](image)
Prior to the test, a baseline calibration was carried out using an empty DSC aluminium pan subjected to the same temperature range for dynamic scanning and the same heating rate as the test. For sample preparation, a small sample of epoxy blend, ranging between 2 – 5 mg, was placed into an aluminium pan and then was transferred into the furnace, with an empty aluminium pan being placed in the other furnace as a reference.

![DSC curve of uncured epoxy blend](image)

**Figure 3.6: DSC curve of uncured epoxy blend.**

Two heating cycles were used in dynamic scanning. First, the temperature was raised from 30 °C to 320 °C for the first run. Then, the sample was cooled down to 30 °C and heated again to 320 °C for the second cycle. Both heating and cooling were run at a rate of 10 °C/min in a nitrogen atmosphere. The second heating cycle is to measure residual heat of reaction due to any unreacted epoxy-amine remaining from the first cycle. Hence, the total enthalpy of reaction is the summation of the two enthalpies of reaction from both cycles. A typical DSC curve for the scanning of uncured epoxy is shown in Figure 3.6, showing heat flow versus temperature during the reaction of a sample. The integrated area under the heat flow-temperature curve will give the enthalpy of reaction (ΔH) for the system.
3.2 Epoxy/GNP Matrices

This subsection describes the materials, methods and procedures used to study the behaviour of epoxy resin when GNPs were added, before being used as matrices with carbon fibre to form multiscale composites.

3.2.1 Materials

The selected epoxy blend was used at this stage. It consisted of 55.56% DGEBF in a blend with TGPAP at stoichiometric ratio of 0.60. All the chemicals used to modify the GNPs were purchased from Sigma Aldrich. 1-methyl-2-pyrrolidinone (1-methylpyrrolidin-2-one) abbreviated as NMP with product number M79063 (purity of reagent 99 %) was used as the solvent. Two types of modifiers were used. First, a surfactant, with the trade name Triton X-100 (4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol), CAS number 9002-93-1 was used to modify the GNPs by a noncovalent method. Second, a coupling agent (3-aminopropyl)triethoxysilane (3-triethoxysilylpropan-1-amine) with CAS number 919-30-2 (purity of reagent 99 %) was used to modify GNPs covalently. Throughout this thesis, Triton X-100 will be denoted as Triton and (3-aminopropyl)triethoxysilane will be referred to as APTS.

Figure 3.7: Chemical structure of (a) NMP (b) Triton X-100 and (c) APTS [194].
Figure 3.7 shows the chemical structures of all the above mentioned chemicals. In this work, GNPs grade M25 from XG Sciences (East Lansing, Michigan, USA) was used with surface area of 120 – 150 m$^2$/g, platelet size of 25 μm, 17-22 number of layers and average thickness 6-8 nm. In addition, M25 has a pristine graphitic surface of sp$^2$ carbon molecules and 3 main peaks in Raman spectroscopy, namely the D peak (~1360 cm$^{-1}$), G (~1560 cm$^{-1}$) and 2D (~2700 cm$^{-1}$) [195]. According to their data sheet for GNPs grade M25 [195], the manufacturing process is non-oxidising with the residual acid and oxygen content being less than 0.5% and 1% respectively.

3.2.2 GNP Treatment Procedures

Modification of GNPs was carried out during sonication in a water bath (Elma sonic P300H). NMP was chosen as a solvent due to its capability in exfoliating graphite [196] and produced stable colloidal suspension [197]. However, the cost of NMP is high. To reduce the cost, water was added to NMP at ratio 45:55 (NMP:water) by volume.

For the treatment, it has been suggested that the modifier concentration should be greater than the nanofiller concentration (mg/mg). It is because in order to establish self-organisation of the modifier agent into micelles, their concentration needs to be above the critical micelle concentration (CMC). This can be achieved with higher ratio of modifier agent to the nanofiller [93], [198], [199]. Previously, Yu et al. [198] reported that the optimum dispersion of nanoparticles in solution is unachievable at lower ratios of modifier to nanoparticles since sufficient modifier is required to provide efficient coating on the surface of the nanoparticles to prevent re-aggregation. They determined that, for effective dispersion, the range of weight ratio of modifier agent to carbon based nanoparticles is between 1.0 – 1.5. Wan et al. [93] also perform the treatment procedure of GNPs using Triton X-100 at a ratio of 1.5 (Triton X-100:GNPs). In this work, 3000 mg of Triton X-100 or APTS was first dissolved in 500 ml of the water/NMP solution. This solution was then sonicated for 15 minutes at 30 °C and 100 % power to give a homogenous mixture and then 2000
mg of GNP was added and further sonication was carried out for 4 hours. The resulting suspension was then filtered and the GNP rinsed 3 times with distilled water to remove NMP and excess modifier before being dried in an oven overnight at 80 °C. The same procedure was repeated using the same batch size to produce sufficient amount of treated GNPs. GNPs treated with Triton X-100 and APTS are abbreviated as T-GNPs and A-GNPs, respectively. Unmodified GNPs (abbreviated as U-GNPs) were prepared using the same procedure but without addition of Triton X-100 or APTS.

3.2.3 Characterisations of GNPs

Characterisation of the modified and U-GNPs was performed to assess the effectiveness of the treatments. Characterisation methods are explained as follows.

3.2.3.1 Scanning Electron Microscopy (SEM)

SEM is widely used to capture the images of microstructure. SEM involves scanning of a high energy electron beam on the specimen, producing signals due to emission of secondary electrons (SE), backscattered electrons (BSE) or X-rays (Figure 3.8). These signals are then picked up by detectors and transformed into an image.

![Figure 3.8: Signals emitted by the electron beam during SEM, with regions the signals can be detected [200].](image-url)
Morphology of as-received GNPs (AR-GNPs) was imaged using a Zeiss SEM EVO 60 at an accelerating voltage of 20 kV. Sample was prepared without coating and placed on the adhesive carbon disc with a 0.52” pin stub (both Agar Scientific). The stub was then pressed onto the GNPs until a sufficient amount of GNPs was attached to the stub.

3.2.3.2 Transmission Electron Microscopy (TEM)

TEM works in a similar way as optical microscope except that it uses electrons for imaging. An electron beam is directed down towards the specimen (focused by a condenser lens). After passing through the sample, the electron beam passes through an objective lens to form, magnify and focus the image and then through a projector lens for magnification before the final image is imaged on the main screen.

In this work, a Philips CM200 TEM was used to image the physical characteristics of GNPs. Images of treated, unmodified and as-received GNPs were captured for comparison. All samples were prepared by placing GNPs into acetone and sonicating for 15 minutes in a water bath. After that, a pipette was used to place a drop of the suspension onto an ultra-thin TEM grid (300 mesh copper, Agar Scientific) which was left to dry for about 10 minutes before being transferred onto a TEM sample holder. Images were captured by a CCD camera with GATAN software at a 200 kV accelerated voltage.

3.2.3.3 Thermogravimetric Analysis (TGA)

TGA measures the change in mass of a sample during a programmed heating cycle and was performed to study the stability of GNPs as a function of temperature. In TGA the sample is placed in a furnace and the variation in mass is monitored by a thermobalance and recorded as an indication for the thermal stability. TGA was carried out using a TGA Q500 (TA Instruments) in a nitrogen atmosphere. Samples were heated from room temperature to 900 °C at a heating rate of 10 °C/min.
3.2.3.4 Raman Spectroscopy

Raman spectroscopy is a common technique used to measure the quality (defects) of GNPs. In this study, the effects of treatment of the GNPs were observed through Raman scattering. It is a technique that uses monochromatic light, usually from a laser source, to create inelastic scattering on the sample. When the laser light hits the sample, most of it will scatter with an unchanged vibration energy level. This phenomenon is known as Rayleigh scattering. Alternatively, a Raman shift occurs upon which photons (are absorbed by the material causing molecules to vibrate and reemit a photon of either increased or decreased energy relative to the initial photon. The case where energy is lost during Raman scattering is designated as Stokes. Raman scattering and where energy is gained is known as anti-Stokes (illustrated in Figure 3.9).

![Figure 3.9: Raman scattering transition scheme](image)

A Raman shift (cm$^{-1}$) is defined as the difference in the incident and scattered wave numbers as shown in equation (3.4) [202]. A Renishaw RM System 2000 Mk1 Raman spectrometer was used to record Raman spectra of GNPs in this work. Before any experiment, a calibration step was carried out by applying a silicon standard exposed to 100% laser power with 1 accumulation and a 10 s exposure time. The excitation will result in a sharp peak at 520 cm$^{-1}$ which was fitted using WIRE software. Calibration offset was applied if the peak was outside 520 ± 1 cm$^{-1}$ range. For the experiments, firstly dried GNPs were placed on a glass slide and compressed using another slide to give a flat surface on the top. These compressed GNPs were transferred onto the optical microscope stage and focussed before the experiment. The excitation was performed using a He Ne laser of 633 wavelength using 10%
laser power in extended mode range from 1000 – 3000 cm\(^{-1}\). Only 1 accumulation of excitation was applied in this work.

\[
Raman \ shift \ (cm^{-1}) = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}
\]

3.2.3.5 Energy Dispersive X-Ray (EDX) Analysis

EDX analysis is used to determine the elemental composition of a material. It works by analysing X-rays characteristic of an element generated when the electron beam strikes the sample during SEM. An incident electron beam may eject an electron from an orbital, hence produce a vacancy to the shell which later will cause an electron from another orbital to move into the inner shell. The transition of the electron from one orbital to fill the vacancy at an inner orbital will produce an X-ray with its respective energy. This X-ray energy will be collected by the detector and converted into voltage signal before being displayed as a spectrum for analysis. Figure 3.10 shows the illustration of an emitted X-ray produced by the transition of an electron from one orbital to another.

![Mechanism of X-ray emitted from the electron transition](image)

Figure 3.10: Mechanism of X-ray emitted from the electron transition [203].
Elemental and composition analysis was performed on all GNP samples by EDX to determine any changes in elemental composition as a result of treatment which will give an indication whether the modifier was successfully grafted onto the GNP. EDX was done using a SEM Zeiss EVO 50 equipped with an Oxford Instruments 250 EDX system. All experiments were conducted at 10 kV by using “point & ID” mode with at least three runs for each sample. An Inca X-sight ATW2 detector was attached in SEM EVO 50 for the X-ray detection. Corresponding EDX spectra were obtained using Oxford Instruments INCA software.

3.2.3.6 X – Ray Photoelectron Spectroscopy (XPS)

In addition to EDX, XPS surface analysis was also carried out to study the effectiveness of the GNP treatments. The XPS principle is explained when an electron at the core level is hit by an X-ray source, overcoming the electron’s binding energy \( E_B \), and emits out from the surface at a certain kinetic energy \( E_{kin} \) which finally is collected by an electron energy analyser. This phenomenon is expressed by the Einstein equation as follows [204].

\[
E_{kin} = h\nu - E_B - \phi
\]

Where, \( E_{kin} \) is kinetic energy of an emitted electron measured by an electron energy analyser, \( h\nu \) is the X-ray energy from its source and \( \phi \) is the instrument’s work function. Therefore, the binding energy, \( E_B \) can be determined.

For the experimental work, XPS was performed using a Kratos Axis Ultra instrument with monochromatic Al K\(_{\alpha}\) source at a base pressure \( 4 \times 10^{-9} \) mbar. Data was displayed using CasaXPS software. Dried GNPs were mounted on a steel bar using double sided tape. The samples were then left overnight in the vacuum chamber for spectral measurements. A wide scan spectrum of the sample was recorded in the range between 0 – 1400 eV, followed by high resolution XPS peak for carbon (C 1s) and oxygen (O 1s). The wide scan spectrum was collected at the pass energy of 200 eV with number of scan =10. Meanwhile, the high resolution spectra were acquired.
at 50 eV (pass energy) with 25 scans. All peaks were centred and normalised at 284.6 eV, relative to the main C 1s peak. Deconvolution of high-resolution peaks was performed by Avantage Software (v. 5.948) from Thermo Fisher Scientific using Shirley background. Elemental composition was determined quantitatively, following the method of Briggs and Seah [204].

3.2.3.7 CHNS Analysis

CHNS (carbon, hydrogen, nitrogen and sulphur) elemental analysis provides rapid determination of these elements. It was performed on as-received GNPs (AR-GNPs) using a CHNS Thermo Scientific Flash 2000 organic elemental analyser. The analysis was conducted at the School of Chemistry, University of Manchester, UK.

3.2.4 Synthesis of Epoxy/GNP Nanocomposites

Epoxy/GNP nanocomposites were prepared by mechanical mixing methods. Firstly, both epoxies (TGPAP and DGEBF) and GNPs were weighed in their required amounts into a glass jar. The jar was then transferred into a silicone oil bath, which was heated at around ~100 °C on a hotplate and the DDS hardener was added. The mixture was stirred by two rotor blades at 2000 rpm for 10 minutes. After that, GNPs were added into mixture and stirring was continued for another 20 minutes. The suspension was then poured into a square mould, fabricated using PTFE-coated glass fabric and then degassed in a vacuum oven at 100 °C for 1 hour. Samples were finally cured at 130 °C, 160 °C and 200 °C for 2 hours at each. The dimension of the square mould used was dependent the type of testing following the required dimensions of the specimens. It is noted that, for all types of testing of nanocomposites, all samples were produced from only one moulding.

3.2.5 Characterisation of Epoxy/GNP Suspensions

Epoxy/GNPs suspensions were characterised using rheometry to study their processing behaviour. In addition, the effects of treatment on the rheological
percolation threshold, at which GNP networks form strong elastic networks in a suspension, could be determined using this technique.

### 3.2.5.1 Rheometry

![Figure 3.11](image)

**Figure 3.11: Schematic representation of a viscous material undergoing simple shear** [205].

Rheology can be defined as a study of the flow behaviour and deformation of matter under an applied force [206]. To illustrate rheological properties of a viscous material, a simple model is shown in Figure 3.11 [205]. Material to be studied is placed in between two parallel plates separated by a distance, $y$. The bottom plate (Figure 3.11) remains at rest while the top plate, with surface area $A$, is moved by an applied force, $F$, at a velocity, $V$ in $x$ direction. The applied force creates a shear stress, $\tau$, of magnitude $F/A$, which is proportional to the velocity gradient developed between the plates, $\frac{dV_x}{dy}$. This can be represented as follows:

\[
\tau = \frac{F}{A} = \eta \frac{dV_x}{dy}
\]

(3.6)

Where, $\eta$ is a proportionality constant known as the Newtonian shear viscosity. At the same time, this shear causes the fluid to move at a shear strain ($\gamma$) and is
equivalent to \( \frac{dx}{dy} (\gamma = \frac{dx}{dy}) \). Shear strain rate (or shear rate) (\( \dot{\gamma} \)) at any point in the gap y will be:

\[
\dot{\gamma} = \frac{dV_x}{dy} = \frac{d(\frac{dx}{dt})}{dy} = \frac{d(\frac{dx}{dy})}{dt} = \frac{dy}{dt}
\]

Therefore, \( \tau \) can be simplified to:

\[
\tau = \frac{F}{A} = \eta \frac{dV_x}{dy} = \eta \dot{\gamma}
\]

Equation (3.8) is the Newtonian fluid model (Newton’s law of viscosity) [207]. It has been reported that many polymers exhibit non-Newtonian behaviour, and when mixed with nanofillers their rheological behaviour will be affected [208]. At small filler loadings, the viscosity of a suspension is low enough to allow Brownian motion (a condition where particles move randomly in a suspended fluid) to become relevant before leading to agglomeration due to particle interaction. As a result, a plateau in storage modulus (G’) is observed at lower strain, which is defined as the linear viscoelastic region (LVR). This region indicates the network stability of a suspension before destruction occurs when a sample is overstrained.

A Thermo Scientific Haake MARS (Modular Advanced Rheometer System) was used for this experimental work, fitted with 35 mm diameter aluminium parallel plates with a 0.5 mm gap. An oscillatory strain sweep measurement was first performed to determine the LVR of the suspension. After that, frequency sweep mode was used to determine the rheological percolation threshold of the epoxy/GNPs suspension within the LVR. All samples tested were resin suspensions without hardener and were run at a temperature of 100 °C. This reflects the environment of suspension at all processing conditions throughout the whole of this research.

### 3.2.6 Characterisation of Nanocomposites

Nanocomposites characterisation was carried out to study the effects of GNPs with different treatment when incorporated into a cured epoxy resin.
3.2.6.1 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was performed to measure the viscoelastic response of the nanocomposites as a function of temperature. A viscoelastic material, when subjected to a sinusoidal stress, will exhibit a sinusoidal strain which is out of phase with the stress by a phase lag, $\delta$. This difference is due to molecular motions and relaxations that occur sometime after a force or stress is applied to a viscoelastic body. These properties can be presented as dynamic storage modulus ($E'$), dynamic loss modulus ($E''$) and mechanical damping behaviour ($\tan \delta$). This is derived and expressed in equations as follows [209].

\[
E^* = \frac{\text{Stress}}{\text{Strain}}
\]  
\[E' = E^* \cos \delta\]  
\[E'' = E^* \sin \delta\]  
\[\tan \delta = \frac{E''}{E'}\]

where, $E^*$ is the complex modulus. In this work, DMTA was performed using a Perkin Elmer 8000, in 3 point bending mode at a frequency of 1 Hz. Rectangular specimens (40 mm x 10 mm x 3 mm) ± 1 mm were cut using a Benetec sliding cutter. Specimens were heated from 30 °C to 300 °C at a rate of 5 °C/min. The curves of $E'$, $E''$ and $\tan \delta$ were displayed as a function of temperature via Pyris software (Perkin Elmer). Three repetitions were performed for each sample.

3.2.6.2 Flexural Testing

Flexural testing of nanocomposites was carried out according to the ASTM D790 – 1 [210]. Specimens were cut using a Benetec sliding cutter to dimensions of (70 mm x 12.7 mm x 3 mm). Specimens were tested using a three point bending fixture with a loading nose of radius 5 mm and lower supports also of 5 mm radius. Support span to thickness ratio was calculated as 16:1, which resulted in a span of 48 mm, and the crosshead speed was calculated according to equation (3.13) to be 1.62 mm/min.
Three specimens were tested for each sample using an Instron 5969 universal testing machine (UTM) fitted with a 10 kN load cell. Segment value in flexural stress-strain curve from 20 MPa to 40 MPa of stress was used to determine the flexural modulus, calculated by Bluehill® software (Instron).

\[ R = \frac{ZL^2}{6d} \]  

(3.13)

where:

- \( R \) = rate of crosshead motion, mm/min,
- \( L \) = support span, mm,
- \( d \) = depth of beam, mm, and
- \( Z \) = rate of straining of the outer fibre, mm/mm/min.

The flexural stress and flexural strain were calculated according to the equations stated in ASTM D790, as follows:

\[ \sigma_f = \frac{3PL}{2bd^2} \]  

(3.14)

where:

- \( \sigma_f \) = stress in the outer fibres at midpoint, MPa,
- \( P \) = load at a given point on the load-deflection curve, N,
- \( L \) = support span, mm,
- \( b \) = width of beam tested, mm, and
- \( d \) = depth of beam tested, mm.

\[ \varepsilon_f = \frac{6Dd}{L^2} \]  

(3.15)

where:

- \( \varepsilon_f \) = strain in the outer surface, mm/mm,
- \( D \) = maximum deflection of the centre of the beam, mm,
- \( L \) = support span, mm, and
- \( d \) = depth, mm.
3.2.6.3 Single Edge Notch Bending (SENB) Fracture Toughness

A fracture toughness study was carried out according to ASTM D5045-99 for single edge notch bending (SENB). Specimens were cut to (10 mm x 5 mm x 44 mm) ± 1 mm and a sharp notch was prepared by machining (Figure 3.12). Subsequently, a natural crack was initiated by tapping a fresh razor blade into the notch using the fixture shown in Figure 3.13a so that crack length, a, will be between 4.5 < a < 5.5 mm [211]. Three samples were used for SENB testing. An Instron 4411 UTM was used for testing with a 500 N load cell, at a crosshead speed at 10 mm/min. The diameter of the loading nose and two support rollers is 6 mm (Figure 3.13b). Stress intensity factor ($K_Q$) was calculated according to the following equation [211]:

\[
K_Q = \left( \frac{P}{\frac{B}{2} W^2} \right) f(x)
\]

(3.16)

\[
f(x) = 6x^{1/2} \frac{[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]}{(1 + 2x)(1 - x)^{3/2}}
\]

(3.17)

Where (0 < x < 1), and $P$ is the critical load for crack propagation, $B$ is specimen thickness, $W$ is specimen width, $a$ is crack length and $x = a/W$. Figure 3.13b shows the experimental set up for SENB testing.

![SENB specimen with dimensions](image)

Figure 3.12: Dimension of SENB specimen.
3.2.6.4 Impedance Spectroscopy

Impedance spectroscopy was used to measure electrical conductivity of the nanocomposites samples and was performed using a NumetriQ PSM1735 system connected to an Impedance Analysis Interface (IAI). Data was displayed by the NumetriQ PSM1735 which also supplied the voltage while IAI provided a wide range of shunts (1 mΩ – 500 mΩ) that enabled the measurement of samples of various resistances. A frequency range of 1 to $10^6$ Hz with voltage at amplitude of 1.0 V was used for all experiments. Electrical conductivity data were converted from the recorded resistance and calculated according to equation (3.18) [212].

$$\sigma (\text{S/m}) = \frac{l}{R \times w \times h}$$

Where $R$ is the measured electrical resistance (Ω) and $l$, $w$ and $h$ respectively is length, width and height (m) as defined in Figure 3.14. For measurement, specimens were cut to (20 mm x 10 mm x 5 mm) ± 1 mm, polished and then coated with silver paint to both ends of samples to minimise the contact resistance between samples and conductive wires. The area covered by the silver paint was kept constant for all
samples. A silver-loaded epoxy adhesive (RS 186-3616 from RS Components) was used to attach conductive wires at both ends of the sample (Figure 3.14). Before measurement, a resistor of known resistance value was tested to verify that the machine was working normally.

![Figure 3.14: Schematic arrangement for conductivity measurement.](image)

3.3 Epoxy/GNP/Carbon Fibre Multiscale Composites

In this section, the materials and methods used to manufacture and characterise epoxy/GNPs/carbon fibre multiscale composites are presented. Selected GNP nanocomposites were used in this section as matrices to manufacture multiscale composites.

3.3.1 Materials

![Figure 3.15: 5 harness satin weave carbon fibre fabric [153].](image)
Epoxy/A-GNPs showed better properties compared to unmodified and T-GNPs nanocomposites. Therefore, in this stage only epoxy nanocomposites containing A-GNPs were used as matrices to manufacture multiscale composites. For the reinforcement, a 5 – harness satin (5 HS) woven carbon fibre (CF) fabric (R100026) with an areal density of 380 g/m² (supplied by Sigmatex UK) was used (Figure 3.15).

3.3.2 Manufacturing of Multiscale Composites

Manufacturing of multiscale composites was done by a Resin Film Infusion (RFI) technique. This technique was employed due to the high viscosity of the resin suspensions, especially when the highest loading of A-GNPs (6 wt. %) was used.

To prepare the resin film, the dispersion of A-GNPs was carried out using the same method as explained in section 3.2.5. The resulting suspension was then poured into a flexible mould, fabricated using PTFE-coated glass cloth, and degassed for about 1 hour in a vacuum oven at 100 °C. Once cool, the mould was left overnight in a freezer to allow the resin/suspension to become a hard film, as shown in Figure 3.16a, which allowed it to be transferred on to CF fabric as shown in Figure 3.16b.

Figure 3.16: (a) Resin/suspension film used in this work (b) Resin film transferred onto carbon fibre fabric.
Eight layers of CF fabric were used to produce laminates approximately 3 mm thick. These were cut into specimens (as in Figure 3.16b) with sizes varying according to the type of test panel. The bigger the size of the rectangle carbon fibre, the more samples it can offer for testing, but the higher the amount of A-GNPs needed to prepare the suspension. Therefore, a detailed plan of how big the composite panels to be produced should be considered before manufacturing to avoid wasting raw materials especially GNPs. At least three specimens were prepared for each sample for all types of testing in multiscale composite which produced by only one moulding. However, for impact testing and compression after impact (CAI), two mouldings are required since dimension of each specimen is relatively large and mould and hot press equipment could not accommodate a sufficiently large single moulding.

Initially in this work, a single (thick) layer of resin film was used as in Figure 3.17a. But, this resulted in composite panels where the outer surface was not fully wetted by the resin due to lack of penetration through the CF fabric in the Z direction.

