Development of Hierarchical Composites for Structural Applications

By

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the Diploma of Imperial College

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Declaration

This dissertation is a description of the work carried out by the author in the Department of Aeronautics, Imperial College London between May 2011 and April 2015 under the supervision of Dr Emile Greenhalgh, Prof Milo Shaffer and Prof Alexander Bismarck. Except where acknowledged, the material presented is the original work of the author and no part of it has been submitted for a degree at this or any other university.

Mohd Shukur Zainol Abidin

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Abstract

The incorporation of carbon nanotubes (CNTs) into the matrix of conventional fibre reinforced composites as fillers offers the potential for mechanical, electrical and thermal multifunctional enhancement without disrupting the pristine in-plane properties. In this research, the CNTs were distributed within a thermosetting matrix system via an extrusion method which alleviated the processing difficulties associated with conventional liquid processing methods. Hierarchical composites (HCs) based on carbon fibres and the manufactured CNT-filled matrix were then produced using a wet powder impregnation technique followed by hot melt consolidation.

The use of pure or mixed matrix powder provided either a homogeneous distribution of CNTs or an engineered heterogeneity at the length scale of the powder particle size (at ~11 μm). Mode I fracture toughness and interlaminar shear strength was measured with double cantilever beam (DCB) and short beam shear (SBS) tests respectively. Through-thickness electrical and thermal conductivities were also characterised to ensure the CNTs had imbued multifunctionality to the HCs.

Heterogeneous HCs had significantly improved initiation fracture toughness (36%) in comparison to that of the baseline carbon fibre epoxy composite. The fracture toughness was also 29% higher than that of HC manufactured with homogenously distributed CNTs, at similar nanoreinforcement content. The interlaminar shear strength increased with average CNT loading up to 5 wt%\textsubscript{E}; weight percent to the weight of the epoxy; (1.38 vol%\textsubscript{C}; volume percent to the volume of the hierarchical composite) but was unaffected by the heterogeneity. The mechanisms for these improvements were investigated through extensive fractography. The through-thickness electrical conductivity exhibited a substantial 357% improvement with the inclusion of 10 wt%\textsubscript{E} (2.67 vol%\textsubscript{C}) CNTs. Through-thickness thermal conductivity exhibited 22% improvement regardless of CNTs content. These physical property improvements implied that multifunctionality in mechanical, electrical and thermal characteristics were achieved.
Acknowledgments

In the name of Allah, the beneficent, the merciful.

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Mohd Shukur Zainol Abidin
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller theory</td>
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<tr>
<td>CF</td>
<td>Carbon Fibre</td>
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<tr>
<td>$E^*$</td>
<td>Complex Modulus</td>
</tr>
<tr>
<td>$E'$</td>
<td>Storage Modulus</td>
</tr>
</tbody>
</table>
$E''$ Loss Modulus

$\sigma$ Stress

$\varepsilon \varepsilon$ Strain

$E_B E_f$ Modulus of Elasticity in Flexure

$P$ Load

$K_{22}^c$ Through-thickness Thermal Conductivity

$\delta$ Crack displacement

$B$ Width of Beam

$a$ Crack Length

$T_g$ Glass Transition Temperature

$\mu m$ Micro-meter

$nm$ Nano-meter

$R$ Electrical Resistance

$V_f$ Fibre Volume Fraction

$E$ Normalised Stiffness

$\mu \varepsilon$ Micro-strain

$wt_{-CNT}$ Weight of the CNTs

$wt_{-epoxy}$ Weight of the Epoxy

$wt\%_E$ Weight Percent With Respect to Epoxy Weight

$wt\%_M$ Weight Percent With Respect to Matrix Weight

$vol\%_M$ Volume Percent With Respect to Matrix Volume
\textit{vol\%}_C \quad \textit{Volume Percent With Respect to Hierarchical Composite Volume}
Chapter 1 : Introduction

1.1 Aim of the study

The objective of this study was to produce carbon fibre reinforced polymer composites enhanced with an unprecedented loading of carbon nanotubes (CNTs). The microstructure within this hierarchical composite was engineered to induce improved interlaminar fracture toughness by modulating the fracture mechanisms and hence promoting crack path tortuosity. Furthermore, the inclusion of CNTs was expected to imbue multifunctionality with improved through-thickness electrical and thermal properties over those of the parent composites.