Figure 3.17: Schematic illustration of RFI technique (a) 1 layer of resin film (b) 3 layers of resin film.
Therefore, three thinner layers of resin film were used which resulted in better wetting of the carbon fabric (a comparison between these techniques will be presented in chapter 6). These three resin films were placed alternately between every two layers of CF fabric as shown in Figure 3.17b. This sandwich construction of CF/resin film was then transferred on to a flat aluminium mould plate and peel ply was placed at top and bottom (outer surface). After that, a permeable mesh was also placed on top and bottom after the peel ply (Figure 3.17b). A spiral tube was taped at one side of the mould to allow suction of trapped air and compression of the sandwiched construction of CF and resin so that complete wetting of the CF fabric could be achieved. Figure 3.17b shows the schematic illustration of the RFI technique used in this work, in which 3 layers of resin film were inserted (1 between every 2 layers of carbon fibre).

![Figure 3.18: Composite layup with pressure gauge attached to check the vacuum condition.](image)

Finally, this constructed layup was covered with Nylon vacuum bagging film and sealed with tacky tape. A valve was connected to this layup and a vacuum pressure
of -100 kPa was then applied using an outlet port connected to a vacuum pump. Using the pressure gauge, the layup was left ~30 minutes to check if the constructed layup had any leakage (Figure 3.18).

Figure 3.19: Membrane press for melting and infusion of resin film.

Figure 3.20: Temperature applied at constant pressure of 6 bars in the hot press during composite fabrication.
An Elkom membrane press preheated to 100 °C. Once the composites layup was fine (showing no leakage), it was transferred onto the membrane press (Figure 3.19). An outlet port was connected to vacuum pump to maintain the pressure at -100 kPa within the bag. Heat supplied by the membrane press melted the resin films which, as vacuum-induced pressure compressed the layup infused through the CF fabric over a period of 1 hour.

The composites layup was then transferred to a hot press (Collin P300) for curing and flattening of the top surface of the composite panels. The hot press was programmed to 130 °C for 2 hours and 160 °C for 2 hours with a pressure applied constantly at 6 bar (Figure 3.20). Once the programme in the hot press completed, the composite panel was removed from the aluminium mould plate and transferred into an oven for postcuring at 200 °C for 2 hours.

The manufacturing of composite panels will follow the requirements for the mechanical test conditions. For instance, to prepare a sample plate for the Mode II fracture toughness test a thin insert of release film, measuring 65 mm wide, was placed in the middle of the layup at one end to ensure a pre-crack was created in the composite panel as required by the testing standard.

3.3.3 Quality of Multiscale Composites

Fabricated multiscale composites were assessed in several ways to measure quality and the feasibility of the method used during manufacturing.

3.3.3.1 Acid Digestion of Matrix

The volume fractions of the composite constituents (matrix, reinforcement and voids) can be determined through the acid digestion method. As the name implies, acid digestion involves removing the matrix from the reinforcement using acid. In this work, acid digestion was carried out following ASTM D3171, method I, procedure B in section 8.2.2 [213] using sulphuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂).
For the measurement, approximately 1cm³ specimens were cut and then placed into an oven for 5 days at 70 °C to dry. The weights and densities of the specimens were measured using a Mettler Toledo XP205 Delta Range electronic balance fitted with a density measurement kit. To digest the matrix, each specimen was immersed into 20 mL of 100% sulphuric acid at 160 °C for about 2 hours, and then approximately 20 mL of hydrogen peroxide (used as a co-digestion reagent) was added slowly drop by drop. Adding hydrogen peroxide changed the solution’s appearance to colourless.

Once the cured epoxy from the composite was fully digested, the mixture was filtered using vacuum filtration and the remaining CF reinforcement was washed a few times using distilled water to remove residual acid. Filtered CF was then placed overnight into an oven at 100 °C for drying before its weight was recorded. Equations (3.19)-(3.23) were used to calculate the constituent percentage of the composites:

\[ W_c = \frac{M_f}{M_i} \times 100 \]  
\[ (3.19) \]

where, \( W_c \) is the fibre content weight percentage, \( M_f \) is the final mass of the specimen after digestion and \( M_i \) is the initial mass of the specimen.

\[ V_f = \frac{M_f}{M_i} \times \frac{p_c}{p_r} \times 100 \]  
\[ (3.20) \]

where, \( V_f \) is the fibre content volume percentage, \( p_c \) is the density of the specimen and \( p_r \) is the density of the fibre.

\[ W_m = \frac{M_i - M_f}{M_i} \times 100 \]  
\[ (3.21) \]

where, \( W_m \) is the matrix content weight percentage.

\[ V_m = \frac{M_i - M_f}{M_i} \times \frac{p_c}{p_m} \times 100 \]  
\[ (3.22) \]

where, \( V_m \) is the matrix content volume percentage and \( p_m \) is the density of the matrix.

\[ V_v = 100 - (W_c + V_m) \]  
\[ (3.23) \]

where, \( V_v \) is the void content by volume.
3.3.3.2 Ultrasonic C-Scan Analysis

In this work, a water-jet ultrasonic C-scan was used to assess the quality of the manufactured composites. Ultrasonic C-scan is a non-destructive test (NDT) and is the most commonly used technique to detect porosity [214]. C scanning has the ability to sense the spatial position and the size of defects in composite plates through ultrasonic transmission [214]. It uses two transducers, the transmitter and the receiver (Figure 3.21). The transmitter sends the ultrasonic signal to the specimen while the another transducer receives the transmitted signal. A C scan is produced when the amplitude of a particular echo is monitored at each point on the specimen. This will give the defect position on the work scanned surface [215]. The grid size and index step during scanning will determine the resolution of the scan (Figure 3.22). The index step is the distance where the transducer (or probes) moves upward at the end of each horizontal scanned segment.

![Figure 3.21: Through transmission method of ultrasonic scan testing][216]

For this test, a Midas NDT C scan system connected to Zeus v3.0 software was used. It consists of two transducers, a transmitter and a receiver. A suitable transducer frequency is required, which depends on the thickness of the composite panel. In
this work, a 10 MHz frequency ultrasonic probe was used. The scan was run at 125 mm/min with 200 μm for both grid size and index step. Two jets of water are directed towards the specimen, which is placed in the middle between the two nozzles. The signal transmitted down one of the jets will be detected as the other (transducer) water jet hits the specimen and is recorded by Zeus v3.0 software, connected to the nozzle with the computer. This signal relates to the non-uniformity of the tested specimen.

![Figure 3.22](image1.png)

Figure 3.22: (a) Grid size and (b) index step of a C scan.

![Figure 3.23](image2.png)

Figure 3.23: Damage profile of composite panel by C-scan [190].
The C scan only provides qualitative data. However, to calculate the damage area after impact testing, Image J software was used to analyse defects, scanned by the C scan. Figure 3.23 shows an example of a scanned image by C scan, indicating the damaged area in the middle of the composite panel.

3.3.4 Mechanical Characterisation of Multiscale Composites

Multiscale composites were tested to assess the effect of GNPs on their properties. A range of mechanical tests were carried out to determine the behaviour of these manufactured composites and the procedures used are explained as follows.

3.3.4.1 Flexural Testing

Flexural testing of multiscale composites was carried out using three-point bending according to ASTM D790 – 10 [210]. Specimens were cut into length according to the thickness of the specimen (specimen thickness varied as a function of A-GNPs loading in the matrices). Unlike flexural testing of the nanocomposites, the ratio of support span to thickness of the sample was set at 40:1 with 10% added at both end to give the final length of the specimen. All samples were cut into 12.7 mm widths. The same formulae used in flexural testing of nanocomposites were applied to calculate the rate of crosshead motion during testing (R). Through calculation, the testing speed was determined to be 4.85 mm/min. Specimens were tested using a three point bending fixture with a loading nose of radius 5 mm and lower supports also of 5 mm radius. Three specimens were tested for each sample using an Instron 5969 universal testing machine (UTM) fitted with a 10 kN load cell. The flexural modulus was calculated by using equation (3.14) and (3.15) as explained in chapter 3.

3.3.4.2 Interlaminar Shear Strength (ILSS) Testing

ILSS (also known as short-beam shear strength) was carried out in accordance with ASTM D2344/D2344M–00. This is a standard test method for short-beam strength
of polymer matrix laminate composite materials [217]. Through ILSS testing, the interlaminar strength of the composite panel could be determined. Depending on thickness, the dimensions of specimens were determined through equations (3.25) and (3.26) [217]. Testing was carried out using an Instron 8862 UTM at a crosshead speed of 1.0 mm/min with three specimens for each sample. The span length between two supports was determined to give a span to thickness ratio of 4.0. Force was applied during the test until either a load drop-off of 30% occurred or the specimen failed. The short beam shear strength was calculated using equation (3.24).

(3.25) \[ \text{Length} = \text{thickness} \times 6 \]
(3.26) \[ \text{Width} = \text{thickness} \times 2 \]

(3.27) \[
F_{sbs} = 0.75 \times \frac{P_m}{b \times h}
\]

Figure 3.24: Diagram of ILSS testing setup.

Where $F_{sbs}$ is short beam shear strength (MPa), $P_m$ is the maximum load observed during the test (N), $b$ is the measured specimen width (mm) and $h$ is the measured specimen thickness (mm). The setup for ILSS testing is shown in Figure 3.24.

3.3.4.3 Mode II Interlaminar Fracture Toughness Testing

Interlaminar delamination of a laminate composite material is one of the important considerations that need to be studied since it represents the common behaviour of
crack propagation for structural applications. Delamination of composite materials is often associated with mode II fracture toughness to predict susceptibility of the material in resisting crack opening or peeling between the plies. Mode II interlaminar fracture toughness was measured using 4-point end-notch flexure (4ENF) testing to characterise the crack propagation behaviour of the multiscale composites.

The testing was performed on an Instron 8862 UTM following the method and procedures described by Kuwata and Hogg [218]. Specimens were prepared the same way as mentioned previously in manufacturing the multiscale composite but a thin release film was inserted in the middle of the carbon fibre fabric, to equally divide the composite panel. The specimen dimension is (140 mm x 20 mm) ± 1 mm. The faces of the specimens were first polished before a white spray was applied at both sides and left to dry. Sprayed specimens were then marked vertically from the edge of the inserted film at every 1 mm up to 50 mm distance. These marks were used to measure the progress of crack propagation during the test. Three specimens were tested for each sample. Specimens were subjected to precracking, performed at a constant crosshead speed of 0.5 mm/min. An event (“pip”) counter was pressed for every 1 mm the crack propagated until when it reached 4 mm, the specimen was then unloaded at the same crosshead speed of 0.5 mm/min back to its start point before the load was reapplied using the same speed without stopping. The pip counter was pressed when the crack moved every 1 mm distance until specimen failed or final crack length was reached. Adjusted compliance versus delamination length data was plotted for the calibration of mode II critical strain energy release rate (\( G_{IIc} \)) by fitting a straight line to the data obtained from the second loading test. The gradient of the line, \( m \), was used to calculate \( G_{IIc} \) using equation,

\[
G_{II} = \frac{P^2 m}{2b}
\]

(3.28)

Where \( P \) is the load, \( m \) is the gradient from the compliance calibration curve and \( b \) is the width of the specimen. Figure 3.25 and Figure 3.26 shows the schematic test set-up and the actual test rig for the test.
3.3.4.4 Impact Resistance

The impact resistance of the composite panels was measured using a Ceast 9350 drop weight impact instrument equipped with CeastVIEW 5.94 3C software as the user interface. Testing followed the method introduced by Prichard and Hogg [219]. Unlike ASTM D 7136 [220] (a standard test method for measuring the damage
resistance of a fibre-reinforced polymer matrix composite to a drop-weight impact event), their procedure uses a reduced size specimen of (89 mm x 55 mm) ± 1 mm. The schematic of the test setup is shown in Figure 3.27. Three specimens were tested for each sample. Specimens were placed in between two plates having a 40 mm diameter circular hole. Specimens were clamped and, during testing, a 5.048 kg impactor fitted with a 20 mm diameter loading nose was used to hit the composite panel. The impact energy levels applied to specimens were 1 J, 3 J, 5 J and 8 J. This was determined at a preliminary stage, before all samples were tested, to obtain meaningful data.

![Figure 3.27: Schematic of impact test setup][219].

### 3.3.4.5 Compression after Impact (CAI)

The residual compressive strength of an impacted specimen was measured to determine its damage tolerance. This is normally done to study the effect of variation in energy level during impact testing. Since the composite panel produced in this experiment had GNPs added, the residual strength as a function of GNPs loading could also be observed. An anti-global buckling fixture was used so that failure during CAI tests failure occurred due to local buckling at the impacted area [221]. Figure 3.28 is a schematic illustration of the CAI test fixture.
In this experiment, CAI tests were performed using an Instron 5989 600 kN electro-mechanical UTM using reduced sized specimens [219]. The same specimens used in impact testing were used for CAI testing in order to find their residual compressive strength after impacting at certain energy levels. Specimens (89 mm x 55 mm) were tested at a constant cross-head speed of 0.5 mm/min. Three specimens were tested for each sample. Figure 3.29 shows the test rig used for testing in this work.
Chapter 4  Epoxy Blend by Response Surface Methodology

4.1  Introduction

Typically, highly crosslinked epoxy resins like TGPAP are used for applications in the aerospace industry. However, due to high viscosity and reactivity the liquid processing of composites using this type of epoxy is difficult. Therefore, in this research it is proposed that an epoxy resin with lower viscosity be blended with TGPAP to improve processability. The blended epoxy resin is expected to facilitate composites processing and offer the desired performance once cured. This chapter discusses the results of mixing DGEBF with TGPAP (to form an epoxy blend) for the manufacture of multiscale composites. Parametric interaction was studied by response surface methodology (RSM) using Design Expert® software. The experiment design used was explained in chapter 3.

4.2  Factor Interaction by RSM

The epoxy blend was characterised in terms of three responses, glass transition temperature ($T_g$), processing window (length of time available until the viscosity of the resin reaches 100 Pa s) and total enthalpy of reaction during cure ($\Delta H$). Two formulation factors were studied. The first was the DGEBF content (wt. %) in the epoxy blend (also denoted as factor A). The second (factor B) was the stoichiometric ratio (g/g) between amine hardener to epoxy. Throughout this thesis, TGPAP is also defined as trifunctional epoxy (Tri) while DGEBF is the bisphenol F epoxy (BPF).

4.2.1  Glass Transition Temperature ($T_g$)

Glass transition temperature ($T_g$) was measured using DMTA as explained in chapter 3 and the presented value in Table 4.1 is the onset $T_g$ determined from storage modulus curves. The interaction between factor A and B for $T_g$ is shown in Figure 4.1. From the 3D and contour plots of surface response, it can be seen that $T_g$ increases as the amount of the trifunctional TGPAP epoxy increases in the epoxy
blend (factor A). This is due to the fact that TGPAP has a higher functionality, compared to a bifunctional epoxy such as DGEBF, resulting in a greater crosslink density. Therefore, a higher \( T_g \) was obtained in epoxy blend with a higher amount of TGPAP. This finding is in agreement with Swanson et al. [223], who investigated the network development of three types of epoxy resins, namely TGDDM, TGPAP and DGEBA (the diglycidylether of bisphenol-A, another type of bifunctional epoxy) with DDS. They found that for all the resins, primary amine was consumed rapidly in the early reaction compared to secondary amines. Under the same conditions, TGPAP reached the gelation level earlier than DGEBA due to its higher functionality.

Table 4.1: Experimental results from experimental design, \( n = 3 \). (Value of glass transition temperature measured from onset storage modulus curve).

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Response 1</th>
<th>Response 2</th>
<th>Response 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:</td>
<td>DGEBF in</td>
<td>Stoichiometry</td>
<td>Glass</td>
<td>Processing</td>
<td>Heat of</td>
</tr>
<tr>
<td></td>
<td>DGEBF/TGPAP (wt. %)</td>
<td>Amine:Epoxy (g/g)</td>
<td>transition</td>
<td>window (min)</td>
<td>reaction (J/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>temperature ( (T_g) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>85.4</td>
<td>0.5</td>
<td>86.6 ± 1.0</td>
<td>251.4 ± 3.0</td>
<td>174.4 ± 2.9</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1</td>
<td>203.2 ± 1.5</td>
<td>59.6 ± 3.7</td>
<td>454.3 ± 6.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0.71</td>
<td>141.2 ± 0.6</td>
<td>206.8 ± 2.7</td>
<td>234.4 ± 3.3</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.71</td>
<td>206.4 ± 1.0</td>
<td>100.9 ± 2.2</td>
<td>423.2 ± 8.2</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
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<td>239.3 ± 0.8</td>
<td>57.2 ± 3.4</td>
<td>507.8 ± 1.2</td>
</tr>
<tr>
<td>6</td>
<td>85.4</td>
<td>0.92</td>
<td>183.8 ± 0.2</td>
<td>105.9 ± 2.0</td>
<td>325.6 ± 6.7</td>
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<td>90.7 ± 2.5</td>
<td>417.1 ± 9.2</td>
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<tr>
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<td>226.2 ± 0.5</td>
<td>53.3 ± 7.1</td>
<td>531.3 ± 3.2</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>0.71</td>
<td>206.4 ± 1.0</td>
<td>92.2 ± 2.7</td>
<td>400.9 ± 7.4</td>
</tr>
<tr>
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<td>224.9 ± 0.2</td>
<td>102.3 ± 1.6</td>
<td>580.3 ± 5.8</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>0.42</td>
<td>134.5 ± 1.0</td>
<td>203 ± 1.3</td>
<td>157.2 ± 2.6</td>
</tr>
</tbody>
</table>

For a fixed amount of DGEBF in the epoxy blend (factor B), as the stoichiometry increases so \( T_g \) increases slightly (as in Figure 4.1a and Figure 4.1b). However, beyond a stoichiometry of 0.71 and at a lower amount of DGEBF in the epoxy blend, the \( T_g \) value was observed to decrease. This is probably due to an increased amount number of secondary amines, which is due to their lower reactivity and possible
steric hindrance may not fully react with the epoxide groups [224]. Thus increased amine content may reduce the value of $T_g$ in an epoxy system by reducing the crosslink density and increasing free volume [225].

![Figure 4.1: Response surface for $T_g$ of DGEBF/TGPAP/DDS epoxy resins (a) 3D plot and (b) contour plot.](image-url)
This finding is in agreement with the study of Palmese and McCullough [226], who reported a significant effect on the modulus and glass transition temperature with a variation in stoichiometry ratio \((r)\). They studied the effect of varying the amount of hardener added into DGEBA, and showed that the highest \(T_g\) was obtained at 30 parts per hundred (pph), beyond which \(T_g\) reduced. They mentioned that using the wrong stoichiometry ratio of curing agent (either more or less) caused the final structures of cured composites to have a lower crosslink density, therefore lowering the \(T_g\). Guerrero et al. [227] also reported similar pattern of \(T_g\) for epoxy resin cured at different stoichiometry ratio, \(r\) which ranging from 0.3 to 1.0. They found the maximum \(T_g\) was obtained when \(r = 0.8 – 0.9\) and decreased thereafter. The following equations are the final empirical regression models, generated by the Design Expert® software for \(T_g\) in both coded and actual factors. It is noted that in the equation DGEBF is the short term used to represent weight of DGEBF from the total weight in the epoxy blend.

**Coded Factor**

\[
\]

**Actual Factor**

\[
56.01 - 2.85\text{DGEBF} + 584.26\text{Stoichiometry} + 3.31\text{DGEBF}\times\text{Stoichiometry} - 0.0063\text{DGEBF}^2 - 443.72\text{Stoichiometry}^2
\]

From the equation in coded factor, A and B are the main effects, AB is the two-level interaction effect and \(A^2\) and \(B^2\) are the second order effects. According to the regression model generated by the Design Expert® software, the two-level interaction between DGEBF content in epoxy blend (A) and stoichiometry (B) is the most significant factor associated with the \(T_g\). This interaction produces the highest value of coefficient, of +14.39 coded value [228]. Also it is noted that the contours are curved as the model contains a strong interaction term. Figure 4.2 shows the normal probability plot of the residual in response to \(T_g\) value. It is a plot to check whether the data set is normally distributed or not. From the plotted data, normal distribution of the points should form an approximate straight line [229]. A check on
the plots for $T_g$ clearly indicates no outliers of residuals are far from the straight line. This is desired and shows that the errors are distributed normally [229].

![Normal Plot of Residuals](image)

**Figure 4.2**: Normal probability plot of residual for $T_g$ data (rectangular plots are the point in CCD).

Summary of the test is presented as in Table 4.2. The confidence level, denoted as P, is usually selected at 95% [230]. The value of “$P > F$” in Table 4.2 for model is less than 0.05 and suggests that the model is significant. Similarly, all other model terms are significant since “pron > F” for each of these terms is also less than 0.05. Therefore, model reduction is not required.

As mentioned previously, different amounts of TGPAP in epoxy blend affect the $T_g$ of the cured epoxy blend due to the different functionality. In addition, as has been discussed earlier, different amounts of amine hardener added into the blended epoxy also produce a significant effect on the $T_g$ [226]. Both factors A and B have a significant effect on the $T_g$, and hence both the two-level interaction (AB) and the second-order effect are also significant. The coefficient of determination, $R^2$ value is
high, close to 1, which is desirable. Adequate Precision measures the signal-to-noise ratio and a ratio greater than 4 is desirable [231], [232]. For this model, the value of adequate precision was 31.541 indicating an adequate signal [229].

Table 4.2: ANOVA table for surface response quadratic model (response: glass transition temperature, $T_g$).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value (Prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>21837.58</td>
<td>5</td>
<td>4367.52</td>
<td>97.95</td>
<td>&lt; 0.0001 (Significant)</td>
</tr>
<tr>
<td>A-DGEBF in DGEBF/TGPAP</td>
<td>2730.24</td>
<td>1</td>
<td>2730.24</td>
<td>61.23</td>
<td>0.0005</td>
</tr>
<tr>
<td>B-Stoichiometry</td>
<td>580.89</td>
<td>1</td>
<td>580.89</td>
<td>13.03</td>
<td>0.0154</td>
</tr>
<tr>
<td>AB</td>
<td>2296.01</td>
<td>1</td>
<td>2296.01</td>
<td>51.49</td>
<td>0.0008</td>
</tr>
<tr>
<td>$A^2$</td>
<td>353.05</td>
<td>1</td>
<td>353.05</td>
<td>7.92</td>
<td>0.0374</td>
</tr>
<tr>
<td>$B^2$</td>
<td>1960.37</td>
<td>1</td>
<td>1960.37</td>
<td>43.96</td>
<td>0.0012</td>
</tr>
<tr>
<td>Residual</td>
<td>222.92</td>
<td>5</td>
<td>44.59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Std. Dev. 6.68  R$^2$ 0.9899
Mean 187.19  Adj. R$^2$ 0.9798
C. V. % 3.57  Pred R$^2$ 0.9281
PRESS 1585.26  Adeq. Precision 31.541

4.2.2 Processing Window (t)

In this work, the processing window (PW) is defined as the length of time until the viscosity of an epoxy blend increases to 100 Pa s. Table 4.1 shows the experimental results for the PW and Figure 4.3 shows examples of the viscosity profiles recorded for two epoxy systems (at the same stoichiometric ratio). The behaviour of the epoxy resin during the measurement can be explained as follows. At the start of the experiment, the temperature of the rheometer was set at 80 °C. It can be seen that the initial viscosity of pure TGPAP epoxy (~0.100 Pa s) is higher than the formulated epoxy blend (~0.080 Pa s) due to the addition of the lower viscosity DGEBF. After 10 minutes at 80 °C, the temperature of the furnace was raised to 130 °C and the viscosity of the resin is seen to decrease. The minimum viscosity recorded for both
profiles is approximately 0.010 Pa s. As the temperature was raised and maintained at 130 °C experiment, the viscosity profile increased due to network formation (crosslinking) and finally reached a plateau, suggesting the system is completely vitrified. The PW was taken as the time at which the viscosity of the resin reached 100 Pa s following ASTM D4473–95a, Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior [233].

Figure 4.3: Isothermal complex viscosity profile for curing of neat TGPAP and a DGEBF/TGPAP blend.

Figure 4.4a and Figure 4.4b show the 3D plots and contour of the response surface of the PW for the interaction between factor A (DGEBF in epoxy blend) and B (stoichiometry). It can be seen from Figure 4.4 that a higher DGEBF (less TGPAP) in epoxy blend resulted in a longer time for the resin to reach 100 Pa s. This means more time will be available to process the blended epoxy during fabrication and manufacturing of composites. As mentioned previously, TGPAP’s nominal functionality of 3 is higher than that of the bifunctional DGEBF. Therefore, as expected, a higher amount of TGPAP in the epoxy blend will reduce the PW due to the system reaching gelation level earlier.
Figure 4.4: Response surface for processing window of DGEBF/TGPAP/DDS epoxy resins (a) 3D plot and (b) contour plot.

Small increases in processing window are observed towards the end of the area on the top-left corner of the response plot in Figure 4.4. The formation of this contour, which shows a small increase in processing window in that area, is probably
influenced by the value of processing window obtained for point (14.6, 0.92). This result could be due to experimental error as indicated by the error value (standard deviation) which is anomalous. During experiments, the control temperature of the rheometer’s furnace is in the range of ± 10 °C. The fluctuation in control temperature within this range could possibly affect the rate of crosslinking and influence the value of processing window for each test from the same sample which finally affects the average value. In addition, to minimise the error for future reference, it is recommended that the three repeats of the test for each sample should be performed at the closest time possible to each other. Otherwise, reaction between epoxy-amine could possibly occur if the epoxy blend was left unused even if the sample was placed in the freezer. This could possibly result in crosslinking prior to the experiment which will affect the measure value of the processing window. The following equations are the final empirical regression models generated by the Design Expert® software for PW in both coded and actual factors:

\[
\text{Coded Factor} = 71.08 + 13.87A - 36.03B - 14.47AB + 6.43A^2 + 17.49B^2
\]

\[
\text{Actual Factor} = 320.84 + 2.39\times\text{DGEBF} - 666.59\times\text{stoichiometry} - 3.33\times\text{DGEBF}\times\text{stoichiometry} + 0.0143\times\text{DGEBF}^2 + 415.99\times\text{stoichiometry}^2
\]

From the regression model, the most significant factor is the level of DGEBF in the epoxy blend at a coefficient of +18.87. The percentage error is also calculated and shown. Figure 4.5 shows the normal probability plot of residual in response to changes in the processing window. As explained previously in T\textsubscript{g} response, it can be observed that all plots are scattered around the straight line which is desirable and illustrates that the distribution of errors is normal [229].

The ANOVA analysis for the PW is shown in Table 4.3. The value of “Prob > F” is less than 0.05 which indicates that the model is significant. The same explanations as in subsection 4.2.1 are applied to describe the ANOVA analysis (Table 4.3).
Figure 4.5: Normal probability plot of residual for processing window data (rectangular plots are the point in CCD).

Table 4.3: ANOVA table for surface response quadratic model (response: processing window, t).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value (Prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>46138.06</td>
<td>5</td>
<td>9227.61</td>
<td>441.82</td>
<td>&lt; 0.0001 (Significant)</td>
</tr>
<tr>
<td>A-DGEBF in DGEBF/TGPAP</td>
<td>2811.65</td>
<td>1</td>
<td>2811.65</td>
<td>134.62</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B-Stoichiometry</td>
<td>6331.62</td>
<td>1</td>
<td>6331.62</td>
<td>303.16</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>AB</td>
<td>2327.10</td>
<td>1</td>
<td>2327.10</td>
<td>111.42</td>
<td>0.0001</td>
</tr>
<tr>
<td>A²</td>
<td>1801.80</td>
<td>1</td>
<td>1801.80</td>
<td>86.27</td>
<td>0.0002</td>
</tr>
<tr>
<td>B²</td>
<td>1727.93</td>
<td>1</td>
<td>1727.93</td>
<td>82.73</td>
<td>0.0003</td>
</tr>
<tr>
<td>Residual</td>
<td>104.43</td>
<td>5</td>
<td>20.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>4.57</td>
<td></td>
<td>R²</td>
<td>0.9977</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>120.29</td>
<td></td>
<td>Adj. R²</td>
<td>0.9955</td>
<td></td>
</tr>
<tr>
<td>C. V. %</td>
<td>3.80</td>
<td></td>
<td>Pred R²</td>
<td>0.9903</td>
<td></td>
</tr>
<tr>
<td>PRESS</td>
<td>449.79</td>
<td></td>
<td>Adeq. Precision</td>
<td>60.041</td>
<td></td>
</tr>
</tbody>
</table>
4.2.3 Heat of Reaction (ΔH)

The reaction of epoxy with hardener during curing is exothermic [234]. The heat produced during cure can be measured in terms of total enthalpy of reaction. This was carried out using DSC.

![Response surface for heat of reaction of DGEBF/TGPAP/DDS epoxy resins](image)

**Figure 4.6:** Response surface for heat of reaction of DGEBF/TGPAP/DDS epoxy resins (a) 3D plot and (b) contour plot.
The heat of reaction (ΔH) was measured to study the effect of the DGEBF composition in the DGEBF/TGPAP mixture and stoichiometry of amine to epoxy group. It will not be taken into consideration for response optimization in RSM. It is because the heat of reaction will not affect the manufacturing process of multiscale composites.

Table 4.1 shows the experimental results for total enthalpy of reaction obtained in this work. Figure 4.6 shows the response surface for ΔH in 3D and contour plots. As expected, for factor A, as the DGEBF content increased the heat of reaction decreases. This is due to lower functionality of DGEBF, which reduces the total enthalpy of reaction during cure of the epoxy blend. For factor B, at a fixed amount of DGEBF in epoxy blend, the heat of reaction increases as the stoichiometry increase. This finding is in agreement with previous work [235]–[237] which indicated that TGPAP has a higher enthalpy of reaction than a bifunctional epoxy resin. The following equations are the final empirical regression models, generated by the Design Expert® software for ΔH in both coded and actual factors.

![Figure 4.7: Normal probability plot of residual for ΔH data (rectangular plots are the point in CCD).](image-url)
\[
\text{Coded factors } = 452.78 - 74.87A + 65.38B
\]

\[
\text{Actual factors } = 332.30 - 3.53\text{DGEBF} + 318.82\text{stoichiometry}
\]

Table 4.4: ANOVA table for surface response linear model (response: heat of reaction, \(\Delta H\)).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value (Prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.000016</td>
<td>2</td>
<td>79377.3</td>
<td>13.92</td>
<td>0.025 (Significant)</td>
</tr>
<tr>
<td>A-DGEBF in DGEBF/TGPAP</td>
<td>0.000012</td>
<td>1</td>
<td>0.000012</td>
<td>21.84</td>
<td>0.0016</td>
</tr>
<tr>
<td>B-Stoichiometry</td>
<td>34193.00</td>
<td>1</td>
<td>34193.00</td>
<td>6.00</td>
<td>0.04</td>
</tr>
<tr>
<td>Residual</td>
<td>45622.90</td>
<td>8</td>
<td>5702.86</td>
<td>58.30</td>
<td></td>
</tr>
</tbody>
</table>

Std. Dev. 75.52  
Mean 382.19  
C. V. % 19.76  
PRESS 0.0000101  

Unlike \(T_g\) and \(PW\), the suggested regression model for \(\Delta H\) is linear with the only significant effects being the level of DGEBF in the epoxy blend (A) and the stoichiometry (B). Figure 4.7 and Table 4.4 respectively show the normal probability plot and ANOVA analysis for the heat of reaction. The same explanation in ANOVA analysis applied as in subsection 4.2.1 for \(T_g\) is applied here.

4.3 Optimization of Epoxy Formulation

In order to optimize the system, a few criteria were set as goals [238]. Table 4.5 shows the criteria used to limit the range of the factors to achieve the optimum goal for each response. The explanation for each criterion is as follows. DGEBF level in epoxy blend was set to “maximize” since more DGEBF in an epoxy blend will give a lower viscosity for better processability of composites. Stoichiometry was set to “minimize” to reduce the viscosity of the epoxy blend. Higher stoichiometry will result in the addition of a higher amount of DDS powder, which will raise the
viscosity of the epoxy. Increase in viscosity will be a disadvantage for composites processing. Responses considered are $T_g$ and PW. The $\Delta H$ was not taken into account since total enthalpy of reaction will not affect the processability of multiscale composite. Therefore, the goal for $\Delta H$ was set to “none” in the software. It has been reported that for structural aerospace applications polymer composites should have a $T_g$ value of at least 180 °C due to high temperature application during service [190]. Therefore, $T_g$ was set to in range between 180-185 °C for the optimization. Finally, the PW was set to be “maximize”, as the epoxy resin system needs to be processed before it starts to cure and its viscosity increase significantly.

The importance column and * symbol as shown in Table 4.5 reflects the priority to achieve optimization. A greater number of * indicate that a higher importance was placed on that particular response or factor [239].

Optimization in targeting the maximum goal yielded 9 suggested solutions for the epoxy formulation. However, the epoxy formulation with the highest desirability was selected. In Design Expert® software, the desirability chart can be viewed in two modes. First, is in ramp mode as shown in Figure 4.8a. View of desirability chart in ramp mode will indicate the individual element for easier interpretation, predicted in actual value. Each ramp in Figure 4.8a shows dot which reflects the optimum value for factors and responses for that solution. To meet the set criteria as in Table 4.5 for optimum response, factors value is achieved at 55.6% of DGEBF in epoxy blend (factor A) and at a stoichiometry of 0.60 (factor B). Both of these values are predicted to give $T_g$ at 180°C and processing window at 136.1 minutes (Figure 4.8a). Second, the desirability value can be viewed in histogram chart (Figure 4.8b). Unlike in ramp mode view, desirability value shown in histogram chart is converted to the value ranging from 0 to 1. This form of graph will indicate how well each variable satisfied the criteria with values near to 1 are good. Desirability for each factors and responses were also indicated as in Figure 4.8b. In this work, the combined desirability was predicted by the Design Expert® at a value of 0.520. A verification test was carried out which gave a $T_g$ at 181.2 ± 0.8 °C which is close to the predicted value. For processing window, the verification run gave a PW of ≈140 minutes. The small discrepancy between verification test and predicted
value for processing window could be associated to the range of control temperature in the furnace which is within ± 10 °C. The fluctuated temperature within this range could affect the test result.

**Table 4.5: Criteria for epoxy blend optimization.**

<table>
<thead>
<tr>
<th>Factor/Response</th>
<th>Goal</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
<th>Importance</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBF in DGEBF/TGPAP</td>
<td>Maximize</td>
<td>0</td>
<td>100</td>
<td>****</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>Minimize</td>
<td>0.42</td>
<td>1</td>
<td>***</td>
</tr>
<tr>
<td>$T_g$ infinity</td>
<td>Is in range</td>
<td>180</td>
<td>185</td>
<td>*****</td>
</tr>
<tr>
<td>Processing window</td>
<td>Maximize</td>
<td>53.28</td>
<td>251.4</td>
<td>*****</td>
</tr>
</tbody>
</table>

![Desirability Chart](image.png)

**Figure 4.8: Desirability chart in (a) Ramp mode of factors for optimum responses of the epoxy blend and (b) Histogram chart with factors and predicted responses.**
4.4 Summary

This chapter presented the findings of experimental work in blending DGEBF and TGPAP to produce an epoxy resin system to be cured with DDS. The effects of the DGEBF content in a DGEBF/TGPAP blend and amine:epoxy stoichiometry ratio with DDS hardener was investigated through response surface methodology using Design Expert® software. The composition of the epoxy blend and the stoichiometric ratio were determined by optimizing the factors to meet the targeted response requirements. The epoxy formulation and stoichiometry with the highest desirability was selected for use in the next stage of this work, which was 55.6% of DGEBF in the DGEBF/TGPAP blend at a stoichiometric ratio of 0.60. At this composition, value predicted was 180 °C for $T_g$ and 136.1 minutes for PW. A verification test was carried out and gave $T_g = 181.2 \pm 0.8$ °C and PW of ≈ 140 minutes which is not far from the predicted value.
Chapter 5  Epoxy/GNPs Nanocomposite Matrices

5.1  Introduction

As reported in chapter 4, an epoxy blend with 55.6% DGEBF and 44.4% TGPAP was chosen for the next phase – a study of the processing, structure and properties of epoxy/GNP nanocomposites.

5.2  Characterisations of GNPs

Firstly, the use of GNPs was maximised by surface modification using covalent and noncovalent treatments. Modified (T-GNP, A-GNP), unmodified (U-GNP) and as-received (AR-GNP), were characterised to assess the effectiveness of treatment.

5.2.1  Microstructural Characterisation

Figure 5.1 shows a typical SEM micrograph of AR-GNPs. It can be seen that the shape of GNPs are platelets type with non-uniform graphene layers stacked upon each other and folded together. This gave transparent and non-transparent images depending on the number of graphene layers in a GNP. The transparent image show fine surfaces of platelets, suggesting thin layers of GNPs. The GNPs shown in Figure 5.1 are essentially as described by the manufacturer with nanoparticles stacks consisting of several layers of graphene sheets having a platelet shape.

![SEM image of as-received GNPs (AR-GNPs), M-25 (XG Sciences).](image)

Figure 5.1: SEM image of as-received GNPs (AR-GNPs), M-25 (XG Sciences).
The platelet-like structure of GNPs was also observed using TEM as shown in Figure 5.2. The TEM image confirmed that AR-GNPs supplied by XG Sciences consist of graphene stacks as reported in their website [240]. Darker areas in Figure 5.2a show that AR-GNPs have stacks of graphene probably 6 to 8 nm thick with 17 to 22 layers as reported by XG Sciences. Similarly, U-GNPs (Figure 5.2b) also produce dark areas in their TEM images, perhaps due to poor exfoliation or reaggregation of graphene sheets.

Figure 5.2: TEM images of GNPs (a) AR-GNP (b) U-GNP) (c) T-GNPs and (d) A-GNPs. Arrows in (a) and (b) indicate obvious folding and wrinkling area for AR and U-GNPs respectively.

Figure 5.2c and Figure 5.2d shows images of GNPs treated by Triton X-100 and APTS, respectively. Both images of the treated GNPs are more transparent
suggesting that thinner stacks of graphene sheets were obtained after the treatment, possibly due to increased exfoliation. The grafting of a surface modifier and sonication creates steric repulsive forces between graphene sheets which will help the exfoliation process and peeling of the stacked layers [98]. Hence, thinner stacks of graphene layers can be observed for both treated GNPs as in Figure 5.2c and Figure 5.2d. In addition, the treatment procedure also affects the GNPs by reducing the platelet size as can be seen in Figure 5.2c and Figure 5.2d compare to as-received GNPs due to effective in sonication process. Previously, similar findings were reported by Khan et al. [241] and Nawaz et al [242], where in their work the length dimensions of graphene flakes were measured as a function of sonication time. They reported that longer sonication in solvent reduced the length of the GNPs from ~3 μm to ~1 μm [241] and from 3.42 μm to 1 μm [242].

Moreover, as indicated by arrows, AR-GNPs and U-GNPs show obvious folding and wrinkling of their surfaces. In contrast, Figure 5.2c and Figure 5.2d show both of the treated GNPs lying flatter on the TEM grid with less folded areas. The folded areas can be identified with the dark streak on the particle image for both treated GNPs.

### 5.2.2 Thermogravimetric Analysis (TGA)

TGA is a useful technique to study thermal stability of a sample. Unstable components may decompose or evaporate at high temperature and provide information about potential mass loss of the sample during processing and in-service. When nanoparticles are modified with chemical agent, it is expected that the grafted modifier will decompose earlier as a function of temperature. In this study, TGA will give an indication as to whether Triton X-100 and APTS molecules were successfully attached onto the surface of the GNPs during treatment.

Figure 5.3 shows TGA curves for both modifiers used in this work, natural graphite, and all the GNPs in nitrogen (N₂) atmosphere. Both modifiers show a very sharp weight loss due to decomposition as a function of temperature. They are volatile hence their TGA curves are not comparable with the GNPs. Graphite proves to be
the most stable material with almost no weight loss observed over the range of temperature studied up to 900 °C. Similar TGA data for graphite was reported by Naebe et al. [243].

As-received GNPs (AR-GNPs) show only a slight weight loss as a function of temperature and a 15% reduction in weight was recorded at 900 °C. For the U-GNPs, a slightly greater decrease in weight (18%) compared to AR-GNPs (15%) was observed. U-GNPs have been sonicated in an NMP/water mixture, potentially leading to greater exfoliation and greater exposed surface area than the AR-GNPs hence giving higher weight loss. From Figure 5.3, it can be seen that both of the treated GNPs experience higher mass loss compared to the graphite, AR-GNPs and U-GNPs. This is most likely due to the decomposition of grafted molecules (Triton X-100 and APTS) attached to their surface. Previously, similar results were observed by another group using Triton X-100 [93], [244] and APTS [81] to modify nanofillers.

Figure 5.3: TGA curves of natural graphite and the GNPs (N₂ atmosphere).
In order to estimate the amount of modifiers attached to the GNPs, TGA analysis was also run in air. In air atmosphere, GNPs will react with oxygen as a function of
temperature, thus their thermal stability in air is lower than what has been observed in nitrogen [245]. The result shown in Figure 5.4 indicates three decomposition steps of GNPs. The first mass loss event occurred at around ~100 to 250 °C which is associated due to loss of moisture and other volatiles [88], [246]. It can be observed that both of the treated GNPs experienced higher mass loss in this region possibly due to desorption, decomposition and evaporation of both modifiers from the nanoparticles’ surface [247]. In order to show the point at which the weight loss is more apparent, differential thermogravimetric (DTG) curve (%/°C) is shown in Figure 5.5. It is estimated that the content of APTS and Triton X-100 attached to the surface of GNPs is 5 and 7 wt. % respectively. The second event of mass loss is observed between ~350 to ~500 °C probably due to degradation of functional group containing oxygen yielding carbon dioxide [67]. At higher temperature all samples oxidised and rapidly lose mass (~70 wt. %). Previously, similar behaviour of thermal stability for GNPs were reported by Ma et al. [248] and B. Alshammari [249].

5.2.3 Raman Spectroscopy

Raman spectroscopy is a useful technique in characterising carbon materials, such as GNPs. In this work it was used to provide quantitative data on the quality of GNPs after treatment and adsorption of the modifier on to the GNP surface. A typical Raman spectrum for a GNP graphene stack consists of three main peaks, a D peak (at around ~1360 cm\(^{-1}\)), a G peak (~1560 cm\(^{-1}\)) and a 2D peak (~2700 cm\(^{-1}\)) [250], [251]. The D peak reflects the disorder of the sp\(^3\) hybridized carbon atoms and only appears when defects are present [252], while the G band peak is related to in-plane vibration of the sp\(^2\) hybridized carbon structure [12].

Figure 5.6 shows Raman spectra for all the GNPs. In Figure 5.6, the 2D peak is observed to shift towards lower energy for both treated GNPs compared to unmodified and as-received GNPs. This could be attributed to a decrease in the number of graphene layers for treated GNPs as further exfoliation may have occurred during treatment. Previously, Ferrari et al. [253] have reported on the evolution of
2D band peak as a function of the number of graphene layers and graphite. They indicated that decrease in the number of graphene layers shifted the 2D band peak towards lower energy.

![Figure 5.6: Typical Raman spectra for all types of GNPs.](image)

Typically, the intensity ratio of the D to the G peak ($I_D/I_G$) was used to measure defects and to quantify the disorder of the GNP structure [254]. Table 5.1 shows $I_D/I_G$ for all types of GNPs used in this work. It can be observed that the intensity ratio of D to G peak is greater and significant for both of the treated GNPs which reflects the effectiveness of treatment due to attachment and adsorption of APTS and Triton molecules onto the GNP [244], supporting the TGA data. According to Hussain et al. [255], the adsorption of functional group onto the nanoparticle’s surface will cause the number of defects to increase. This is because the treating agents could disturb relevant bonds located on the nanoparticle’s surface which may contribute to physical defects in its structure [256]. This could be observed through
the ratio of $I_D/I_G$ in Raman spectroscopy. Previously, other research groups also have observed similar behaviour in Raman analysis for functionalised GNPs where higher levels of defects are reported compared to unmodified GNPs [81], [95].

Table 5.1: Ratios $I_D/I_G$ for all GNPs. Data are mean ± standard deviation (n=5).

<table>
<thead>
<tr>
<th>GNPs type</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>0.24 ± 0.05</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>0.38 ± 0.09</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>*0.76 ± 0.04</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>*0.61 ± 0.03</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant calculated against AR-GNPs at 95% confidence level and degree of freedom (df) of 8 with t-value from standard table is 1.860.

The disorder in the GNP structure is higher for A-GNPs compared to the T-GNPs, which may be due to the mechanism of grafting. APTS molecules could be attached to the GNP surface through covalent bonding, perhaps through Si-O [84], [257]. Functionalization through covalent bonding will induce hybridisation changes in the carbon structure from sp² to sp³ that is reflected in an increasing D band intensity (increasing the $I_D/I_G$ ratio) [257]. On the other hand, the adsorption of Triton X-100 on to the surface of GNP could possibly occur through noncovalent bonding, for instance, by weak hydrogen bonding [98], [258] which will not disturb the carbon structure as intensely. Defects may also be generated during the sonication process [259], [260]. Thus, on comparing the $I_D/I_G$ of the AR-GNPs (unsonicated) and U-GNPs (sonicated for 4 hours) the latter sample was found to have a slightly higher ratio (+17%).

5.2.4 Energy Dispersive X-Ray (EDX)

Figure 5.7 shows the EDX spectrum for all types of GNPs used. There are three main elements in all samples which are carbon, oxygen and sulphur. In the case of A-GNPs, the silicon peak also appeared indicating that the treatment was successful in attaching APTS to the GNP. This finding is in agreement with Ma et al. [261]
who functionalized carbon nanotubes using (3-glycidyloxypropyl) trimethoxysilane (GPTMS) and Kim et al. group [187] who functionalized GNPs using three different types of silane coupling agents.

![Figure 5.7: EDX spectrum of all the GNPs.](image)

**Table 5.2: Elemental composition of GNPs by EDX spectroscopy.**

<table>
<thead>
<tr>
<th>GNPs type</th>
<th>Element (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>93.3</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>92.4</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>94.1</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>95.5</td>
</tr>
</tbody>
</table>

For non-covalent treatment using Triton X-100, no other elements could be detected, since the chemical structure of this surfactant consists of carbon, hydrogen and
oxygen, which are already present in GNPs. Therefore, evidence of change is not obvious. However, the elemental composition as in Table 5.2 shows that the carbon to oxygen ratio increased after GNPs were treated by Triton X-100. This change is attributable to the attachment of the surfactant since Triton X-100 molecules possess a high ratio of carbon to oxygen in its chemical structure.

5.2.5 X–Ray Photoelectron Spectroscopy (XPS)

XPS was also used to study the effects of surface modification on the GNPs. Figure 5.8 shows wide scan surveys of all GNPs types. In general, two main peaks appear in the spectra which are the C 1s and O 1s. Carbon and oxygen are the two main elements in GNPs. There is no obvious difference in the spectra of the U-GNPs and T-GNPs, relative to AR-GNPs. However, a new peak appeared at around 100 eV for the A-GNPs, indicating silicon. Once again, this indicates grafting of APTS onto the GNPs surface. This is in agreement with the results reported by other groups for surface modification using APTS with GNPs [84] and CNTs [261].

![Figure 5.8: XPS wide scan spectra for AR-GNPs, U-GNPs, A-GNPs and T-GNPs.](image)
In addition to the wide scan survey, Figure 5.9 shows the high resolution scan of C 1s spectra for all the GNPs. The deconvolution of C 1s spectra consisted of four peaks at 284.6, 285.6, 287.6 and 291.2 eV [84], [135], [244], [261], [262]. The percentage and assignation for each peak to their respective element is summarized as shown in Table 5.3. The appearance of groups on the GNPs surface like C-OH and C=O could have been introduced during preparation of the GNPs. The peak for the $\pi-\pi$ chemical environment at 291.2 eV is due to the interaction between aromatic carbon structures between graphene layers in the GNPs. The main peak appearing at 284.6 eV corresponds to C-C binding energy which normally has been used as a reference for peak calibration [244] and corresponds to sp$^2$ carbon atoms.

Figure 5.9: Deconvolution of C 1s high resolution scan for (a) AR-GNPs (b) U-GNPs (c) A- GNPs and (d) T-GNPs.
Table 5.3: Summary of relative percentage (%) of carbon and assignation.