1.2 Introduction

The application of polymer composites as primary structures is hindered by their sensitivity to damage and defects [1]. Whilst polymer composites have excellent in-plane tensile performance, they suffer from relatively poor compression, interlaminar and other matrix dominated properties [2]. Approaches to address these concerns include through-thickness reinforcement and advanced toughening of matrix resins [3], but these are expensive and sensitive to processing conditions which tend to lead to reductions in pristine and fatigue performance [2]. Recently, the inclusion of CNTs into the matrix of fibre reinforced composites to produce hierarchical composites (HCs) has been identified as a promising means of improving damage tolerance without compromising pristine in-plane properties [4].

Ideal CNTs intrinsically possess excellent mechanical properties, with the Young’s modulus of the nanotubes having been measured as 270-950 GPa [5] and experimentally
determined tensile strengths of between 11-63 GPa [5]. They also offer significant electrical and thermal conductivity [6], as well as chemical stability [7]. Hence, they have the potential to improve a range of key characteristics such as lightning strike and solvent resistance [7]. In some cases additional functions such as self-healing [8], self-sensing [9] or energy storage [10] have been demonstrated. In general, CNTs can be introduced in the fibre reinforced composite via two major routes; CNTs grafted/grown onto primary fibre surfaces [11] or dispersion of CNTs within the matrix [12] as shown in Figure 1-1.

Figure 1-1: Schematic diagram of fibre reinforced hierarchical composites [11].

Excellent interlaminar toughness enhancement over the parent material has been reported [11,13] with the CNTs grafted/grown technique although this method presents challenging processing hurdles particularly to avoid parent fibre damage. A variation of this approach includes the transfer of CNT arrays/forests to critical locations in the composite [14,15]. The second technique, dispersing CNTs within the matrix, may be simpler to implement for large scale manufacturing and has been commercialised at low CNT loadings. However the CNT loading is limited by filtration and viscosity issues [11].

In previous nanocomposite (NC) studies, the focus has been on individually dispersed and a homogenised distribution of CNTs within the matrix [12,16,17]; with various functionalization and processing methods having been explored to achieve a uniform CNT
distribution. Toughening mechanisms such as crack deflection [18], crack pinning [18], CNT pull-out [19], matrix deformation [18], void nucleation [20], crack bridging [21], and CNT fracture [22] have been proposed to explain the observed improvements in fracture toughness of these nanocomposites. However, all these mechanisms require some degree of interaction between the crack front and the nanofillers. When the NCs are used as a matrix in HCs, the fracture toughness improvement does not fully translate to toughness improvement in HCs [11] except at very low CNTs loadings (<0.5wt%) [23].

Kim and Mai have presented an extensive review on methodologies to achieve the fracture toughness enhancement within a fibre reinforced composite [24]. One methodology, intermittent of weak and strong interfacial bonding between the matrix and the fibre, has been scarcely explored in comparison to other methods such as rubber toughening and thermoplastic modification in the matrix [25]. Nonetheless, Atkins [26] showed that improved fracture toughness within a composite could be achieved by modulating the bonding strength of the fibre/matrix interphase. An engineered fracture promoting layer within a composite panel has been shown to promote multiple crack deflection mechanisms thus increasing energy absorption from impact damage [27]. Mai [28] demonstrated that a controlled fibre/matrix bonding is a viable route to improve toughness without significant loss to pristine intralaminar mechanical properties. These studies show that engineered weakened topography could improve the overall toughness of the composite instead of homogeneous toughening by modulating the crack propagation path. Indeed such hierarchical morphology has been observed in natural materials [29] such as bones, abalone shell and crab exoskeletons, but generating this methodology using CNTs has yet to be unexplored.