<table>
<thead>
<tr>
<th>GNPs type</th>
<th>284.6 eV</th>
<th>285.6 eV</th>
<th>287.4 eV</th>
<th>291.2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-C</td>
<td>C-OH</td>
<td>C=O</td>
<td>π-π</td>
</tr>
<tr>
<td>AR- GNPs</td>
<td>69.4</td>
<td>16.5</td>
<td>10.9</td>
<td>3.2</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>60.1</td>
<td>25.2</td>
<td>13.1</td>
<td>1.6</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>67.9</td>
<td>19.5</td>
<td>7.3</td>
<td>5.3</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>69.3</td>
<td>18.7</td>
<td>6.8</td>
<td>5.2</td>
</tr>
</tbody>
</table>

![Figure 5.10: Deconvolution of O 1s high resolution scan for A-GNPs.](image)

Grafting of APTS molecules on GNPs structure was further evidenced by high resolution scan of O 1s (Figure 5.10). The spectra were deconvoluted into two peaks at 531.8 eV which is assigned for C=O and 533.3 eV which is an indicator of Si-O chemical environment in A-GNPs [263], [264]. In the case of T-GNPs, since Triton X-100 molecules consist of only carbon, oxygen and hydrogen atoms, no obvious differences can be observed on the wide scan spectra. Therefore, once again due to the high ratio of carbon to oxygen in the structure of the Triton X-100 molecule, the carbon to oxygen ratio was calculated [95]. Figure 5.11 shows that treatment of GNPs by Triton X-100 increased the C/O ratio relative to AR-GNPs...
from 18.1 to 26.2. Table 5.4 shows the amount of each element in every type of GNP, which indicates that Triton X-100 was grafted on to the GNP surface. Quantification of the elemental composition using XPS shows general agreement with the data from EDX but shows a different value since the sensitivity and mechanism of the two instruments are different.

Figure 5.11: XPS spectrum of C1s and O1s for (a) AR-GNPs (b) U-GNPs (c) A-GNPs and (d) T-GNPs.

Table 5.4: Summary of elemental composition by XPS.

<table>
<thead>
<tr>
<th>GNP type</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Si (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>94.8</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>91.7</td>
<td>8.3</td>
<td>-</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>94.5</td>
<td>5.1</td>
<td>0.4</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>96.3</td>
<td>3.7</td>
<td>-</td>
</tr>
</tbody>
</table>
The presence of sulphur in GNPs as detected by EDX and XPS in this work was further confirmed using CHNS elemental analysis as shown in Table 5.5. CHNS results indicated that GNPs supplied from XG sciences contained sulphur at 0.9 %, which could have been produced during processing of the GNPs. However, it is not clear what type of method was used to manufacture the GNPs to give sulphur in the structure. Perhaps, it may come from acid treatment during processing since the technical data sheet stated there is a residual acid in GNPs and the content is less than 0.5 wt. %. Unfortunately, no information was provided on what type of acid has been used [195]. It is noted that the process is non-oxidising as mentioned in the data sheet provided by XG sciences.

Table 5.5: Elemental composition by CHNS analyser.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>91.5</td>
</tr>
</tbody>
</table>

As discussed earlier regarding TEM images, treatment of GNPs in this work caused a reduction in the platelet size. If it is assumed that the GNPs are round in shape and that the percentage of oxygen reported by EDX or XPS were obtained from the edge of the platelets with all the edges oxygen-terminated, the composition of oxygen can be estimated for smaller platelet. If 5.5 % of oxygen content for AR-GNPs (25 μm platelet diameter) as detected by EDX is used as reference (Table 5.2), the quantity of oxygen will directly proportionate to the perimeter of the platelets, which is given by the equation \( \pi d \) where \( d \) is the diameter of the platelets. Therefore, if the diameter of the GNPs is reduced to 2.5 μm and 0.25 μm, the quantity of oxygen will reduce to approximately ~0.55 % and ~0.055 % respectively. Similarly, a smaller quantity of oxygen can be predicted for both treated GNPs for smaller particle size as indicated in TEM images (Figure 5.2c and Figure 5.2d). However, the amount of oxygen detected by EDX and XPS is not decreasing, for example comparing the oxygen contents of AR-GNPs and A-GNPs (Table 5.6). Therefore, it can be
concluded that the oxygen moieties as observed by EDX and XPS may also occur on the basal plane and not predominantly on the edges of the GNPs.

### Table 5.6: Summary of oxygen content (%).

<table>
<thead>
<tr>
<th>Characterisation</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AR-GNPs</td>
</tr>
<tr>
<td>EDX</td>
<td>5.5</td>
</tr>
<tr>
<td>XPS</td>
<td>5.2</td>
</tr>
</tbody>
</table>

### 5.3 Characterisations of Suspensions

The rheological behaviour of epoxy/GNPs suspensions in oscillatory-shear was studied under frequency sweep mode to determine the rheological percolation threshold of the GNPs [265]. This frequency sweep study was conducted at a fixed strain ($\gamma_o = 3\%$) within the linear viscoelastic region (LVR), determined earlier in a strain sweep measurement. The LVR is the region in which the GNP network formed within the suspension remains stable before its destruction at a higher strain. The method reported by Kinloch et al. was used in this test [266]. All resin suspensions were prepared without hardener and were tested at 100 °C, the same temperature used for all processing operations including dispersion of GNPs in epoxy and fabrication of multiscale composites (as explained in chapter 3).

#### 5.3.1 Rheology Frequency Sweep

Figure 5.12 shows the storage or elastic modulus ($G'$) of suspensions versus frequency (range between 0.1 – 100 rad/s). $G'$ are seen to increase as a function of filler loadings for all cases in Figure 5.12a, b, c and d. In addition, the neat resin and suspensions with 2 wt. % loading of the GNPs show a frequency dependent behaviour throughout the whole range of frequency, indicating liquid-like characteristics of the suspension and suggesting these systems remain viscous.
A plateau at low frequency was observed starting at around 4 wt. % of GNP for Figure 5.12a, b, and d. This plateau becomes wider at higher loadings of GNP within the suspensions. The frequency independent behaviour of the plateau suggests a solid-like (elastic) behaviour of the suspensions due to the formation of continuous GNP networks before changing to frequency dependent behaviour at higher frequency as the GNP networks break down. This phenomena is usually known as the rheological percolation threshold [267], [268], a term used to describe the condition whereupon a critical loading, the filler forms a continuous network in the suspension [267], [269]. Typically, the transition of suspension behaviour from frequency dependent (liquid-like) to frequency independent (solid-like) at low frequency is used to predict the occurrence of the rheological percolation threshold [116], [270]–[272]. Therefore, an estimate may be made that the percolation threshold
threshold for all types of GNP suspension occurs at around between 2 – 4 wt. % of loadings.

Above the percolation threshold, the suspension will show solid-like behaviour. If the loading of nanofillers within the resin is high enough, the suspension will show a constant value of storage modulus (\(G'\)) throughout the whole range of frequency studied, due to solid-like (elastic behaviour) dominating the viscous behaviour. This can be seen in Figure 5.12 for all the GNPs at 8 wt. %. An attempt to add 7 wt. % of GNPs into the epoxy resin for composite processing failed, as the suspension became too difficult to process (the degassing process to remove air bubbles failed due to the solid-like behaviour). The same situation was faced by Yasmin and Daniel [57] using GNPs and a DGEBA epoxy system. Hence, 6 wt. % of GNPs is the highest loading used in this work for composite processing.

In addition, it is also observed that both of the treated GNPs have lower values of \(G'\) (about an order of magnitude) compared to the AR-GNPs and U-GNPs. This may be attributed to less solid-solid interactions due to better dispersion and distribution for both treated GNPs within the epoxy. The reason behind this finding can be explained as follows. The sonication of GNPs in a mixture of surface modifier and solvent gives steric repulsive forces between the graphene layers. This causes exfoliation of the GNPs in which, separation of graphene layers occurs and the stacks becomes thinner. The TEM images shown previously in section 5.2.1 support this proposal. Therefore, a higher surface area is created and exposed to the epoxy matrix upon mixing [124]. Moreover, after treatment, GNPs were encapsulated with APTS and Triton X-100 producing a “soft layer” which reduces solid-solid interactions between the GNPs and inhibits agglomeration [115], thus reducing the value of \(G'\) compared to the AR- and U-GNPs [273], [274].

5.3.2 Percolation Threshold

In order for nanocomposites to be effective in their performance, the nanoparticles are often required to reach their percolation threshold [268]. Therefore, it is
imperative to predict and determine the critical loadings where GNPs form a continuous network within the epoxy system. Previously, it was proposed that the GNP started forming a continuous network when the transition between a liquid to a solid-like structure occurred. In this section, the rheological percolation threshold will be determined using percolation theory which predicts an elastic network to grow with increasing filler loading ($p$) following power law equation as explained in chapter 2, in subsection for percolation theory. The value of percolation threshold, $p_c$ was determined using Solver data analysis from Microsoft Excel with residual between data and the model set as the target objective and at minimum value. GRG (generalised reduced gradient) nonlinear was used as the solving method for optimisation to fit the data with the model.

Figure 5.13: Semi log plot of $G'$ (within LVR at a frequency 2.91 rad/s) as function of GNP loading (a) AR-GNPs (b) U-GNPs (c) A-GNPs and (d) T-GNPS.
Figure 5.13 shows the $G'$ values plotted in on a semi-log scale as a function of GNPs loading. The data fitting yielded respective $p_c$ values of 3.9, 3.6, 3.2 and 3.5 wt. % for the AR-GNPs, U-GNP, A-GNP and T-GNPs. From Figure 5.13, data which does not fit with the model indicate the GNP loading before the percolation threshold. The values of $p_c$ obtained indicate that the rheological percolation threshold for these suspensions varies with surface treatment of the GNPs. Both treated GNP shows lower percolation threshold than the AR-GNPs and U-GNPs. The U-GNPs, which has been sonicated for 4 hours, also showed lower percolation threshold compared to the AR-GNPs. This difference may reflect different degrees of exfoliation of the U-GNPs which improved their dispersion and distribution with less aggregate within epoxy resulted to lower percolated loading. For both treated GNPs, surface modification also may have improved the dispersion of the GNPs, altered their surface characteristics and affected the wetting of the GNPs within epoxy [116].

The treatment of the A-GNPs generates covalent bonding with APTS molecules [87], [261]. This ultimately converts the surface from hydrophobic to hydrophilic allowing dispersion of A-GNPs more uniformly within the suspension compared to the untreated [87]. In contrast, for the T-GNPs electrostatic or hydrogen bonding may have formed between the surfactant and the GNP surfaces [93], [275]. The hydrophobic side of this surfactant can interact with GNPs by adsorption whilst its hydrophilic side can be attached to epoxy through hydrogen bonding [97]. The adsorption of surfactant on the GNPs surface may lower the surface tension of the GNP, inhibiting aggregation of particles as van der Waals attractions between them are overcome by electrostatic or steric repulsive forces from the surfactant [98].

In addition, as mentioned previously, both modifiers (APTS and Triton X-100) may have been attached to the GNPs surface and form an additional layer, possibly wrapping the GNP particles [99], [115]. Unlike AR-GNPs, where aggregation can easily happen to form a cluster, the layer introduced to both treated GNPs may reduce particle solid-solid interactions within suspension which will prevent reaggregation whilst simultaneously promoting slip between the GNPs. Moreover, surfactant treatment of GNPs may overcome van der Waals attractions by
electrostatic or steric repulsive forces [96], [276] thus helping achieve a uniform dispersion and distribution within the epoxy matrix [277]–[279]. The more uniform distribution of particles (less agglomeration of particles) for both treated GNPs within the epoxy matrix resulted to lower requirement of particles loading to form a percolated network.

Since rheological studies related to epoxy/GNPs are still rare and to our knowledge percolation data for this system have not been reported so far, systems containing other types of nanoparticles will be used as references for discussion. For example, Zhu et al. [115] investigated the rheological behaviour of epoxy resin suspensions with as-received carbon nanofibers (CNFs). The comparison was made with other CNFs treated using 3-aminopropoxyltriethoxysilane (APTS), the same coupling agent used in this work. They found the viscosity of suspensions reduced with treated CNFs due to an introduction of a “soft layer” of APTS that encapsulated the surface of the GNPs after treatment. According to the authors, this layer prevented aggregation of CNFs which subsequently improved their dispersion. They also showed that storage modulus (\(G^\prime\)) decreased with the incorporation of treated CNFs into epoxy resin compared to as-received CNFs. They determined the rheological percolation threshold with treated CNFs suspension yielded at 0.3 wt. % and 0.5 wt. % for as-received CNFs. Their finding is in agreement with the result showed in this work where lower percolation threshold is predicted for treated GNPs compared to as-received GNPs. They also proposed improved dispersion of treated CNFs as the reason for lower percolation threshold compared to as-received CNFs suspension.

Similar behaviour was also observed by Yuan et al. [277] who studied the rheological percolation using CNT-filled poly(butylene succinte) nanocomposites. They determined that the percolation threshold occurred at lower loadings with increasing temperature which was attributed to lower matrix viscosity. Similarly, lower \(G^\prime\) value and lower matrix viscosity is recorded for epoxy containing treated GNPs compared to AR-GNPs in this work. This has resulted from reduced aggregation of particles within the suspension and hence more effective distribution to cause the formation of a percolated network at lower loadings [277]. The
elasticty and structure of GNP networks was also investigated by Filippone et al. [114], who studied the rheological behaviour of polystyrene-GNP nanocomposites. From the power law relationship, they determined that the rheological percolation threshold occur at $p_c = 3.8$ wt. %. Other studies using GNPs found critical loadings of 4 wt. % for GNP–polycarbonate (PC) [116] and 3–4 wt. % for GNP–poly(arylene ether nitrile) [271].

5.3.3 Pot life of Epoxy/GNPs Suspension

The pot life of epoxy/GNPs suspension was studied with the inclusion of curing agent (DDS) in the system. It was observed that 100 °C was high enough to make the DDS melt and mix homogenously within the epoxy blend. Even though a higher temperature would reduce the viscosity of the suspension and ease the dispersion of GNPs, crosslinking could also occur earlier which would be a disadvantage. An isothermal rheology study which was conducted at 130 °C indicated that curing starts after 80 minutes for the neat epoxy system (Figure 5.14). At 100 °C, the viscosity
remains constant (crosslinking not occurring) even after 3 hours. This represents the pot life and process ability of these matrices. In this work, the time required in order to complete all stages of preparation during composite processing was 2.5 hours, consisting of 0.5 hours of mixing using a mechanical stirrer, 1 hour for degassing using a vacuum oven and 1 hour for the resin film infusion (RFI) procedure.

During preparation of epoxy/GNP suspensions it was identified that the viscosity of the mixture was high enough to prevent full degassing when it reached 7 wt. % of GNPs. Hence, 6 wt. % of GNPs was added as the maximum nanofiller into the resin. Similar behaviour was also observed by other groups [69].

### 5.4 Characterisation of Cured Nanocomposites

Cured nanocomposites were characterised to study the effects of the surface modifications of GNPs when mixed with epoxy resin. The characterisations are made with U-GNPs as a reference for comparison to the nanocomposites made with treated GNP. In addition, for an additional comparison AR-GNPs nanocomposites at 4 wt. % were also prepared, a loading chosen based on the rheological percolation threshold result as discussed in the previous section.

#### 5.4.1 Dynamic Mechanical Thermal Analysis (DMTA)

In this work, DMTA was used to characterise the viscoelastic behaviour of the cured nanocomposites. Measurement was carried out at a frequency of 1 Hz and each sample was measured three times. The data were presented as storage modulus ($E'$), loss modulus ($E''$) and tan $\delta$ curves.

Figure 5.15 shows typical dynamic storage modulus ($E'$) curves for all the cured epoxy nanocomposites (NCs) containing GNPs. Due to the increase in chain mobility upon heating, the values of $E'$ drop slowly starting at room temperature and then decrease more significantly by nearly two orders of magnitude at around 175 °C as they reach their $T_g$. After the transition, $E'$ was observed to remain essentially
constant throughout the remainder of the temperature range studied. The region of \( E' \) before \( T_g \) shows the glassy behaviour of the NCs whilst the region after shows their rubbery behaviour.

**Figure 5.15:** Storage modulus (\( E' \)) for cured nanocomposites at 1 Hz frequency for (a) U-GNPs and AR-GNPs (b) A-GNPs (c) T-GNPs and (d) Unfilled cured epoxy resin containing 4 wt. % Triton X-100 and APTS.

In general, the NCs for all types of GNPs show higher \( E' \) compared to the neat epoxy. This can be observed at both regions, glassy and rubbery. Table 5.7 shows the values of \( E' \) from both regions, taken at 100 °C and 250 °C respectively. For example, NCs containing 6 wt. % of loading in the glassy region, U-GNPs show a 33% increase, A-GNPs 17% and T-GNPs 41% relative to the neat epoxy. This increase can be attributed to the exfoliation of GNPs during sonication which increased the surface area of GNPs in contact with the epoxy matrix. Uniform
dispersion and distribution of exfoliated particles within the epoxy resin also may contribute to higher storage modulus as the load transfer from the resin to the reinforcement may occur more effectively. In addition, GNP s are known to have a high modulus of ~1000 GPa [195], [280]. Therefore, embedding (GNPs) into epoxy resin will increase the storage modulus of the NCs [281], [282]. For 4 wt. % of AR-GNPs in the glassy region, E’ is lower compared to neat epoxy. This could be due to agglomeration of AR-GNPs which contributed to poor dispersion and distribution in the epoxy matrix as the AR-GNPs were not sonicated for further exfoliation compared to other types of GNP s. In addition, Figure 5.15d shows that the inclusion of Triton X-100 and APTS to the epoxy resin reduces the storage modulus, due to plasticization effect [283].

**Table 5.7: Storage modulus (E’) within the glassy and rubbery regions at 100 °C and 250 °C, respectively. Data are mean ± standard deviation (n=3).**

<table>
<thead>
<tr>
<th>Epoxy/GNPs</th>
<th>Storage modulus at 100 °C</th>
<th>Storage modulus at 250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
<td>2 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>(4.2 ± 0.5) x 10^9</td>
<td>* (2.8 ± 0.4) x 10^9</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>(4.4 ± 0.1) x 10^9</td>
<td>* (5.3 ± 0.5) x 10^9</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>(4.7 ± 0.3) x 10^9</td>
<td>(4.8 ± 0.4) x 10^9</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>*(5.0 ± 0.2) x 10^9</td>
<td>*(5.3 ± 0.5) x 10^9</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0 wt. % GNP s) at 95% confidence level and degree of freedom (df) of 4 with t-value from standard table is 2.132.

Similar trends in the results of E’ of NCs have been reported. For example, Ganguli et al. [84] measured the thermomechanical properties of epoxy NCs containing
untreated GNPs and GNPs treated with APTS. As a result, higher values of $E'$ were shown for both systems compared to the neat epoxy. Similar to the results in this work (Figure 5.15) their data shows no obvious difference in $E'$ for NCs containing untreated and treated GNPs. However, the authors reasoned that the enhancement in $E'$ for NCs relative to neat epoxy was due to strong interfacial bonding between epoxy/GNPs. Zhang et al. [284] compared functionalised (f-GNPs) and untreated GNPs in an epoxy resin up to 0.5 wt. % maximum loading. At 0.5 wt. % of GNP, they reported an increase of up to 42% in storage modulus relative to the neat epoxy for the f-GNPs compared to an increase of 27% for the untreated GNPs. These results were also claimed to be due to strong interfacial interaction between GNPs and epoxy especially in the case of functionalised GNPs.

![Figure 5.16](image-url)

**Figure 5.16:** Loss factor ($\tan \delta$) profile for (a) U-GNPs and AR-GNPs (b) A-GNPs (c) T-GNPs and (d) Unfilled cured epoxy resin containing 4 wt. % Triton X-100 and APTS.
Table 5.8: $T_g$ values determined by DMTA at peak tan δ. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>$T_g$ value (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>*194.5 ± 0.4</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>201.2 ± 0.4</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>*196.0 ± 0.6</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>*197.0 ± 0.8</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat resin (0 wt. % GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

The $T_g$ for NCs was also determined by DMTA. $T_g$ is defined as the temperature at which the epoxy matrix changes from glassy to rubbery behaviour. Here, $T_g$ for the NCs was determined at the peak of tan δ [285]. Figure 5.16a to Figure 5.16c show the tan δ vs. temperature curves for cured NCs for all types of GNPs. The data is presented in Table 5.8. The peak value of tan δ shift towards lower temperature as a function of filler loading for all types of NCs relative to cured neat epoxy with all reductions being statistically significant. The $T_g$ of a crosslinked polymer is typically associated with the degree of restriction in polymer chain mobility and crosslink density. Many groups have reported an increase in $T_g$ on incorporating GNPs into a matrix polymer, for instance GNPs–PMMA [286], GNPs–epoxy [287], GNPs–elastomer [288] and GNPs–PPCPA [289]. However, in this work, the data in Figure 5.16 show that the tan δ peaks shifted systematically to lower temperatures, as a function of filler loadings for all types of GNPs.

A few studies report lowering of $T_g$ by the addition of nanoparticles, reasoning that the drop was due to aggregation of fillers and weak interfaces [286], [290]. In this work, the reduction in $T_g$ for NCs with respect to neat epoxy is speculated due to the greater immiscible interfacial area generated by the presence of GNPs [281]. This may introduce mobility at the immiscible interface between matrix-GNPs within NCs when the specimen is subjected to cyclic load as a function of temperature. In contrast, the formation of network in the case of neat resin is without immiscible interface which decreased mobility within the system at glass-transition region and
lower the energy dissipation [281]. Figure 5.17 shows the summary of T$_g$ for all NCs as a function of GNPs concentration.

Similar observation in the reduction of T$_g$ with incorporation of GNPs into epoxy was reported by Bose and Drzal [291]. By incorporate 2 wt. % of GNPs into epoxy, the position of tan δ peak for nanocomposites is shifted towards lower temperature (~10 °C) relative to neat epoxy. They stated that the reason could be attributed to immiscibility interface between matrix and filler which resulted to poor interaction and weak bonding between the phases.

Figure 5.17: T$_g$ values of epoxy/GNPs nanocomposites, epoxy/APTS and epoxy/Triton X-100. Data are mean ± standard deviation (n=3).

Figure 5.17 also shows that the T$_g$ of the epoxy resin decreased with the inclusion of both organic modifiers at 4 wt. % which could be attributed to a plasticization effect. Previously, the same behaviour was observed by other groups when they added organic modifier into epoxy resins. For example, Cui et al. [292] added different amount of Tergitol (a type of non-ionic surfactant) into an epoxy resin. At 4 wt. % of Tergitol a ≈18% reduction in T$_g$ was observed. Park and Jana [293] also reported a decrease in T$_g$ (-38 °C) with addition of ammonium chloride into an epoxy resin. Figure 5.17 also shows that the value of T$_g$ values for all the nanocomposites are
higher than the $T_g$ for epoxy which contains only APTS or Triton X-100. The addition to epoxy of both modifiers resulted in plasticization, perhaps by lowering the crosslinking density which finally reduced the $T_g$ [294]. Table 5.8 shows the calculated t-value from t-testing which was calculated against neat resin (0 wt. % GNPs). From the t-test, it can be observed that the incorporation of GNPs into epoxy resin reduced the $T_g$, significantly.

5.4.2 Flexural Testing

Flexural testing was carried out according to ASTM D790 to assess the flexural properties of cured NCs. Figure 5.18 shows the stress-strain curves for the flexural test.

![Stress–strain curves of epoxy NCs containing (a) AR-GNPs and U-GNPs (b) A-GNPs (c) T-GNPs and (d) Summary of flexural strain versus GNPs content for all the NCs.](image)

**Figure 5.18:** Stress–strain curves of epoxy NCs containing (a) AR-GNPs and U-GNPs (b) A-GNPs (c) T-GNPs and (d) Summary of flexural strain versus GNPs content for all the NCs.
All the figures show that as a function of filler loadings the failure strain reduces. For example, relative to neat epoxy, addition of 4 wt. % of GNP reduced the failure strain by 46% for AR-GNPs, 48.6% (U-GNPs), 4.6% (A-GNPs) and 30.8% (T-GNPs) as summarised in Figure 5.18d. This reduction suggests that the NCs become more brittle with GNP inclusion. However, it can be observed that the flexural stress–strain curves for the NCs are above that of the neat resin, suggesting an improvement in flexural modulus (Figure 5.18).

Figure 5.19: Relative modulus of NCs in the present work to that flexural modulus of neat epoxy (NCs/neat epoxy).

The relative flexural modulus was calculated to illustrate the increase of flexural modulus of NCs with respect to the flexural modulus of the neat epoxy (NCs/neat epoxy) and is shown in Figure 5.19. The result shows that, as an example, at 6 wt. % of GNP, the relative flexural modulus of the NCs increased by 4.2% for U-GNPs, 8.4% (A-GNPs) and 6.1% (T-GNPs) relative to neat epoxy. This can be attributed to the high modulus of GNP (~1000 GPa) [195], [280] which when embedded in epoxy, impart higher moduli to the resultant NCs. Although the increase in modulus is inconsistent as a function of GNP content (perhaps due to particle aggregation),
all epoxy/GNPs NCs shows higher modulus than the neat epoxy as observed in stress-strain curve in Figure 5.18. Table 5.9 shows the summary of data for flexural strain and flexural modulus in this work. NCs containing A-GNPs indicated higher flexural strain than the NCs containing T-GNPs which could be attributed to stronger interface adhesion introduced by covalent functionalisation compared to noncovalent method [243], [295].

**Table 5.9: Flexural strain, modulus and strength for epoxy/GNP NCs. Data are mean ± standard deviation (n=3).**

<table>
<thead>
<tr>
<th>Epoxy/GNPs</th>
<th>Flexural Strain at break (%)</th>
<th>Flexural Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>5.00 ± 0.00</td>
<td>3.09 ± 0.12</td>
<td>122.28 ± 0.72</td>
</tr>
<tr>
<td>AR-GNPs 4 wt. %</td>
<td>*2.70 ± 0.41</td>
<td>*3.29 ± 0.04</td>
<td>*74.97 ± 3.09</td>
</tr>
<tr>
<td>U-GNPs 2 wt. %</td>
<td>*3.76 ± 0.95</td>
<td>*3.31 ± 0.06</td>
<td>*86.87 ± 12.26</td>
</tr>
<tr>
<td>U-GNPs 4 wt. %</td>
<td>*2.57 ± 0.19</td>
<td>*3.32 ± 0.01</td>
<td>*79.48 ± 4.52</td>
</tr>
<tr>
<td>U-GNPs 6 wt. %</td>
<td>*2.00 ± 0.09</td>
<td>3.22 ± 0.07</td>
<td>*58.47 ± 1.22</td>
</tr>
<tr>
<td>A-GNPs 2 wt. %</td>
<td>5.00 ± 0.00</td>
<td>3.13 ± 0.05</td>
<td>*113.63 ± 1.31</td>
</tr>
<tr>
<td>A-GNPs 4 wt. %</td>
<td>*4.77 ± 0.16</td>
<td>*3.31 ± 0.05</td>
<td>*110.45 ± 2.0</td>
</tr>
<tr>
<td>A-GNPs 6 wt. %</td>
<td>*3.26 ± 0.17</td>
<td>*3.35 ± 0.03</td>
<td>*88.49 ± 0.60</td>
</tr>
<tr>
<td>T-GNPs 2 wt. %</td>
<td>*3.96 ± 0.75</td>
<td>*3.30 ± 0.07</td>
<td>*116.22 ± 2.52</td>
</tr>
<tr>
<td>T-GNPs 4 wt. %</td>
<td>*3.46 ± 0.57</td>
<td>*3.28 ± 0.05</td>
<td>*99.87 ± 4.28</td>
</tr>
<tr>
<td>T-GNPs 6 wt. %</td>
<td>*2.99 ± 0.21</td>
<td>*3.28 ± 0.04</td>
<td>*77.41 ± 3.34</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) of 4 with t-value from standard table is 2.132.

To develop a better understanding of the influence of GNPs on the modulus of NCs obtained through experimental work, a comparison was made with predicted values using simple models. The simplest model that can be used to predict the modulus for a two phase system is the iso-strain rule of mixtures (upper bound), as shown in equation (5.1) [296]. Equation (5.2) is an extension or the modified iso-strain rule of mixture [297]. Note that this model make a number of assumptions which include that both matrix and reinforcement material are isotropic, that bonding between these two materials is perfect and that the matrix is void free [298].
Respectively, $E_c$, $E_f$ and $E_m$ are the moduli of the composite, reinforcement and matrix. Similarly, $V_f$ is the (nominal) volume fraction of the reinforcement (GNPs), $V_m$ is the volume fraction of matrix (epoxy) where both were determined through calculation using equation (5.5) [299].

$$V = \frac{m}{\rho}$$

(5.3)

$$V_{\text{GPNP}} = \frac{V_{\text{GPNP}}}{V_{\text{GPNP}} + V_{\text{epoxy}}}$$

(5.4)

$$V_{\text{GPNP}} = \frac{m_{\text{GPNP}}/\rho_{\text{GPNP}}}{m_{\text{GPNP}}/\rho_{\text{GPNP}} + m_{\text{epoxy}}/\rho_{\text{epoxy}}}$$

(5.5)

Where $V$ is the volume, $m$ is the weight percent and $\rho$ is the density. Density of GNPs ($\rho_{\text{GPNP}}$) is 2.2 g/cm$^3$ as provided by XG Sciences. Density of the blended epoxy ($\rho_{\text{epoxy}}$) is 1.3 g/cm$^3$, which was determined by measurement using a Mettler Toledo Excellence XP205 Delta Range electronic balance fitted with a density function. In this work the value of $E_m$ was 3.09 GPa (Table 5.9)

In equation (5.2), $\eta_o$ is the Krenchel orientation factor and a value of 8/15 was used in this work as suggested by Young [300] and Li et al. [297] for 3D random orientation of nanoplatelets. $\eta_i$ is the length efficiency factor and was determined through calculation using equation (5.6) [301].

$$\eta_i = 1 - \left(\frac{l_c}{2l}\right)$$

(5.6)

Where $l_c$ is critical filler length, for which 3 μm was used as the length required for graphene flakes to give good reinforcement in polymer nanocomposites [302], and $l$ is filler length (25 μm).
Figure 5.20 shows the experimental and predicted modulus using modified rule of mixtures, equation (5.2). Theoretically, it is well known that the moduli of NCs increase with higher $E_f$ values. From Figure 5.20, it can be observed that the experimental modulus values followed closely the predicted modulus calculated for $E_f = 50$ GPa at GNPs ≤ 2 wt. %. Beyond 2 wt. % of GNPs, discrepancies between predicted and experimental modulus increase probably due to aggregation of GNPs with higher volume of particles in the system. Previous work by Gong et al. [303] who studied the level of reinforcement by graphene flakes consisting different number of layers indicated that, the effectiveness of graphene in load transfer decrease as the number of layers increased. In addition, Young et al. [304] also concluded that the level of efficiency of graphene as a reinforcement is reducing with the increase of graphene layers.
Figure 5.21: Flexural modulus of epoxy/GNPs in the present work relative to the result from previous studies using different types of epoxy.

Similar to the findings that has been presented in this work, other studies also have reported increase in flexural modulus for NCs over neat epoxy. Figure 5.21 shows the flexural modulus of epoxy/GNPs in the present work relative to the results from previous studies using different types of epoxy resin [123], [124], [78]. For example, Jana et al. [124] studied the flexural properties of epoxy/GNPs NCs by preparing the GNPs from graphite flake. They reported a 13% increase in flexural modulus for NCs containing 5 wt. % of GNPs relative to neat epoxy. They reasoned the superior properties exhibited by the NCs were due to the high surface area and aspect ratio of GNPs. Wang et al. [123] also reported increases in flexural modulus of up to 25.7% improvement with inclusion of 5 wt. % GNPs into epoxy (Figure 5.21). They also reasoned that the improvement in modulus was due to high aspect ratio which facilitates effective load transfer from the matrix to the reinforcement. Coupled with high filler modulus and uniform dispersion of GNPs, higher flexural modulus was obtained in their work. Prolongo et al. [305] studied the effect of as-received GNPs as nanofillers in epoxy matrix. They presented fluctuating data for flexural modulus
at different concentration of GNPs (Figure 5.21). They concluded that the flexural modulus obtained for the NCs was inferior relative to neat epoxy resin (between 2.7 – 2.9 GPa). They stated that the reason was due to low interaction between interfaces of the two phases. Moreover, according to them, the nanofillers caused stress concentration, leading to poor mechanical properties for the NCs compared to neat epoxy.

Figure 5.22 shows the flexural strength of neat epoxy and cured NCs as a function of filler loading. The data is presented as in Table 5.9. In general, the trend of the graph shows the flexural strength of the NCs is decreasing as a function of GNP's concentration over neat epoxy. However, comparing different types of cured NCs, NCs manufactured using A-GNPs and T-GNPs show superior results than U-GNPs. For example, at 4 wt. % of GNP, AR-GNPs show the most significant drop (38.5%) in flexural strength relative to neat epoxy followed by U-GNPs (35%), T-GNPs (18.3%) and A-GNPs (9.7%). This can be attributed to agglomeration of AR-GNPs while further exfoliation of U-GNPs and both treated GNPs during sonication in the NMP/water mixture subsequently improved filler dispersion and distribution within epoxy materials. A few studies have reported that by using various types of solvent the sonication of GNPs can exfoliate the graphene stacks and increase the number of outer surface layers in contact with the matrix polymer [196], [241], [250], [306]–[310]. In addition, higher flexural strength for both treated GNPs compared to U-GNPs was observed in this work which could be attributed to a reduction in reaggregation of fillers which improves the dispersion and distribution leading to effective load transfer within the NCs.

Similarly, Wang et al. [123] and Prolongo et al. [305] also reported that higher particle loading decreased the flexural strength of their cured GNPs NCs relative to flexural strength for neat epoxy (Figure 5.22). They speculated a few reasons that may cause the inferior properties of NCs including the adhesion between GNPs and epoxy was weak, indicated by SEM images of fracture surfaces which show clean separation along the interface between epoxy/GNPs, resulting in pull-out of GNPs due to interfacial debonding. In addition, they also speculated that aggregated GNPs
act as stress concentrators for failure. Jana et al. [124], on the other hand, reported increased flexural strength for NCs relative to neat epoxy (Figure 5.22) and, as with their data for modulus (Figure 5.15), they proposed that the increase in strength was due to the high surface area and aspect ratio of their GNPs.

![Figure 5.22: Flexural strength of epoxy/GNPs in the present work relative to the result from previous studies.](image)

5.4.3 Single Edge Notch Bending (SENB) Fracture Toughness

It has been reported that the use of nanoparticles can inhibit crack propagation in polymer NCs [295], [311]. If this behaviour could also be achieved to form multiscale composite with CF, the contribution will be useful for the structural application. Therefore, the fracture toughness of the NCs was studied using SENB testing to understand the role of GNPs before further step to apply them in multiscale composite. The toughening effects of the GNPs in the epoxy NCs can be observed through changes in their load–displacement curves as shown in Figure 5.23.
Figure 5.23: Load–displacement curve for cured epoxy nanocomposites containing (a) U-GNPs and AR-GNPs (b) A-GNPs and (c) T-GNPs.
Figure 5.24: Fracture surface by SEM for (a) Neat epoxy and (b) NC of epoxy/U-GNPs at 4 wt. %.

The neat epoxy exhibits brittle behaviour, with an abrupt failure on crack initiation due to rapid crack propagation giving the relatively smooth fracture surface as shown in Figure 5.24a. In contrast, signs of plastic deformation are visible for the epoxy/GNP NCs. Starting at 2 wt. % of nanofiller, plastic deformation becomes
more pronounced as a function of filler loading which possibly results from
deflection and branching of the crack due to the embedded GNPs. This provides a
rougher fracture surface as in Figure 5.24b. Consequently, the area under the load–
displacement curves for the epoxy/GNP NCs also becomes greater as a function of
filler concentration which reflects the energy required to initiate and propagate the
crack during fracture of the NCs [312], [313].

Figure 5.24a show an SEM image of a fracture surface of the neat epoxy, which can
be seen to be smooth and relatively featureless, indicating brittle behaviour with
weak resistance to crack initiation and propagation [314]. In contrast, Figure 5.24b
presents the fracture surface of a NC with 4 wt. % of U-GNPs which is much rougher
with smaller-scale texture due to the embedded flakes of the GNPs. This rougher
surface suggests stronger resistance to cracking with significant small-scale plastic
deformation.

Table 5.10: Plain strain fracture toughness, $K_{1C}$ from SENB testing. Data are
mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>Plain strain fracture toughness, $K_{1C}$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>0.80 ± 0.04</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>*1.12 ± 0.01</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>*1.17 ± 0.01</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>*1.15 ± 0.04</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0
wt. % GNPs) at 95% confidence level and degree of freedom (df) of 4 with t-value
from standard table is 2.132.

Fracture toughness ($K_{1C}$) was calculated as explained in chapter 3. It is a measure of
the resistance of a material to fracture [211]. The result is presented as in Table 5.10
and Figure 5.25. It shows that the $K_{1C}$ of the cured NCs increase as a function of
filler content for all types of GNPs. For example, the value of $K_{1C}$ for U-GNPs NCs
increased from 0.80 ± 0.04 MPa.m$^{1/2}$ for neat epoxy to 1.12 ± 0.01 MPa.m$^{1/2}$ at 2 wt.
% of U-GNPs, 1.24 ± 0.06 MPa.m$^{1/2}$ (4 wt. %) and 1.32 ± 0.01 MPa.m$^{1/2}$ (6 wt. %).
A similar pattern of results has been reported for other graphene/epoxy systems [95], [315]. The increase in $K_{IC}$ as a function of filler concentration relative to neat epoxy is as explained in load-displacement curve (Figure 5.23) with SEM image of fracture surface in Figure 5.24.

![Figure 5.25: Fracture toughness, $K_{IC}$ of cured epoxy NC as a function of GNPs content. Data are mean ± standard deviation (n=3).](image)

The value of $K_{IC}$ for NCs containing both treated GNPs was also observed to be higher than NCs containing U-GNPs. For instance, at 6 wt. % of fillers, the $K_{IC}$ value for the A-GNP and T-GNP NCs was increased to $1.44 \pm 0.02$ MPa.m$^{1/2}$ and $1.35 \pm 0.10$ MPa.m$^{1/2}$ respectively from $1.32 \pm 0.01$ MPa.m$^{1/2}$ for U-GNP NCs. This may be due to the improved dispersion and distribution of treated GNPs compared to U-GNPs within the epoxy matrix and better interface interaction, resulting from surface treatment [12]. These will allow a greater degree of yielding to be induced by the GNPs. The dispersion and distribution of different types of GNPs within the epoxy can be observed in the SEM images in Figure 5.26.
Figure 5.26: SEM images of fracture surfaces of NCs containing 4 wt. % of (a) U-GNPs (b) A-GNPs and (c) T-GNPs.
In general, all fracture surface images in Figure 5.26 show a rough surface for NCs which suggests the toughening effect of GNP s to resist crack propagation. The image at low magnification indicates a non-uniform pattern of stress whitened areas possibly due to difference in height of the topography of the fracture surface. This could be formed from different resistance capability during fracture due to obstacles by GNP s that bridged and inhibited the crack propagation to progress. Subsequently, the crack path is deflected and branching to another direction. As a result, a rougher fracture surface is produced for epoxy/GNP NCs compared to neat epoxy (Figure 5.24a). The feature circled in Figure 5.26a appears to be an aggregation of particles resulting from poor distribution of U-GNP s. On the other hand, images in Figure 5.26b and Figure 5.26c show more uniform textured surfaces, suggesting improved dispersion and distribution of A-GNP s and T-GNP s within the epoxy resulting from increased exfoliation of GNP s during treatment. Consequently, efficiency of reinforcement was enhanced to resist crack propagation.

In addition to $K_{IC}$, the critical strain-energy release rate, $G_{IC}$ (or fracture energy) was also calculated. In SENB testing, $G_{IC}$ represents the energy required in order to cause fracture [211]. The data is presented in Table 5.11 and Figure 5.27 shows the plot of $G_{IC}$. The trend of the graph shows $G_{IC}$ increasing with the increase of filler concentration. For example, the value of $G_{IC}$ for U-GNP s NCs was increased from $0.18 \pm 0.01 \text{kJ/m}^2$ for neat epoxy to $0.26 \pm 0.01 \text{kJ/m}^2$ at 2 wt. % of U-GNP s, $0.38 \pm 0.03 \text{kJ/m}^2$ (4 wt. %) and $0.42 \pm 0.03 \text{kJ/m}^2$ (6 wt. %). This suggests that, as a function of filler loadings, more energy is required in order to cause the NCs to fail. Generally, both treated GNP s possess higher $G_{IC}$ values compared to the U-GNP s. For instance, at 6 wt. % of GNP s the $G_{IC}$ values for NCs containing A-GNP s and T-GNP s increased by 16% and 7% respectively, relative to the value of $G_{IC}$ for NCs which contain U-GNP s. This could be attributed to better exfoliation of modified GNP s leading to improved dispersion and distribution which enhance reinforcement efficiency in toughening due to greater interfacial area for the GNP s to be surrounded by the epoxy matrix. Higher $K_{IC}$ and $G_{IC}$ for NCs containing A-GNP s than T-GNP s could be attributed to stronger interface adhesion for treatment by covalent functionalisation relative to noncovalent method [243], [295].
Table 5.11: Critical strain-energy release rate, $G_{1C}$ from SENB testing. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>Critical strain-energy release rate, $G_{1C}$ (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>*0.26 ± 0.01</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>*0.29 ± 0.04</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>0.27 ± 0.09</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) of 4 with t-value from standard table is 2.132.

Figure 5.27: Critical strain energy release rate, $G_{1C}$, of cured epoxy/GNP NCs as a function of GNP content. Data are mean ± standard deviation (n=3).

Similar patterns of results for SENB were reported previously for $K_{1C}$ and $G_{1C}$ by other groups for epoxy/GNP NCs. For example, Zaman et al. investigated the effect of GNPs modification using 4,4’-Methylene diphenyl diisocyanate (MDI) [12],
polyoxyalkyleneamine (B200) [95] and polyoxypropylenediamine (J2000) [295]. They also observed the trend of $K_{IC}$ and $G_{IC}$ increasing as a function of filler content, similar to the results obtained in this work. For example, for polyoxyalkyleneamine (B200) treatment [95], they reported $K_{IC}$ values increases from $0.657 \pm 0.034$ MPa.m$^{1/2}$ for neat epoxy to $1.004 \pm 0.033$ MPa.m$^{1/2}$ for 0.122 vol.% of GNPs, $1.258 \pm 0.030$ MPa.m$^{1/2}$ (0.244 vol%) and $1.472 \pm 0.023$ (0.489 vol.%). Similarly, they reported the $G_{IC}$ increase as a function of GNPs concentration from $140.7 \pm 7.9$ MPa.m$^{1/2}$ for neat epoxy to $295.6 \pm 4.1$ MPa.m$^{1/2}$ for 0.122 vol% of GNPs, $439.7 \pm 8.8$ MPa.m$^{1/2}$ (0.244 vol%) and $557.3 \pm 2.7$ MPa.m$^{1/2}$ (0.489 vol%). They proposed that the toughening mechanism of GNPs in an epoxy matrix was due to crack deflection [12]. In addition, the authors reasoned that the increase in toughening with incorporation of GNPs was due to their modification which promoted better exfoliation, dispersion, and distribution compared to unmodified GNPs. For unmodified GNPs, surface area can be reduced due to restacking of graphene sheets upon mixing with the epoxy matrix [295]. They also mentioned that the load transfer from a matrix to nanofillers becomes more effective with the presence of modifier agent on the GNPs surface [295].

Other group have reported similar pattern of result where increased fracture toughness was observed with incorporation of GNPs in comparison to neat epoxy. Generally, they also stated that the reason for the increase in resistance to crack was due to crack deflection [126], [127], [132], [284] and crack bridging [284] as well as stronger interfacial interaction between epoxy/GNPs resulting from grafted modifiers attached during treatment [284].

5.4.4 Impedance Spectroscopy

Figure 5.28 shows electrical conductivity as a function of frequency for NCs containing all types of GNPs used in this work. As expected, the neat epoxy shows electrically insulative behaviour, displaying scattered data points that are highly frequency dependent.
Figure 5.28: Electrical conductivity as a function of frequency for epoxy nanocomposites containing (a) U-GNPs and AR-GNPs at 4 wt. % (b) A-GNPs and (c) T-GNPs.
At 2 wt. % of U-GNPs, the frequency dependent response of the NCs was superior to the neat epoxy, but still the material acted as an insulator over the full experimental frequency range. At 4 and 6 wt. % of U-GNPs, the conductivity shows frequency-independent behaviour at the lower range of frequency (<100 Hz), indicative of the percolation threshold of GNPs for electrical conductivity [212]. The NCs containing 4 wt. % of AR-GNPs showed higher conductivity than the equivalent U-GNP NCs and their frequency-independent region also extended to a higher value (just >100 Hz). This could be due to exfoliation of the U-GNPs during sonication, resulting in a more extensive GNP network compared to the AR-GNPs. The conductive paths created by both NCs containing AR-GNPs and U-GNPs could be attributed to good dispersion but poor distribution of GNPs within the NCs as discussed in subsection 2.3.1 of chapter 2.

Figure 5.29: Formation of GNPs network (a) Conductive network and (b) and (c) nonconductive network (the yellow coating represents surface modifier encapsulating the surface of the GNPs [103].
In contrast, both A-GNPs and T-GNPs epoxy nanocomposites show insulative behaviour up to 6 wt. % filler loading. This may happen for two reasons. Firstly, both of these treated GNPs are better dispersed and distributed more uniformly within the epoxy matrix than the U-GNPs and therefore do not as readily form a conductive network (as illustrated in Figure 5.29b). Ma et al. [87] observed the same behaviour when they modified CNTs with APTS for epoxy NCs. In contrast, the U-GNPs form clusters due to less efficient dispersion and distribution (as shown in the SEM image in Figure 5.26a) which more readily form a continuous network (as illustrated in Figure 5.29a). Secondly, after modification with APTS and Triton X-100, the GNPs are coated with molecular layers of surface modifier which inhibit direct contact between nanofillers, inhibiting the formation of a continuous network (Figure 5.29c). Similar behaviour was observed by Zhu et al [115] for their surface-modified GNPs.

5.5 Summary

GNPs were successfully modified with APTS coupling agent and Triton X-100 surfactant. Characterisation of the modified GNPs was carried out in order to investigate whether grafting of APTS and adsorption of Triton X-100 on to the surface of the GNPs had occurred. TEM indicated that better exfoliation of GNPs were achieved after treatment in solvent containing modifiers which produced thinner stacks of graphene flakes compared to U-GNPs. Mass loss from TGA indicated that both treated GNPs experienced higher mass loss compared to U-GNPs and AR-GNPs. Raman spectroscopy indicated that the modifications of GNPs resulted to higher intensity ratio between D to G peak. The $I_D/I_G$ increased from 0.24 for AR-GNPs to 0.28 (U-GNPs), 0.76 (A-GNPs) and 0.61 (T-GNPs). In addition, EDS and XPS showed that elemental composition after the treatment had changed. A rheological percolation threshold occurred at around 4 wt. % for U-GNP suspensions, and at around 5 wt. % for both treated GNP suspensions. Properties of composites were compared using impedance spectroscopy and several mechanical tests. The results indicated that epoxy nanocomposites with A-GNPs gave better mechanical performance speculated to be due to stronger adhesion introduced by
covalent functionalisation using APTS compared to U-GNPs and T-GNPs. Both modified GNPs, however, were found to form electrically insulative NCs despite highest loading of 6 wt. % of GNP is included. Therefore, due to better performance in mechanical properties, epoxy/A-GNPs nanocomposite matrices were chosen to manufacture multiscale composites since the focus of this work is to study the potential use of GNPs for structural application in aerospace composite. This topic is presented in the next chapter of this thesis.
Chapter 6  Epoxy/GNPs/Carbon Fibre Multiscale Composites

6.1  Composite Manufacturing

The techniques used in composite manufacturing are important in ensuring the production of high quality composite panels. In this work, it was necessary to use vacuum-assisted resin film infusion (VARFI) to manufacture multiscale composites due to the high viscosity of the epoxy/GNPs suspension. The manufacturing of composites by VARFI is discussed in the next subsection.

6.1.1  Flow of Resin Film within Carbon Fibre Lay-ups

Initially using VARFI, one layer of resin film was placed in the middle of eight layers of carbon fibre fabric. Unfortunately, the quality of composite panel manufactured by this approach is poor. This is because, by using only one layer of resin film to encapsulate eight layers of carbon fibre fabric requires the resin to move in the z direction through 4 layers of carbon fibre from the middle to the top and bottom. As a result, fabricated composite suffered from inadequate wetting of the carbon fibre (as shown in Figure 6.1a).

Therefore, another approach was proposed to improve the manufacturing process, where three layers of resin film were prepared and each film was placed alternately between two layers of carbon fibre fabric. A schematic illustration of this lay-up structure was shown in chapter 3 (subsection on manufacturing of multiscale composites). To show the effect of both approaches, fabricated composites are shown in Figure 6.1. Figure 6.1a and Figure 6.1b show composite panels manufactured by one and three layers of resin film, respectively. It can be seen that for one layer of resin film, inadequate wetting of the carbon fibre fabric was observed after the composite panel was cut as shown by the arrows in Figure 6.1a. In contrast, the composite panel manufactured using three layers of resin film have a sharp and fine edge when cut (Figure 6.1b). This suggests fibre yarns are
encapsulated with matrix. Therefore, in the rest of this work, composite panels were prepared using three layers of resin film.

Figure 6.1: Composite panel produced by (a) 1 layer of resin film (b) 3 layers of resin film.
6.2 Quality of Manufactured Composites

Before the fabricated composite panels were used for characterisation, their quality was assessed. Defects in manufactured composite panels are inevitable especially porosity (voids), which is the most common fault. The quality of composite panels was observed qualitatively using ultrasonic C-scanning and optical microscopy. Quantitatively, void content measurements were performed using acid digestion of the matrix to analyse the quality of the composite panel. Throughout this chapter, the term multiscale composite refers to fabricated composite panels consisting of three constituents, epoxy/CF/A-GNPs while conventional composite refers to the system consisting of epoxy/CF only.

6.2.1 C Scan Analysis

Ultrasonic inspection is an important tool and the most common non-destructive method used to evaluate the quality of laminated composites [316], [317]. Figure 6.2 shows the example of C scan image of composite panels manufactured in this work. In the image, the composite panel appears as a uniform grey colour produced by the lower amplitude of interface echo of the transducers [318]. The green colour in the image indicates the surrounding air included during scanning. Appearing as black at the bottom of the composite panel is the image of the sample holder. As can be seen in Figure 6.2, a non-uniform dashed black line appears in the image speculated to be due to attenuation resulting from an inhomogeneous composite panel in terms of its density. This discontinuous area will cause the ultrasonic signal to scatter resulting in more rapid loss in its energy [319]. Typically, defects or voids in composite panels will appear as dark regions in C scan images. This is due to flaws in the composite panel reflecting back the acoustic wave towards the transducer, creating a shadow in the flawed area [320]. However, information provided by C scans with regards to the effects of manufacturing techniques on the panel quality is usually inadequate in detecting microdefects [190], [319]. In addition, the use of C scan is more effective to evaluate defects on the composite panel after mechanical testing for...
example impact test [179], [321]. Hence, optical and electron microscopy were also used to assess the quality of manufactured composite panels in this work.

![Composite panel, Sample holder, Air](image)

**Figure 6.2:** An example of C scan image of epoxy/CF composites manufactured in this work.

### 6.2.2 Microscopy Techniques

Porosity in composite materials is known to be the most common defect in the manufacturing process [214], [322], [323]. It is imperative for the quality of the composite panel to be assessed in order to know how good the manufacturing process is. Microscope is usually used to identify failure modes in composites by examining the cross sectional area of a specimen. Since C scan does not sensitive to microdefects like small voids, characterisation of the cross section of a composite panel by using microscope is valuable. **Figure 6.3** shows an example of the cross
sectional area of a multiscale composite containing 4 wt. % of A-GNPs. The dashed circled in the image indicated voids within the composite structure.

Based on observation of all the composites in this work, voids can only be seen by microscope and not by the naked eye. The lack of porosity could be due to a good degassing process as well as continuous air suction during resin film infusion. Nonetheless, the volume percentage of void content ($V_v$), for each manufactured composite in this work was determined by acid digestion. In addition, the fibre volume fractions of the composites ($V_f$), were calculated, and the results obtained from mechanical testing were normalised according to the value of fibre volume fraction ($V_f$).

![SEM image showing voids in a multiscale composite of epoxy/CF/A-GNPs (4 wt. %).](image)

**Figure 6.3:** SEM image showing voids in a multiscale composite of epoxy/CF/A-GNPs (4 wt. %).

### 6.2.3 Composite Constituent Volume Percentage

Composite constituent volume percentage was determined by acid digestion technique as explain in subsection 3.3.3.1. Table 6.1 shows the vol. % of fibre ($V_f$), matrix ($V_m$) and void content ($V_v$) in the composite panel as a function of A-GNPs
concentration. The result shows that, as a function of A-GNPs, $V_m$ and $V_v$ increases significantly. This could be attributed to the increase in viscosity of suspension which has been observed during preparation of the suspensions.

Table 6.1: Composite constituent volume percentage. Data are mean ± standard deviation ($n = 4$).

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Fibre ($V_f$)</th>
<th>Matrix ($V_m$)</th>
<th>Void ($V_v$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>65.6 ± 1.3</td>
<td>32.8 ± 1.3</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>*62.4 ± 1.3</td>
<td>34.9 ± 1.4</td>
<td>*2.7 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>*56.5 ± 1.4</td>
<td>*40.0 ± 1.4</td>
<td>*3.5 ± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>*51.2 ± 1.7</td>
<td>*44.4 ± 1.8</td>
<td>*4.4 ± 0.1</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant, calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) of 6 with t-value from standard table is 1.943.

Table 6.2: Viscosity of suspension and thickness of fabricated composite containing different amounts of A-GNPs. For thickness measurement, data are mean ± standard deviation ($n=3$).

<table>
<thead>
<tr>
<th>A-GNPs (wt. %)</th>
<th>Epoxy/A-GNPs suspension</th>
<th>Epoxy/CF/A-GNPs multiscale composite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity at 80 °C (Pa s)</td>
<td>% Increase</td>
</tr>
<tr>
<td>0</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
<td>+100%</td>
</tr>
<tr>
<td>4</td>
<td>0.62</td>
<td>+182%</td>
</tr>
<tr>
<td>6</td>
<td>0.87</td>
<td>+295%</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant, calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) 4 with t-value from standard table is 2.132.

Tabulated data for the increase in viscosity of suspension (with hardener) as a function of A-GNPs loading is presented in Table 6.2. For example, it can be observed that the viscosity of a suspension shows a significant increase by 100% with addition of 2 wt. % of GNPs relative to the viscosity of the neat epoxy. Similar behaviour was reported by Seyhan et al. [169] using CNTs added into a resin blend to be used for vacuum assisted resin transfer moulding (VARTM). This indicates that the viscosity of suspension is significantly affected by nanoparticle addition. As the viscosity of the suspension increases with A-GNP content, areas within the fibre
with greater complexity of gaps such as the region between individual fibres are harder to be penetrated and filled by the matrix. Therefore, these unoccupied regions may cause void formation within the composite structure and this effect increases as a function of A-GNPs content as a result of the increase in viscosity of suspension.

A study by Vaxman and Narkis [324] also showed using SEM that cavities appear at the fibre-matrix interface which was attributed to poor wetting of the carbon fibre by the matrix as a result of low resin-fibre compatibility. According to Kamar et al. [182], in conjunction with higher viscosity and poor wetting of the CF, voids can also appear due to the manufacturing process. Two regions where voids can form are within a tow, where there are gaps between individual fibres, and in the resin-rich areas where each warp and fill tow of a fabric, cross each other [182]. These are known as “tow voids” and “channel voids”, respectively [325]. Research reported by other groups also stated that void content increased with higher nanoparticle concentration in their fabricated composites [163], [326], [327].

The viscosity of the epoxy/GNP suspension also affects the fibre volume fraction ($V_f$) of the composites. Increasing viscosity at higher A-GNPs content (for example at 6 wt. %) inhibits the flow of a suspension. As a result, more matrix remains in the composite and less is forced out from the CF fabric lay-up during VARFI process. Therefore, matrix volume fraction ($V_m$) is increasing as a function of A-GNPs concentration while fibre volume fraction ($V_f$) of composites is reduced. The effect of higher matrix volume fraction ($V_m$) as a function of A-GNPs content can be seen to increase the thickness of multiscale composites as shown in Table 6.2. For example, thickness of the composite increase by 6% with the inclusion of 2 wt. % of A-GNPs relative to the composite made by neat epoxy resin.

SEM images in Figure 6.4 shows the reason for these circumstances where all the images were taken at the middle layer of the fabricated composites. Figure 6.4a shows the composite containing 0 wt. % of A-GNPs and Figure 6.4b the composite containing 6 wt. % of A-GNPs. In Figure 6.4a, due to low viscosity of neat epoxy at the 100 °C processing temperature, the resin can flow easily throughout the fabrics
including in the z direction to penetrate the small gaps between the individual fibre. As vacuum-only pressure is continued during the VARFI process, any excess neat epoxy will flow out from the CF fabric. As a result, the texture in Figure 6.4a shows needle-like features following the shape of CF. In contrast, for epoxy/A-GNPs (6 wt. %), the high resin viscosity slows the flow excess of suspension out from the CF fabric which therefore leave significant amount of matrix within the laminate. Hence, higher $V_m$ and lower $V_f$ was obtained for the multiscale composites. Figure 6.4c also indicates that for the composite fabricated using 6 wt. % of A-GNPs there is the possibility that the resin will not be able to flow to the edge of laminate, due to high viscosity, leaving some part of the CF uncovered. However, this condition was avoided during manufacturing by preparing resin films with surface areas large enough to cover the CF fabric.

![Figure 6.4](image)

**Figure 6.4:** Surface of composite in the middle layer with epoxy/CF containing A-GNPs at (a) 0 wt. % (b) 6 wt. % and (c) 6 wt. % at low magnification.
6.3 Mechanical Testing of Epoxy/CF/A-GNP Multiscale Composites

Characterisation of the fabricated multiscale composites was carried out by means of mechanical testing to assess the effects of A-GNPs addition into the epoxy/CF composites. As published work on the inclusion of GNPs into epoxy/CF is still rare, multiscale composites which consist of different constituents will be used as a reference for analysis and discussion of results.

6.3.1 Flexural Strength Properties

Flexural strength properties of fabricated composites were characterised by three point bending according to ASTM D790 [210]. Figure 6.5 shows typical stress–strain curves of the multiscale composites that have not been normalised for the differences in $V_f$. The failure mode of all specimens in flexural testing can be classified as brittle, showing abrupt failures as in Figure 6.5. It was observed that as GNP loading increased, the failure of multiscale composites occurred at lower flexural stress and strain which explains significant decrease in flexural strength (as shown in Table 6.3), suggesting that the multiscale composites become more brittle with the addition of A-GNPs. Unlike the flexural properties for cured nanocomposites (discussed in chapter 5), the stress–strain curve for multiscale composites is below the stress–strain curve for epoxy/CF composites as presented in Figure 6.5. This reflects that the flexural modulus for multiscale composites decreased with addition of A-GNPs despite the fact that GNP are known to have a high modulus (~1 TPa) [63] coupled with modulus for CF ~260 GPa [328].

The stress-strain curves shown in Figure 6.5 are affected by the variation in $V_f$ of the composites as discussed previously. As the $V_f$ reduced with higher A-GNPs content in the multiscale composite, the matrix volume fraction ($V_m$) increased. As a consequence, the reinforcement effect is reduced and consequently flexural modulus, which is dominated by the CF in the laminated composite, also decreased since $V_f$ decreased. Previous work by Ramanaiah et al. [329] and He and Gao [330] also indicated that the flexural modulus of composite decrease with lower fibre volume.
fraction. He and Gao [330] for example stated that at lower $V_f$, the ability for the load transfer between fibres to matrix is low, hence lower flexural modulus is exhibited.

![Figure 6.5: Typical un-normalised stress–strain curves of multiscale composite containing A-GNPs at all loadings.](image)

Table 6.3: Data for flexural strength and flexural modulus normalised to the respective $V_f$ of the composites. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Normalised Flexural Modulus (GPa)</th>
<th>Normalised Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81.8 ± 2.4</td>
<td>1043.9 ± 2.2</td>
</tr>
<tr>
<td>2</td>
<td>*77.7 ± 0.7</td>
<td>*909.1 ± 14.9</td>
</tr>
<tr>
<td>4</td>
<td>82.1 ± 0.4</td>
<td>*887.4 ± 18.1</td>
</tr>
<tr>
<td>6</td>
<td>81.5 ± 0.8</td>
<td>*872.8 ± 5.6</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant, calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) 4 with t-value from standard table is 2.132.

In contrast, at higher $V_f$, early sliding of the polymer phase is prevented since the CF has started to show the reinforcement effects [330]. Table 6.3 shows that the flexural modulus data in this work did not change significantly as a function of A-GNPs.
content after being normalised to the respective $V_f$ for each composite. In addition to the effect of $V_f$, higher void content for composites fabricated using higher A-GNPs loading in this work also could possibly reduce the flexural modulus. A previous study by Liu et al. [331] on the effects of void content on composite properties indicated that flexural modulus decreases as a function of void content.

![Figure 6.6](image-url)

**Figure 6.6:** Normalised flexural strength (with $V_f$) as a function of A-GNPs content. Data are mean ± standard deviation (n=3).

Table 6.3 and Figure 6.6 also show the result of flexural strength as a function of GNPs loading, which was normalised according to the respective $V_f$. It can be observed that the flexural strength of epoxy/CF composites decreases significantly as A-GNPs was added (Table 6.3). This reduction could be due to poor interaction at the matrix/CF interfaces which creates weak adhesion bonding. This could result from the increase in viscosity of the matrix resin containing A-GNPs compared to neat epoxy, since higher viscosity reduces the ability of the suspension to flow throughout the laminate tows and within the tows. In addition to higher viscosity, the filtering effect of the CF during film infusion may also contribute to poor encapsulation of CF by the matrix [332]. Hence, the roles of the matrix to bind the
CF together and to transfer load is deteriorated and will decrease the mechanical properties. Moreover, the filtering effect by the CF may also cause aggregation of the A-GNPs between the fibres which has been proposed to create stress concentrated areas when subjected to load [15].

Figure 6.7: SEM image of epoxy/CF containing A-GNPs at (a) 0 wt. % and (b) 6 wt. %.
Figure 6.7 show typical examples of SEM images for epoxy/CF containing A-GNPs at 0 wt. % (Figure 6.7a) and 6 wt. % (Figure 6.7b). Figure 6.7a indicates that the neat epoxy matrix is distributed more uniformly with greater coverage on the CF. In contrast, Figure 6.7b shows that more individual fibres are not encapsulated by the matrix and aggregated GNP on the outside of tows, suggesting a severe filtering effect by the CF. This reflects that lower viscosity for the neat epoxy contributed to encapsulate the CF more effectively compared to the matrix materials which contain A-GNPs.

Several other groups characterised their multiscale composites using 3-point bend flexural testing but reported contradictory results for epoxy/CF/GNPs [24] and epoxy/CF/GNPs + CNTs [188]. For example, Qin et al. [24] reported a 82% increase in flexural strength for composites containing GNPs over neat epoxy composites. They reasoned that stronger interfacial adhesion was introduced with GNPs inclusion in the epoxy/CF composites of their work. Wang et al. [188] reported that the combination of CNTs/GNPs caused a complementary structure between the nanofillers, in that the increase in flexural strength and modulus in their work was due to CNTs being able to permeate between the GNPs providing good interaction and preventing aggregation due to van der Waals attraction. Kamar et al. [182] reported an increase of 29% in flexural strength for epoxy/glass fibre/GNPs at 0.25 wt. % of GNPs compared to a pristine epoxy matrix. GNPs levels beyond that content resulted in a decrease in the strength of the multiscale composites. They reasoned that the deterioration was due to interlaminar adhesion decreasing at filler loadings above 0.25 wt. %.

### 6.3.2 Interlaminar Shear Strength (ILSS)

In this work ILSS was carried out using short-beam shear tests according to ASTM standard D2344 [217]. Figure 6.8 shows typical stress–strain curves from ILSS testing for each sample. It can be seen that the composite panel with neat epoxy breaks in a brittle manner, where a sudden drop of stress is recorded at the end of the curve. In contrast, the multiscale composites with epoxy/A-GNPs as the matrix
show plastic deformation, allowing the sample to support a higher strain before failing. Furthermore, it can be seen that, as a function of filler loading and at higher content of A-GNPs, the maximum stress value for multiscale composites is lower compared to the neat epoxy matrix material. This appears to suggest inferior properties with the inclusion of A-GNPs in composites. However, this behaviour could be affected by the decrease in $V_f$ and increase in $V_m$ for the fabricated composite as a function of A-GNPs content.

![Figure 6.8: Un-normalised stress–strain curves for composite containing different concentration of A-GNPs.](image)

The effect of fibre volume fraction ($V_f$) on the ILSS properties was studied by Romanzini et al. [333]. Data from their group indicated that the ILSS of composites decreased at lower $V_f$. Therefore, if the $V_f$ can be controlled and kept constant, perhaps more consistent results can be observed in the stress-strain curves and ILSS. The lower value in maximum stress for the multiscale composite relative to the conventional composite also could be attributed to weak interfacial adhesion between the matrix and carbon fibres as indicated in the SEM images shown in Figure 6.9. Moreover, the filtering effect of the CF, and poor distribution of matrix within CF
tows due to the high viscosity resulting from the inclusion of A-GNPs (discussed earlier and shown in Figure 6.7), also could contribute to give the inferior properties of multiscale composite over conventional composite. In addition, aggregation of A-GNPs in multiscale composites may contribute to increased stress concentration and reduce the value of ILSS.

Figure 6.9: SEM images of the edge of epoxy/CF composites tested ILSS specimens containing A-GNPs at (a) 0 wt. % (b) 2 wt. % (c) 4 wt. % and (d) 6 wt. %.

SEM images of the delaminated region of tested ILSS specimens are presented in Figure 6.9. As shown in Figure 6.9a, the darker area in the image is the region rich with CF and the lighter area is the region rich with matrix (epoxy/A-GNPs). According to the SEM images failure of these short beams specimens occurred in interlaminar shear failure mode, as referred to in the ASTM D2344 standard. At the same magnification, the crack in the neat epoxy resin matrix is not as obvious as in the multiscale composites, especially for the panel containing 6 wt. % of filler loading. This suggests the breaking resistance of multiscale composites with higher
GNPs content is lower compared to composites with neat epoxy. Figure 6.9 also indicates that the crack initiated by the applied force propagated along the carbon fibre/matrix interface. This type of failure can be attributed to weak interfacial adhesion between CF/matrix that causes delamination of reinforcement.

Table 6.4: Normalised interlaminar shear strength of multiscale composite as a function of A-GNPs content (wt. %). Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Interlaminar shear strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.1 ± 1.6</td>
</tr>
<tr>
<td>2</td>
<td>*51.1 ± 2.8</td>
</tr>
<tr>
<td>4</td>
<td>*51.3 ± 1.0</td>
</tr>
<tr>
<td>6</td>
<td>*28.8 ± 0.4</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) 4 with t-value from standard table is 2.132.

Figure 6.10: Normalised interlaminar shear strength with the respective V_f as a function of A-GNPs content. Data are mean ± standard deviation (n=3).
Table 6.4 and Figure 6.10 shows the summary of ILSS data, which was normalised according to the respective $V_f$. Similar to flexural properties, ILSS of the multiscale composites decreases significantly as a function of A-GNPs content relative to the neat epoxy matrix. For example, from Figure 6.10 the ILSS decreases from 88.1 ± 1.6 MPa for neat epoxy to 28.8 ± 0.4 MPa for multiscale composites with 6 wt. % A-GNPs. The same explanations proposed previously for the stress-strain curves could also be reasons for the inferior ILSS properties of the multiscale composites. It has been reported that if good matrix-reinforcement interaction is achieved, the ILSS performance of composites is improved [166].

Several other groups have reported an increase in ILSS when they incorporate nanofillers into composite panels consisting of epoxy/CF/GNPs [24], epoxy/CF/GNPs + CNTs [188] and epoxy/glass fibre/clay [334]. Qin et al. [24] stated that adding GNPs into composites caused mechanical interlocking between fibre and matrix hence reduced the interlaminar shear concentrations. The same reasons for superior properties in ILSS as for flexural strength were given by Wang et al. [188], namely interlacing and complementary interaction between CNTs and GNPs. They stated that the hybrid nanoparticles restricted the crack growth which subsequently gave higher ILSS for multiscale composites over conventional composites.

6.3.3 Mode II Interlaminar Fracture Toughness (ILFT)

Mode II ILFT was carried out using four point end-notched flexure (4ENF) following the method reported in Kuwata and Hogg [218]. Figure 6.11 shows representative compliance curves for each composite system, plotted against the crack length of the specimen. Compliance, $C$, was determined by the ratio of displacement to load ($\delta/P$) [15]. All the graphs in Figure 6.11 indicate that specimen compliance increased linearly with crack propagation. Fitting the data with a linear function using OriginPro 8.5 software showed that the value of gradient (compliance) decreased as a higher content of A-GNPs was incorporated into the composites, as the stiffness of the composites panels increase with a higher content
of A-GNPs. The gradient of the compliance–crack length graph in Figure 6.11 was used to calculate $G_{II}$.

![Compliance vs Crack Length Graphs](image)

**Figure 6.11**: Representative compliance curves from 4ENF tests for epoxy/CF composites containing A-GNPs at (a) 0 wt. %, (b) 2 wt. %, (c) 4 wt. %, and (d) 6 wt. %.

Figure 6.12 shows the crack growth plotted in load–displacement graph from the 4ENF tests. It shows that the maximum load the epoxy/CF composites can sustain is approximately 650 N before the specimen yields upon reaching ~4.0 mm of displacement. In contrast, as a function of GNPs content, the maximum load that the multiscale composite specimens can sustain is around 250-300 N. This could be due to the effect of $V_f$ as in general load-displacement curves for composites would display lower loads for lower values of $V_f$. Moreover, the same reasons as discussed in the previous section could also be the cause of the lower load recorded for the multiscale composites compared to conventional composites in this characterisation.
method. These reasons include poor interface adhesion of the matrix/carbon fibre
[335], higher void contents as a function of A-GNPs [163], [326] and filtration of A-
GNPs by the CF fabric causing aggregation [332], which together can create a stress
concentration area in the composite panel. In addition to possessing lower load-
carrying capability, multiscale composites exhibit different characteristics in their
load–displacement curves relative to conventional composites. The load slightly
dropped when displaced at around 1 – 1.5 mm but afterwards increased, until the
 crack length was ~4 mm, before the load was released to end the test. Previously,
similar pattern of load-displacement curve was reported by Kuwata and Hogg [336].
The initial linear section of the load–displacement curves in Figure 6.12 represents
an elastic region and at any point within this region, if the load is released, the
sample will return to its original shape. This elastic region shows that the multiscale
composite exhibit a higher load compared to epoxy/CF composites at any given
displacement. In order to show the difference in this region more clearly, data up to
250 N in Figure 6.12 is presented in Figure 6.13.

Figure 6.12: Crack propagation of composite panel measured in 4ENF test
plotted in load–displacement graph for all types of multiscale composites.
Figure 6.13 indicates that the addition of A-GNPs into the matrix system increases the stiffness of the composites, supporting the reductions in the compliance slopes in Figure 6.11 as well as being in agreement with the flexural test data discussed previously. Moreover, a higher content of A-GNPs in multiscale composites shortens the displacement that the specimen can undergo when subjected to load, reflecting their stiffer behaviour.

**Figure 6.13: Enlarged view of the elastic regions of the load–displacement curves in Figure 6.12.**

Figure 6.14 shows typical R–curves (resistance curves) for all specimens, normalised to their respective $V_f$. The highest value of $G_{II}$ was found for composite panels with the neat epoxy matrix, followed by multiscale composites with the order of A-GNPs containing 2, 4 and 6 wt. % accordingly. From R–curves (Figure 6.14), composite panels containing neat epoxy show an increase in $G_{II}$ and then decrease due to a sudden drop in load as observed previously in Figure 6.12. In the case of multiscale composites containing A-GNPs, $G_{II}$ increases by a small amount initially followed by a slight drop.
Figure 6.14: Typical R-curves normalised to the respective $V_f$ for composites containing different amount of A-GNPs.

Table 6.5 and Figure 6.15 shows the $G_{II}$ values of multiscale composites as a function of A-GNPs, which were normalised to their respective $V_f$. It can be seen the $G_{II}$ decrease significantly with higher content of A-GNPs in the composites for example from 1.68 kJ/m$^2$ (epoxy/CF) to 0.25 kJ/m$^2$ for multiscale composite containing 6 wt. % of A-GNPs. Improvement in fracture toughness for NCs is not reflected in multiscale composite perhaps due to, with the incorporation of A-GNPs, multiscale composite introduced another interfacial area primarily at matrix-CF interface which could affect their load resistance capability [337], [338].

Table 6.5: Normalised mode II fracture toughness as a function of A-GNPs content (wt. %). Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Normalised mode II fracture toughness (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.68 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>*0.41 ± 0.10</td>
</tr>
<tr>
<td>4</td>
<td>*0.35 ± 0.04</td>
</tr>
<tr>
<td>6</td>
<td>*0.25 ± 0.03</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) 4 with t-value from standard table is 2.132.
Figure 6.15: Mode II fracture toughness normalised to the respective $V_f$ for composites panel as a function of A-GNPs content. Data are mean ± standard deviation (n=3).

Previously, Mode II ILFT was studied by Wichman et al. [175] using double wall carbon nanotubes (DWCNT) and amino-functionalised double wall carbon nanotubes (DWCNT-NH$_2$) incorporated into epoxy/glass fibre composite. The CNTs were added at the same concentration (0.3 wt. %) with the $V_f$ for both composites controlled at 50 %. As a result, mode II ILFT in their study indicated no changes for both systems containing DWCNTs and DWCNTs-NH$_2$ relative to specimen control containing no DWCNTs. They speculated the reason as being due to the influence of fibre-matrix interface debonding but no further explanation is provided in their report.

Similar results were observed by Ahmadi-Moghadam and Taheri in mode II fracture toughness testing for epoxy/E-glass composites containing unmodified GNPs, abbreviated as U-GNPs [332]. They also made the comparison with multiscale composites using GNPs treated with NH$_2$ (GNPs-NH$_2$) and with glycidyloxypropyl-trimethoxysilane (GNPs-Si). All types of GNPs were added at 0.5 wt. % to form the multiscale composites. The result shows inferior properties for multiscale composites containing U-GNPs relative to the control sample with an approximately 21.3% reduction in mode II fracture toughness. In contrast, both GNPs-NH$_2$ and
GNPs-Si gave values improved by 12% and 11%, respectively. Their discussion of these results only stated that the mechanism of crack propagation subjected to mode II fracture was influenced by macro-crack nucleation, which occurred in the matrix rather than along the matrix/fibre interface in their study.

Zhu et al. [15] investigated the effect of various types of modified CNTs on the properties of epoxy/S2-glass composites. They have used CNT functionalised with carboxyl groups (COOH-CNTs and both long (aspect ratio 660-6250) and short CNTs (aspect ratio 25-200) treated with glycidylxypropyl-trimethoxysilane (GPS-CNTs). Method of composites manufacturing was also studied using two approaches similar to the method used in this work (explained in chapter 3). First, resin with CNTs was placed in the middle of a composite layup and second, the resin with CNTs was placed alternately between the layers of glass fibres. They reported no significant effect from mode II fracture toughness testing for COOH-CNTs and short GPS-CNTs using the first approach of composites manufacturing. By the same method of composites manufacturing, only a 10% increase in mode II fracture toughness was observed with addition of long GPS-CNTs at 0.25 wt. %. For the second approach to composites manufacturing, they reported a significant increase in mode II fracture toughness with a 91% improvement for long GPS-CNTs at 0.25 wt. % and 74% improvement for short GPS-CNTs at 0.5 wt. %. For the composites manufactured by interlayer placement of epoxy-CNTs suspension (2nd approach), they observed a uniform thickness for all specimens which indicates that the resin bled out evenly during the consolidation process. They also stated that CNTs remained entrapped, leaving them concentrated on the glass fibre surface which subsequently served as an effective obstacle for matrix/fibre debonding. Bridging of cracks by the long CNTs was observed which contributed to superior properties in the multiscale composites structure.

6.3.4 Impact Resistance

Impact testing was carried out to characterise the behaviour of the manufactured multiscale composites as a function of A-GNPs content. Low-energy impact
resistance was applied at 1 J, 3 J and 5 J, determined through preliminary testing. Based on this preliminary study, the conventional composite (epoxy/CF) was also tested at an energy level of 8 J, as epoxy/CF specimen produces smaller damage areas compared to the multiscale composites.

![Image](image.png)

Figure 6.16: Impact resistance of energy–time curves for epoxy/CF composites panel containing A-GNPs at (a) 0 wt. % (b) 2 wt. % (c) 4 wt. % and (d) 6 wt. %.

Figure 6.16 shows typical energy–time curves from impact testing for the composites containing 0, 2, 4 and 6 wt. % of A-GNPs. In general, the energy curves increase as the impact energy level increases. This type of pattern in energy–time curve is commonly observed for impact resistance at different energy levels [179], [339]. The formation of the curve during testing can be explained as follows. As the impactor hits the specimen at a specified energy level, the energy increases over time and reaches a peak, indicating the amount of energy that has been transferred to the specimen. However, during impact and not all of the energy is absorbed and some is
returned to the impactor [340]. Therefore, as shown in Figure 6.16, after reaching the peak the energy–time curve decreases to a constant value which reflects the amount of total energy absorbed by the specimen. The amount of energy returned to the impactor is called the inelastic returned energy [180]. The sum of absorbed and inelastic returned energy will equal the impact energy transferred [179]. In addition, it can be observed that the peak of the curve is shifted towards longer times for composite panela containing A-GNPs relative to epoxy/CF composite. The peak is also shifted accordingly with A-GNPs concentration. For example, at 1 J of impact energy, the peak of the curve for composite containing 0 wt. % of A-GNPs is positioned at around 1.4 ms, and for the multiscale composites at 2 ms (2 wt. %), 2.2 ms (4 wt. %) and 2.4 ms (6 wt. %). This suggests the same level of impact energy imparted by the impactor to the multiscale composites takes a longer time to be transferred, compared to conventional composites. Moreover, the multiscale composites were observed to absorbed higher energy relative to the conventional composite in which the absorbed energy was determined from the energy–time curve as discussed in chapter 2 (subsection on damage tolerance).

Table 6.6: Normalised absorbed energy respective to Vf at different impact energy level for all composite systems. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised absorbed energy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>32.3 ± 5.1</td>
</tr>
<tr>
<td>3 J</td>
<td>70.2 ± 6.6</td>
</tr>
<tr>
<td>5 J</td>
<td>88.9 ± 4.6</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which calculated against neat epoxy (0 wt. % GNPs) at 95% confidence level and degree of freedom (df) 4 with t-value from standard table is 2.132.

Summary of the absorbed energy data is presented in Table 6.6 and Figure 6.17. It shows that the decrease in Vf as a function of A-GNPs concentration does not affect the impact test result perhaps due to the rate of the test. The reason for higher energy absorption by the multiscale composite could be related to their higher Vm than the
conventional composite and could also be attributed to A-GNPs providing additional absorption processes [179] when added into epoxy. Unlike in the conventional composite, the existence of A-GNPs in the multiscale composite has introduced interfacial area between epoxy/A-GNPs in the matrix phase. The interfacial area generated by the A-GNPs reduces the density of the matrix which imparts higher tolerance of in-plane compression to the multiscale composite. Hence, higher energy will be absorbed by the multiscale composite and less energy returned to the impactor. In addition, as mentioned previously, the existence of A-GNPs in the matrix phase resulted in weaker interface bonding between matrix/CF. Therefore, when the impactor hits the multiscale composite panel, impact energy is easily distributed to the other area from the point of impact which resulted in interlaminar cracking due to the weaker interface bonding between matrix/CF. In contrast, impact energy is concentrated at the point of impact for the case of neat epoxy in the conventional composite which creates translaminar and intralaminal cracks. Figure 6.18 shows SEM images of composite panel containing neat epoxy after impact at an energy level of 3 J (Figure 6.18a) which shows translaminar failure, in comparison with a composite panel containing 4 wt. % of A-GNPs which shows interlaminar failure (Figure 6.18b).

![Figure 6.17: Normalised absorbed energy with respective to V_f at different impact energy level for all composite systems. Data are mean ± standard deviation (n=3).](image)
The effect of $V_f$ on the impact properties of polymer matrix composites was carried out by Parvatham et al. [341] which emphasized on the impact strength. They found that the impact strength of composite is increase by the decrease of $V_f$. As an example from their work, decrease of $V_f$ from 43% to 35% has increased the impact strength from 36.4 to 46.2 kJ/m$^2$ respectively. They stated that the increase in $V_f$
cause inefficient capsulation of fibres by the matrix which subsequently reduced the strength of composite.

Although the multiscale composites exhibit higher energy absorption compared to the conventional composite, no significant changes in absorbed energy are observed as a function of A-GNPs content. For example, at 1 J the absorbed energy of the composites are 21.2% (0 wt. % of A-GNPs), 39.9% (2 wt. %), 47.5% (4 wt. %) and 39.6% (6 wt. %). In addition, absorbed energy generally increases as impact energy is increased. This observation has also been reported by other groups [342]–[345]. From Figure 6.17, the effect of A-GNPs concentration on the absorbed energy during impact also could be observed. As mentioned previously, the presence of A-GNPs provides additional mechanisms to increase the absorbed energy of multiscale composite relative to the conventional.

Inam et al. [181] also reported increases in absorbed energy for multiscale composites of epoxy/CF/DWCNT-NH₂ in drop-weight impact tests. The DWCNT-NH₂ content was varied to 0.025 and 0.05 wt. % giving a 3% and 6% improvement to the energy absorption, respectively. Unfortunately, they did not discuss why DWCNT-NH₂ gave higher absorbed energy for the multiscale composites.

Force–displacement and force–time curves are shown in Figure 6.19 and Figure 6.20. The graphs were constructed and arranged according to the energy level during impact. Here, force, or contact force, is defined as the load exerted by the specimen on the impactor. It is also known as the reaction force returned to the impactor from the specimen. In general, maximum force and displacement of the impactor is greater at higher impact energy. It has been reported that the maximum contact force increases as a function of impact energy until it becomes constant as higher impact energy is applied. This suggests there will be a limit for the manufactured composites in carrying a given load [180], [346]. In this work, the maximum contact force that can be carried by the specimen is determined to be around 3000 N as shown in both Figure 6.19 and Figure 6.20.
Figure 6.19: Force–displacement for all composites panel impacted at (a) 1 J (b) 3 J and (c) 5 J.
At 1 J of impact energy, epoxy/CF composites show a very different curve compared to other specimens. This suggests 1 J of impact energy is insufficient to create significant damage in the specimen such as delamination [346]. This indicates elastic deformation. The maximum contact force was reached at around 2500 N and returned to zero displacement at the end of the impact event. For 3 J and 5 J of impact energy, the epoxy/CF composite shows curves with initial maximum force (or also known as incipient force or delamination onset) followed by a sudden load drop [347], [348] and afterwards a fluctuation in load. This unstable force corresponds to unstable propagation of delamination, which is related to matrix cracking [349].

![Figure 6.20: Force–time for all composites panel impacted at (a) 1 J, (b) 3 J and (c) 5 J.](image)

Before the incipient force, the specimen shows elastic behaviour, which is the region where the specimen could revert to its original shape if the force is released. Beyond the incipient force, the load drops and the specimen exceeds the yield point of elastic
deformation. At this point onwards, a plastic deformation occurs [343]. This behaviour can also be observed by analysing the force–time curves shown in Figure 6.20. Lower incipient forces for the multiscale composite relative to conventional composite (epoxy/CF) can be observed in both Figure 6.19 and Figure 6.20. This could be attributed to the decrease in strength retention of composite with the inclusion of A-GNPs compared to unfilled.

The closed curves for all the graphs in Figure 6.20 reflect the impactor not perforating the specimen during the test. The sudden decrease after the incipient force does not necessarily reduce the load-carrying capability of epoxy/CF composites. It is because this behaviour may occur at load levels lower than the maximum attainable load (or also known as maximum contact force) for a particular specimen. This can be seen from Figure 6.20c for the case of 5 J of impact energy in epoxy/CF composites [349].

For multiscale composites impacted at 1 J (Figure 6.20a) the incipient force was around 1000 N. The force beyond the incipient force shows a small increase as a function of time, due to low impact energy imparted to the specimen. This indicates that even though the multiscale composite is affected by 1 J of impact energy, the dissipated energy from the impact point is insufficient for the specimen to show the resistance to load. A similar observation was reported by Iqbal et al. [19] when they applied low impact energy to epoxy/CF composites filled with nanoclay particles. At 3 J and 5 J of impact energy the multiscale composites show similar incipient forces of 1000 N, however their respective maximum contact forces (~2500 and ~3000 N) are higher than the sample impacted by 1 J (Figure 6.20c). This suggests that at higher impact energy, the unperforated multiscale composite will exhibit higher load carrying capability. In addition, an increase in force beyond the point of incipient force for multiscale composites can be observed through the curve in Figure 6.20, suggesting that the failure characteristic of multiscale composites exhibited plastic deformation behaviour. Perhaps, upon impact and reaching the incipient load, the load received by the specimen is distributed by the A-GNPs to the side area from the point of impact. As a consequence, dissipated force is absorbed, created crack which
propagate rather than concentrated as in conventional composite. Hence, higher maximum contact force can be observed than the incipient force for the multiscale composites.

Table 6.7: Normalised incipient force respective to $V_f$ at different impact energy level for all composite systems. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised incipient force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>3633.4 ± 32.0</td>
</tr>
<tr>
<td>3 J</td>
<td>4091.6 ± 11.1</td>
</tr>
<tr>
<td>5 J</td>
<td>4179.9 ± 68.6</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

Figure 6.21: Normalised incipient force with respective $V_f$ at different impact energy levels for composites containing different amount of A-GNPs. Data are mean ± standard deviation (n=3).
Table 6.7 and Figure 6.21 summarises the normalised incipient force as a function of impact energy for the composites containing different amount of A-GNPs. It can be seen that the epoxy/CF recorded much higher incipient forces relative to the multiscale composites systems and the difference are significant with A-GNPs loadings. The result also shows that the incipient force changes relatively little over the range of energy levels used. This shows that higher concentration of A-GNPs did not affect the incipient force of the multiscale composites. There is some evidence of the incipient force reaching a threshold for the epoxy/CF composite at ~3 J whereas the threshold value when A-GNP is included in the composites could be <1 J. Furthermore, the conventional composite shows higher maximum contact force values compared to the multiscale composites. Similar behaviour was reported by Mathivanan and Jerald [345] for epoxy/glass fibre system containing 3 wt. % of graphite. However, no reason was discussed in their report on the effect of graphite particles on the results.

Table 6.8: Normalised maximum contact force respective to $V_f$ at different impact energy level for all composite systems. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised maximum contact force (N)</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td></td>
<td>2387.0 ± 31.7</td>
<td>*1190.0 ± 38.1</td>
<td>*1121.3 ± 69.1</td>
<td>*1079.5 ± 35.2</td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>2965.3 ± 114.2</td>
<td>*2217.8 ± 106.2</td>
<td>*2387.1 ± 53.6</td>
<td>*2524.1 ± 91.6</td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>2986.9 ± 53.6</td>
<td>*2612.2 ± 271.9</td>
<td>*2743.6 ± 96.8</td>
<td>2866.6 ± 144.4</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

Table 6.8 and Figure 6.22 present the summary of normalised maximum contact force data determined from the maximum point in the force–time data in Figure 6.20. Addition of A-GNPs at all loadings decreases the maximum contact force significantly as in Table 6.8. The trend of the result for conventional composite is similar comparing the incipient force with maximum contact force as a function of impact energy. In contrast, for multiscale composites, the trend of the result shows a significant different between incipient force and maximum contact force (Figure 6.21
and Figure 6.22) particularly at 3 J. As an example, maximum contact force for multiscale composites containing 6 wt. % of A-GNPs is around ~1100 N (1 J) and ~2500 N (3 J). This was not observed in incipient force. As mentioned previously, this could be attributed to the distribution of force by the A-GNPs which allow multiple small cracks to propagate rather than the force concentrated at the impact point as in conventional composite.

![Figure 6.22: Normalised maximum contact force with respective V_f impacted at different energy level for composites containing different amounts of A-GNPs. Data are mean ± standard deviation (n=3).](image)

The contact time between the impactor and the specimen as a function of impact energy level is shown in Table 6.9 and Figure 6.23. Generally, the contact time increased as higher impact energy was applied to the specimen. This is related to an increase in the damage area as the impact energy increased, which therefore resulted in an increase in the contact time between the impactor and the sample. In addition, there is a significant difference in contact time between the epoxy/CF and multiscale composites. This is probably due to the introduction of additional interface area with the inclusion of A-GNPs resulted to higher tolerance in in-plane compression when multiscale composite was hit by the impactor.
Table 6.9: Normalised contact time respective to $V_f$ at different impact energy level for all composite systems. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised contact time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>6.6 ± 0.4</td>
</tr>
<tr>
<td>3 J</td>
<td>17.2 ± 0.1</td>
</tr>
<tr>
<td>5 J</td>
<td>20.6 ± 0.1</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

Figure 6.23: Normalised contact time impacted at different energy level for composites containing different amount of A-GNPs. Data are mean ± standard deviation (n=3).

The maximum deflection increases linearly with impact energy as shown in Table 6.10 and Figure 6.24. This is a common behaviour which was also observed by other groups, for instance Aktas et al. [350]. In comparison, multiscale composites show a significant higher maximum deflection compared to conventional composites. This could be attributed to the failure characteristics, in which conventional composites break in an abrupt rupture during the impact event. Multiscale composites with A-GNPs, on the other hand, show a plastic deformation failure characteristic (as discussed previously) which provides more damage tolerance and an ability to absorb
energy during impact. Hence, the impactor travelled slightly deeper upon hitting the specimen before rebound, thereby giving a higher maximum deflection to multiscale composite relative to conventional composite. A more detailed explanation is given in the next paragraph for the after-impact image from the C scan. No significance changes in maximum deflection can be observed with the inclusion of A-GNPs at different wt. % despite the value of $V_f$ decreasing as a function of A-GNPs content.

Table 6.10: Normalised maximum deflection respective to $V_f$ of composite at different impact energy level. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised maximum deflection (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>1.26 ± 0.02</td>
</tr>
<tr>
<td>3 J</td>
<td>2.49 ± 0.06</td>
</tr>
<tr>
<td>5 J</td>
<td>3.91 ± 0.27</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

Figure 6.24: Normalised maximum deflection with respective $V_f$ impacted at different energy level for composites containing different amount of A-GNPs. Data are mean ± standard deviation (n=3).
Figure 6.25: 5 J impacted composites panel at different loadings of A-GNPs.
Figure 6.26: C scan image of impacted composites panel at 1 J, 3 J and 5 J containing (a-c) epoxy/CF, (d-f) epoxy/CF/A-GNPs 2 wt. %, (g-i) epoxy/CF/A-GNPs 4 wt. %, (j-l) epoxy/CF/A-GNPs 6 wt. %.
Figure 6.25 shows images of the front and back faces of specimens impacted at 5 J. Figure 6.26 shows C scan images of specimens which contain different concentrations of A-GNPs impacted at different energy levels. Both of these Figures support the previous data in explaining the mechanism of failure in composites panel with or without A-GNPs in epoxy/CF system. At the time of impact, the energy is transferred from potential to kinetic and passed to the composite panel when the impactor hits the specimen. In the case of epoxy/CF, the impact energy is concentrated at the contact point between the impactor and specimen, therefore, severe splitting or delamination occurs at the back face of the specimen (Figure 6.25b). Due to this concentration of impact energy at the contact point in epoxy/CF, the C scan image revealed a relatively small damage area (Figure 6.26c). However, the fracture of the internal structure of epoxy/CF is possibly severe, considering the image on the lower surface of specimen as in Figure 6.25b which indicates a relatively greater matrix crack, more delaminated and fibre breakage than multiscale composites. Introduction of A-GNPs to form multiscale composite was found to increase the total energy absorption relative to conventional composite. Upon load impact, the imparted energy was dissipated radially to the surrounded area, at all angles and more effectively for multiscale composite than in the epoxy/CF system. Less splitting and fibre breakage on the impacted specimen was observed for multiscale composites (Figure 6.25h) compared to conventional composite. However, C scan images revealed a bigger damage area, as an effect of energy dissipation during the impact event.

Table 6.11: Normalised damage area respective to V of composite at different impact energy level. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised damage area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>29.5 ± 0.3</td>
</tr>
<tr>
<td>3 J</td>
<td>236.9 ± 16.6</td>
</tr>
<tr>
<td>5 J</td>
<td>356.3 ± 22.2</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.
Figure 6.27: Normalised damage area respective to $V_f$ of composite, impacted at different energy level for composites panel containing different amount of A-GNPs. Data are mean ± standard deviation (n=3).

The damage areas in Figure 6.26 were measured using Image J software. Prior measurement, all C scan images were set at the same scale using “set scale” function. “Polygon selection” was used to draw the damage area and analysed using “measure” functions to calculate the area. Figure 6.25 shows images of the front and back faces of specimens impacted at 5 J. Figure 6.26 shows C scan images of specimens which contain different concentrations of A-GNPs impacted at different energy levels. Both of these Figures support the previous data in explaining the mechanism of failure in composites panel with or without A-GNPs in epoxy/CF system. At the time of impact, the energy is transferred from potential to kinetic and passed to the composite panel when the impactor hits the specimen. In the case of epoxy/CF, the impact energy is concentrated at the contact point between the impactor and specimen, therefore, severe splitting or delamination occurs at the back face of the specimen (Figure 6.25b). Due to this concentration of impact energy at the contact point in epoxy/CF, the C scan image revealed a relatively small damage area (Figure 6.26c). However, the fracture of the internal structure of epoxy/CF is possibly severe, considering the image on the lower surface of specimen as in Figure 6.25b which indicates a relatively greater matrix crack, more delaminated and fibre breakage than multiscale composites. Introduction of A-GNPs to form multiscale
composite was found to increase the total energy absorption relative to conventional composite. Upon load impact, the imparted energy was dissipated radially to the surrounded area, at all angles and more effectively for multiscale composite than in the epoxy/CF system. Less splitting and fibre breakage on the impacted specimen was observed for multiscale composites (Figure 6.25h) compared to conventional composite. However, C scan images revealed a bigger damage area, as an effect of energy dissipation during the impact event.

Table 6.11 and Figure 6.27 summarises the damage area according to the impact energy and type of composite. As explained previously, due to the abrupt rupture during the impact event and inability to dissipate the energy away from the impact point, the epoxy/CF shows a smaller damage area compared to the multiscale composite system. Obvious differences in the damage areas can be seen in Figure 6.27 between the multiscale and conventional composites. In the case of epoxy/CF subjected to 1 J of impact energy, no visible damage area is seen in the C scan image in Figure 6.26a. As mentioned previously, this is due to an insufficient amount of impact energy to cause damage on the structure of the epoxy/CF composites. A damage area is clearly seen on the inclusion of A-GNPs and increases as a function of A-GNPs in the multiscale composites. For example, the damage area of the composites at 1 J of impact energy is ~29.5 mm² for 0 wt. % of A-GNPs, 1447.9 mm² (2 wt. %), 1855.8 mm² (4 wt. %) and 2444.4 mm² (6 wt. %) as shown in Figure 6.26a, d, g and j. Similarly, this behaviour also can be observed for both the 3 J and 5 J of impact energy. This is attributed to the increase in energy dissipation radially to the side area from the impact point during the impact. Higher impact energy also increases the damage area of the impacted specimen, which is a common behaviour due to the higher force imparted to the specimen.

### 6.3.5 Compression after Impact (CAI)

Figure 6.28 shows the load–displacement curves for compression tests for all the composites impacted at different energy levels. The maximum compressive load of multiscale composites is lower relative to the conventional composite. The load–
displacement curves for the multiscale composites show no significant differences despite different $V_f$ and different amounts of A-GNPs. This suggests that the different in $V_f$ does not affect the load–displacement curve in the CAI test. Figure 6.29 is a summary of CAI values for all of the composites. This figure reflects the residual strength of the damaged structure after impact. The effect of A-GNPs addition to the composite can be observed by analysing data according to the impact energy. For example, the non-impacted specimen (0 J) shows that compressive strength decreases with the inclusion of A-GNPs and continues to decrease with increased A-GNPs concentration. This suggests that the strength retention of the multiscale composites is lower compared to the conventional composite.

Figure 6.28: Load–displacement curve for compression test, presented in different scale for all types of composites panel impacted at energy level of (a) 0 J - unimpacted (b) 1 J (c) 3 J and (d) 5 J.
The failure characteristics for conventional composite indicate an abrupt rupture with sudden drop in compressive load upon fracture. In contrast, the failure characteristics of multiscale composites show plastic deformation behaviour (Figure 6.29) suggesting that slippage in microcracks might occur during the compression test. From Figure 6.29, the compressive strength of the non-impacted specimens is reduced significantly from ~462 MPa for the conventional composite (0 wt. % A-GNPs) to the following for the multiscale composites ~202 MPa (2 wt. %), ~121 MPa (4 wt. %) and 107 MPa (6 wt. %).

To the best of our knowledge, characterisation of multiscale composites with the inclusion of nanoparticles has received little attention. Yokozeki et al. [184] reported the effect of CNF on the CAI strength of epoxy/CF composites. By incorporate 5 wt. % of CNF into the composite, no significant effect was observed. They reported the CAI data for epoxy/CF composite as 175 MPa. For system containing 5 wt. % of CNF, the CAI data was 176 MPa.

Table 6.12: Normalised compressive strength respective to \( V_f \) of composite impacted at different energy levels. Data are mean ± standard deviation (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Normalised compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>0 J</td>
<td>462.3 ± 7.6</td>
</tr>
<tr>
<td>1 J</td>
<td>378.4 ± 23.0</td>
</tr>
<tr>
<td>3 J</td>
<td>320.5 ± 14.5</td>
</tr>
<tr>
<td>5 J</td>
<td>132.1 ± 10.9</td>
</tr>
</tbody>
</table>

*Indicates the value is statistically significant which was calculated against the neat resin (0 wt. % A-GNPs). The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132.

The compressive strength data of the composites shows a significant reduction as a function of A-GNPs loadings as shown in Table 6.12 and Figure 6.29. In addition considerable reduction in compressive strength also can be observed as a function of
impact energy. This observation is a common finding in which a specimen impacted at a higher energy level exhibits a greater stress concentration at the damaged zone, resulting in higher local instability during the compression test. Therefore, a lower value of compressive strength is recorded for an impacted sample compared to a non-impacted specimen.

Figure 6.29: Normalised compressive strength with respective $V_f$ impacted at different energy levels for composites containing different amount of GNPs. Data are mean ± standard deviation (n=3).

6.4 Summary

Epoxy/CF composites at different concentrations of A-GNPs were fabricated by VARFI. Three layers of resin film were prepared to consolidate eight layers of CF. It was found that the void content ($V_v$) increased and fibre volume fraction ($V_f$) decreased as a function of A-GNPs content in the fabricated multiscale composites, resulted from the increase in viscosity of the resin-GNP suspensions. Mechanical testing was performed with no significant changes observed in flexural modulus with
the inclusion of A-GNPs in epoxy/CF. ILSS tests showed a 67.3% decrease for the epoxy/CF composite containing 6 wt. % of A-GNPs relative to the conventional epoxy/CF. Mode II 4ENF tests indicated that the stiffness of the multiscale composites increased as a function of A-GNPs content and were greater than that of the conventional. However, mode II fracture toughness ($G_{11C}$) showed a substantial reduction from 1.68 kJ/m$^2$ (epoxy/CF) to 0.25 kJ/m$^2$ (epoxy/CF/A-GNPs 6 wt. %). In impact testing, multiscale composite exhibited higher energy absorption compared to conventional composite but no significant changes can be observed between the multiscale composite at different A-GNPs concentration.

For example, the energy absorbed at 1 J of energy was 32.3% for the conventional composite compared to 63.9% for the multiscale composites containing 2 wt. % of A-GNPs, 84.1% (4 wt. % A-GNPs) and 77.3% (6 wt. % A-GNPs). Similarly, the damage area was 29.5 mm$^2$ for 0 wt. % of A-GNPs, 1447.9 mm$^2$ (2 wt. %), 1855.8 mm$^2$ (4 wt. %) and 2444.4 mm$^2$ (6 wt. %). In CAI testing, the multiscale composites showed inferior properties in compressive strength relative to the conventional composite. For example, 56.3% decrease was observed for a multiscale composite containing 2 wt. % of A-GNPs relative to the conventional composite.
Chapter 7  Conclusions and Future Work

7.1  Conclusions

TGPAP and DGEBF were used in this work to form a miscible epoxy resin blend. The effects of DGEBF content in DGEBF/TGPAP mixture and stoichiometry ratio of amine-epoxy to the glass transition temperature \( (T_g) \) and processing window (PW) of the epoxy blend were studied in this work. Through response surface methodology (RSM) by Design Expert® software, the optimum values for both variables (high \( T_g \), long PW) were determined at 55.56% of DGEBF in the DGEBF/TGPAP blend at a stoichiometric ratio of 0.60. These values give the highest desirability value of 0.520 with \( T_g = 180 \) °C and PW = 136.1 minutes. Verification test for both values were determined at 181.2 ± 0.8 °C for \( T_g \) and ≈140 minutes for PW. Therefore, 55.56% of DGEBF in DGEBF/TGPAP mixture at 0.60 stoichiometry ratio was used for the next stage of work where GNPs was incorporated.

GNPs were modified using a surfactant, Triton X100 and a silane modifier, 3-Aminopropyl triethoxy silane (APTS) to produce treated GNPs (abbreviated as T-GNPs and A-GNPs). TGA for both treated GNPs shows a higher mass loss compared to graphite and unmodified GNPs (U-GNPs) speculated due to earlier decomposition of grafted modifier molecules. Raman spectroscopy revealed the intensity ratio between D to G peak for treated GNPs increased to 0.76 (A-GNPs) and 0.61 (T-GNPs) from 0.28 for U-GNPs which suggest the degree of disorder on GNP’s surface increased with the attachment of modifier molecules. Elemental analysis using XPS indicated that new peak appear at around 100 eV for A-GNPs representing silicon while for T-GNPs, C/O ratio was increased to 26.2 from 11.0 for U-GNPs speculated due to high carbon element in Triton X100 molecules.

Frequency sweep study by rheometer indicated that the suspension started to show frequency independent behaviour at lower frequency with the inclusion of 4 wt. % of GNPs. The rheological percolation threshold was determined and yield 4.1 wt. % for AR-GNPs, 4.2 wt. % (U-GNPs), 5.1 wt. % (A-GNPs) and 5.3 wt. % (T-GNPs).
Characterisation using DMTA indicated that the storage modulus of nanocomposites (NCs) increased relative to neat epoxy except for AR-GNPs at 4 wt. % perhaps due to aggregation. $T_g$ which was determined from the position of tan $\delta$ peak indicate an inferior behaviour of NCs relative to neat epoxy. Flexural strain reduced as a function of GNPs content which suggests the NCs become more brittle relative to neat epoxy but their modulus is improved. At 4 wt. % of GNPs, the flexural modulus of NCs increased by 6.4% for AR-GNPs, 7.4% (U-GNPs), 7.1% (A-GNPs) and 6.1% (T-GNPs) relative to neat epoxy. The value of fracture toughness ($K_{IC}$) increased with GNPs addition. $K_{IC}$ for NCs containing U-GNPs increased from $0.80 \pm 0.04$ MPa.m$^{1/2}$ for neat epoxy to $1.12 \pm 0.01$ MPa.m$^{1/2}$ at 2 wt. % of U-GNPs, $1.24 \pm 0.06$ MPa.m$^{1/2}$ (4 wt. %) and $1.32 \pm 0.01$ MPa.m$^{1/2}$ (6 wt. %). The results also indicated that NCs containing A-GNP gave better mechanical performance compared to U-GNP and T-GNP NCs (eg: higher $T_g$ and $K_{IC}$ value). Therefore, A-GNP was brought forward to fabricate CF multiscale composites.

Vacuum-assisted resin film infusion (VARFI) technique was used to manufacture multiscale composite with three resin films were placed alternately between 2 layers of CF. Acid digestion analysis indicated that the void content and matrix volume fraction ($V_m$) in laminated composites increased as a function of GNP loadings which resulted from the increase in viscosity. The thickness of multiscale composite was also increased for example by 6.0% when manufactured using 2 wt. % of A-GNPs, 15.8% (4 wt. %) and 23.8% (6 wt. %) relative to epoxy/CF composite.

Flexural properties, interlaminar shear strength (ILSS) and interlaminar fracture toughness mode II ($G_{11C}$) for multiscale composite decreased as a function of A-GNPs content which attributed to weak interface bonding between matrices-CF and increase in void formation. For example, $G_{11C}$ of multiscale composite containing 6 wt. % of A-GNPs decrease to 0.13 kJ/m$^2$ from 1.10 kJ/m$^2$ for neat epoxy. The C scan image indicated increase in damage area as a function of A-GNPs content. In addition, the CAI strength of composite panel decreases as a function of GNPs content. The failure characteristic for multiscale composites however indicate plastic deformation behaviour as observed in load-displacement curve.
7.2 Recommendations for Future Work

7.2.1 Epoxy/GNP Nanocomposite Matrices

In previous studies, NC’s containing GNPs with larger flake size were reported to show better mechanical properties than NCs containing smaller size of GNPs flake [123], [133]. This observation is typically associated due to higher aspect ratio for the larger size of GNPs for instance to support the crack deflection and crack bridging more effectively than the smaller size of GNPs [133]. However, the proposed study in this work is to further evaluate the contribution of GNPs to the properties of epoxy/CF composite. Since the gap between individual fibres within the tow is relatively small, it is predicted that the larger flake size of GNPs has greater difficulty to permeate between the gaps of individual fibres. Therefore, the use of smaller flake size of GNPs is recommended to improve the permeability within the tow. This could possibly give better quality of multiscale composite, for example lower void content is expected. Hence, the use of smaller flake size of GNPs for instance 5 μm is recommended and introduced to study the behaviour of nanocomposites matrices for CF multiscale composite.

7.2.2 Epoxy/GNP/CF Multiscale Composites

It is recommended for the characterisation of multiscale composites which consist of epoxy/GNP/CF to be extended for the mode I fracture toughness testing. This is considered important since loading by mode I is a matrix dominated properties testing. A recent work by Moghadam and Taheri [332] indicated that for multiscale composite manufactured by epoxy/E-glass with GNP treated using silane coupling agent (glycidoxypropyl-trimethoxysilane), 35% improvement was observed with respect to neat epoxy.

Hybrid GNPs with another type of nanoparticles was also reported to result in an improvement to the properties of multiscale composites. For example, a recent work by Wang et al. [188] indicated that by combining GNPs with CNTs at ratio 1:1 to
form 1 wt. % hybrid nanoparticles multiscale composite, 33% improvement was recorded in tensile strength. In addition, at the same ratio of GNPs to CNTs, 21% and 23% improvement was observed respectively for flexural strength and flexural modulus. Therefore, if GNPs is to be combined with another type of nanoparticles, possible increase in the properties of fabricated composite could be achieved.

In this work, the multiscale composite was fabricated using vacuum assisted resin film infusion (VARFI) due to the increase in viscosity of suspension especially for the highest loading applied at 6 wt. %. As a result, fibre volume fraction \(V_f\) of composite decrease as a function of GNPs content. The variation in \(V_f\) due to viscosity perhaps could be controlled by preparing the multiscale composite using a prepregs process as shown in Figure 7.1. To maintain the suspension at low viscosity, resin bath could be heated to a required temperature. Dies and flattening pins can also be applied and placed between the resin bath and mandrel in order to control the resin or suspension content in the prepreg CF [14]. At the same time, dies and flattening pins should also to be maintained at the required temperature. Fabricating multiscale composite by this method could possibly give the composite constituent volume fraction at a similar content.

It is also recommended for the techniques that have been used in this work to manufacture the multiscale composite to be combined. In this matter, the vacuum-assisted resin film infusion (VARFI) could be used at the same time with the hot press during composite manufacturing. This could possibly help to achieve a uniform thickness of composite as a function of GNPs.
Furthermore, GNPs is also known as a thermally conductive nanomaterial with thermal conductivity of graphene was reported in the range between ~3080–5150 W m\(^{-1}\) K\(^{-1}\) [65]. The use of GNPs to improve thermal conductivity of polymer has been studied by several groups. For example, a study by Ganguli et al. [84] and Wang et al. [123] indicated that, thermal conductivity of epoxy resin was increased with the inclusion of GNPs. Ganguli et al. [84] reported increase in thermal conductivity from 0.2 W/mK for neat epoxy to 5.8 W/mK for cured epoxy which contains 20 wt. % of GNPs. Wang et al. [123] who studied the effect of GNPs addition to the epoxy resin using ~5 and 1 μm size reported 115% increase in thermal conductivity with the inclusion of 5 wt. % of 5 μm GNPs, relative to neat epoxy. Therefore, the use of GNPs to manufacture multiscale composite could be benefited in their thermal behaviour. Heat generated or concentrated at an area could be dissipated to other area more effectively within the composite panel to enhance their service life.

In addition, a recent work by Prolongo et al. [305] also shows a reduction in water uptake properties of epoxy/GNPs nanocomposites relative to neat epoxy. The increase in hydrophobicity behaviour by the inclusion of GNPs into polymer could be worth for the use of composite panel in an environment with high humidity. Therefore, it is suggested that the incorporation of GNPs to form multiscale composite to consider the study of thermal conductivity and water uptake behaviour.
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Figure A.1: Multiscale composite which contains A-GNPs at (a) 0 wt. % and (b) 6 wt. %.

Figure A.1(b) indicates weaker bonding at matrix-CF interface for multiscale composite with cracking occurring along the interface compared to epoxy/CF composite in Figure A.1(a).
Appendix B

Steps to perform the statistical test (t-test):

\[ t_{calc} = \frac{X_1 - X_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \]

Where \( X_1 \) and \( X_2 \) are the mean values of each sample groups, \( s_1^2 \) and \( s_2^2 \) are sample variances and \( n_1 \) and \( n_2 \) are sample size.

1. Calculate t-value using formula using formula above
2. Set a risk level where in this work, \( p < 0.05 \).
3. Determine degree of freedom, \( df = n_1 + n_2 - 2 \).
4. Compare \( t_{calc} \) and t-value from the standard table of t-distribution (below).
5. If \( t_{calc} > t \)-table, the difference is statistically significant. If \( t_{calc} < t \)-table, the difference is not statistically significant


### t-distribution table

<table>
<thead>
<tr>
<th>df</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.314</td>
<td>2.921</td>
<td>2.353</td>
<td>2.132</td>
<td>2.015</td>
<td>1.943</td>
<td>1.895</td>
<td>1.860</td>
<td>1.833</td>
</tr>
</tbody>
</table>

Table B.1: Statistical t-value for ratio \( I_D/I_G \) for all GNPs by Raman spectroscopy. *Indicates the value is statistically significant which calculated against AR-GNPs at 95% confidence level and degree of freedom (df) of 8 with t-value from standard table is 1.860 (n=5).

<table>
<thead>
<tr>
<th>GNP type</th>
<th>( I_D/I_G )</th>
<th>t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>0.24 ± 0.05</td>
<td>n/a</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>0.38 ± 0.09</td>
<td>0.87</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>*0.76 ± 0.04</td>
<td>18.16*</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>*0.61 ± 0.03</td>
<td>14.19*</td>
</tr>
</tbody>
</table>
Table B.2: Statistical t-value for storage modulus of nanocomposites (NCs) at 100 °C and 250 °C, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/GNPs</th>
<th>Calculated t-value for storage modulus at 100 °C</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
<td>0.68</td>
<td>2.69*</td>
<td>2.82*</td>
<td></td>
</tr>
<tr>
<td>U-GNPs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-GNPs</td>
<td>1.49</td>
<td>1.62</td>
<td>2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-GNPs</td>
<td>2.57*</td>
<td>2.69*</td>
<td>5.73*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Epoxy/GNPs</th>
<th>Calculated t-value for storage modulus at 250 °C</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
<td>0.46</td>
<td></td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>U-GNPs</td>
<td></td>
<td>0.46</td>
<td>6.90*</td>
<td>11.44*</td>
<td></td>
</tr>
<tr>
<td>A-GNPs</td>
<td>3.67*</td>
<td>6.08*</td>
<td>5.26*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-GNPs</td>
<td>0.35</td>
<td>6.90*</td>
<td>4.28*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.3: Statistical t-value for $T_g$, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>Calculated t-value for $T_g$</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
<td>-5.89*</td>
<td>n/a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-GNPs</td>
<td>-20.51*</td>
<td>-30.13*</td>
<td>-34.82*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-GNPs</td>
<td>-12.48*</td>
<td>-29.79*</td>
<td>-55.38*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-GNPs</td>
<td>-8.13*</td>
<td>-17.77*</td>
<td>-21.30*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.4: Statistical t-value for flexural strain, modulus and strength, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/GNPs</th>
<th>Calculated t-value</th>
<th>Flexural Strain at break (%)</th>
<th>Flexural Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>AR-GNPs 4 wt. %</td>
<td>-9.72*</td>
<td>2.74*</td>
<td>-25.82*</td>
<td></td>
</tr>
<tr>
<td>U-GNPs 2 wt. %</td>
<td>-2.26*</td>
<td>2.84*</td>
<td>-4.99*</td>
<td></td>
</tr>
<tr>
<td>U-GNPs 4 wt. %</td>
<td>-22.15*</td>
<td>3.31*</td>
<td>-16.19*</td>
<td></td>
</tr>
<tr>
<td>U-GNPs 6 wt. %</td>
<td>-57.74*</td>
<td>1.62</td>
<td>-78.01*</td>
<td></td>
</tr>
<tr>
<td>A-GNPs 2 wt. %</td>
<td>0</td>
<td>0.53</td>
<td>-10.02*</td>
<td></td>
</tr>
<tr>
<td>A-GNPs 4 wt. %</td>
<td>-2.49*</td>
<td>2.93*</td>
<td>-9.63*</td>
<td></td>
</tr>
<tr>
<td>A-GNPs 6 wt. %</td>
<td>-17.73*</td>
<td>3.64*</td>
<td>-62.44*</td>
<td></td>
</tr>
<tr>
<td>T-GNPs 2 wt. %</td>
<td>-2.40*</td>
<td>2.62*</td>
<td>-4.00*</td>
<td></td>
</tr>
<tr>
<td>T-GNPs 4 wt. %</td>
<td>-4.68*</td>
<td>2.53*</td>
<td>-8.94*</td>
<td></td>
</tr>
<tr>
<td>T-GNPs 6 wt. %</td>
<td>-16.58*</td>
<td>2.60*</td>
<td>-22.75*</td>
<td></td>
</tr>
</tbody>
</table>

Table B.5: Statistical t-value for plain strain fracture toughness, $K_{1C}$ where t-value was calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>Calculated t-value for $K_{1C}$ against neat resin (0 wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>13.40*</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>15.89*</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>14.66*</td>
</tr>
</tbody>
</table>

Table B.6: Statistical t-value for critical strain energy release rate, $G_{1C}$ where t-value was calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Type of epoxy/nanocomposite</th>
<th>Calculated t-value for $G_{1C}$ against neat resin (0 wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>AR-GNPs</td>
<td>n/a</td>
</tr>
<tr>
<td>U-GNPs</td>
<td>9.80*</td>
</tr>
<tr>
<td>A-GNPs</td>
<td>4.62*</td>
</tr>
<tr>
<td>T-GNPs</td>
<td>1.72</td>
</tr>
</tbody>
</table>
Table B.7: Statistical t-value for composite constituent volume % where t-value was calculated against the neat resin (0 wt. %). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 6 is 1.943 (n=4). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Calculated t-value for volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibre ($V_f$)</td>
</tr>
<tr>
<td>0</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>-3.01*</td>
</tr>
<tr>
<td>4</td>
<td>-8.25*</td>
</tr>
<tr>
<td>6</td>
<td>-11.65*</td>
</tr>
</tbody>
</table>

Table B.8: Statistical t-value for thickness of fabricated composite containing different amounts of A-GNPs, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Thickness (mm)</th>
<th>t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>multiscale composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 wt. %</td>
<td>2.98 ± 0.04</td>
<td>n/a</td>
</tr>
<tr>
<td>2 wt. %</td>
<td>3.16 ± 0.04</td>
<td>5.51*</td>
</tr>
<tr>
<td>4 wt. %</td>
<td>3.45 ± 0.02</td>
<td>18.20*</td>
</tr>
<tr>
<td>6 wt. %</td>
<td>3.69 ± 0.02</td>
<td>27.50*</td>
</tr>
</tbody>
</table>

Table B.9: Statistical t-value for normalised flexural strength and modulus containing different amounts of A-GNPs, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Normalised Flexural Strength (MPa)</th>
<th>Normalised Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated t-value</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>n/a</td>
<td>m/a</td>
</tr>
<tr>
<td>2</td>
<td>-15.50*</td>
<td>-2.84*</td>
</tr>
<tr>
<td>4</td>
<td>-14.87*</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>-49.26*</td>
<td>-0.21</td>
</tr>
</tbody>
</table>
Table B.10: Statistical t-value for interlaminar shear strength for composite containing different amounts of A-GNPs, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Interlaminar shear strength (MPa)</th>
<th>Calculated t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.04 ± 1.6</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>51.1 ± 2.8</td>
<td>-20.11*</td>
</tr>
<tr>
<td>4</td>
<td>51.3 ± 1.0</td>
<td>-33.99*</td>
</tr>
<tr>
<td>6</td>
<td>28.8 ± 0.4</td>
<td>-63.26*</td>
</tr>
</tbody>
</table>

Table B.11: Statistical t-value for mode II fracture toughness, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Epoxy/CF/A-GNPs (wt. %)</th>
<th>Mode II fracture toughness (kJ/m²)</th>
<th>Calculated t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.68 ± 0.05</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>0.41 ± 0.10</td>
<td>-12.84*</td>
</tr>
<tr>
<td>4</td>
<td>0.35 ± 0.04</td>
<td>-24.53*</td>
</tr>
<tr>
<td>6</td>
<td>0.25 ± 0.03</td>
<td>-28.99*</td>
</tr>
</tbody>
</table>

Table B.12: Statistical t-value for energy absorbed in impact resistance, calculated against the neat resin (0 wt. % GNPs). *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td></td>
<td>n/a</td>
<td>5.06*</td>
<td>3.77*</td>
<td>8.34*</td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>-0.33</td>
<td>0.44</td>
<td>2.21*</td>
<td></td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>6.22*</td>
<td>3.86*</td>
<td>9.76*</td>
<td></td>
</tr>
</tbody>
</table>
Table B.13: Statistical t-value for incipient force in impact resistance, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the hypothesized mean.

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>n/a</td>
<td>-44.14*</td>
<td>-57.14*</td>
<td>-51.85*</td>
<td></td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>-35.95*</td>
<td>-68.22*</td>
<td>-98.75*</td>
<td></td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>-58.48*</td>
<td>-51.80*</td>
<td>-43.34*</td>
<td></td>
</tr>
</tbody>
</table>

Table B.14: Statistical t-value for maximum contact force, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3). Negative sign implies that the sample mean is less than the value of the hypothesized mean.

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Maximum contact force (N)</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>n/a</td>
<td>-41.87*</td>
<td>-28.84*</td>
<td>-47.84*</td>
<td></td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>-8.31*</td>
<td>-7.94*</td>
<td>-5.23*</td>
<td></td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>-2.34*</td>
<td>-3.81*</td>
<td>-1.35</td>
<td></td>
</tr>
</tbody>
</table>

Table B.15: Statistical t-value for contact time, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>n/a</td>
<td>1.56</td>
<td>6.79*</td>
<td>7.53*</td>
<td></td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>3.55*</td>
<td>71.75*</td>
<td>112.55*</td>
<td></td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>10.47*</td>
<td>41.46*</td>
<td>25.96*</td>
<td></td>
</tr>
</tbody>
</table>

Table B.16: Statistical t-value for maximum deflection, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
<th>0 wt. %</th>
<th>2 wt. %</th>
<th>4 wt. %</th>
<th>6 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>n/a</td>
<td>36.13*</td>
<td>26.56*</td>
<td>7.72*</td>
<td></td>
</tr>
<tr>
<td>3 J</td>
<td></td>
<td>9.18*</td>
<td>45.18*</td>
<td>52.60*</td>
<td></td>
</tr>
<tr>
<td>5 J</td>
<td></td>
<td>6.51*</td>
<td>11.52*</td>
<td>10.56*</td>
<td></td>
</tr>
</tbody>
</table>
Table B.17: Statistical t-value for damage area of composite, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>1 J</td>
<td>n/a</td>
</tr>
<tr>
<td>3 J</td>
<td>258.45*</td>
</tr>
<tr>
<td>5 J</td>
<td>175.73*</td>
</tr>
</tbody>
</table>

Table B.18: Statistical t-value for compressive strength, calculated against the neat resin (0 wt. % GNPs) at respective energy level. *Indicates the value is statistically significant. The t-value obtained from standard table with 95% confidence level and degree of freedom (df) of 4 is 2.132 (n=3).

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Calculated t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>0 J</td>
<td>n/a</td>
</tr>
<tr>
<td>1 J</td>
<td>-19.55*</td>
</tr>
<tr>
<td>3 J</td>
<td>-18.14*</td>
</tr>
<tr>
<td>5 J</td>
<td>-0.36</td>
</tr>
</tbody>
</table>