The hypothesis which underpins the present study proposes that with HCs containing high CNTs loadings, the crack propagation within the matrix is hindered by the tough modified matrix, and thus the crack path is deflected into the fibre/matrix interface region which is devoid of CNTs. To achieve the full potential toughening mechanisms of incorporating CNTs into the matrix, the crack path must be driven to propagate within the modified matrix. This study uniquely explores the fracture mechanisms and mechanical properties of a carbon fibre HCs modified with CNTs where controlled crack propagation was promoted through engineering heterogeneity within the matrix. To introduce (regions with) high loading of CNTs into the fibre tows, a novel nanocomposite powder impregnation route was used to avoid the problems associated with high viscosity and self-filtration of CNTs. Mixing
powders of different compositions modulates the matrix microstructure on the length scale of the powder particles (and parent fibres).

1.3 Research objectives
The specific research objectives during the course of the study were as follows;

   a) Optimising the production process of HCs with CNT weight fractions of the matrix between 0 wt\%$_E$ and 25.0 wt\%$_E$ via a powder impregnation route.
   b) Production of HCs with a tailored and optimised microstructure.
   c) Mechanical property characterisation of the HCs which included Mode I fracture toughness, interlaminar shear strength and flexural properties.
   d) Characterising the fracture surface morphologies of the HCs via scanning electron microscopy (SEM) and optical microscopy.
   e) Characterising the imbued multifunctionality of the HCs via through-thickness electrical and thermal properties.

1.4 Structure of the thesis
This thesis is divided into eight chapters. This chapter briefly gives the problem statement and motivation for the study. Chapter 2 reviews the relevant background literature encompassing the previous work with similar materials and their findings. The chapter captures the common trends presented in the literature and the proposed enhancement mechanisms. Chapter 3 draws together the literature findings and presents the resulting research plan. Chapter 4 presents the experimental section which includes the materials used, the NC production method and the optimisation of the HC production method. Chapter 5 explains the characterisation methods used to evaluate the physical and mechanical properties of the HCs. Chapter 6 presents the experimental results and findings before evaluation and interpretation of the results as detailed in Chapter 7. Chapter 8 concludes the findings of the research and proposed future work.

1.5 List of publications and conferences

1.5.1 Publications


1.5.2 Conferences

M. Shukur Zainol Abidin, Tomi M. Herceg, Emile S. Greenhalgh, Milo S.P. Shaffer, and Alexander Bismarck, *Development of hierarchical composites with extremely high CNTs content via wet powder impregnation route*. 6th International Conference on Carbon NanoParticle Based Composites 2013, Sept 22-25, Dresden, Germany.

Chapter 2 : Literature Review

This chapter presents the state of the art of CNT enhanced fibre reinforced composites. The improved mechanical, electrical and thermal properties in comparison to those of the parent composites after the inclusion of CNTs have sparked considerable research interest over the past decade. The challenges regarding the CNT reinforced hierarchical composites (HCs) processing methodologies are explored and their reported property enhancements were analysed in this Chapter. Furthermore, the mechanisms which had contributed to these enhanced properties were critically reviewed in this Chapter.

2.1 Composite materials

Some of the major drawbacks in employing carbon fibre reinforced polymer (CFRP) composites for structural applications have been their relatively poor compression performance and interlaminar toughness. These mechanical properties are dominated by the matrix and the interphase properties which are often orders of magnitude inferior to the fibre dominated properties, hence making CFRP composites susceptible to premature and unexpected failures when loaded under compression or subjected to delamination damage [1]. Employing composite materials in critical load bearing structures therefore needs to be supported by extensive verification and testing [3].

Significant studies have been conducted to improve the damage tolerance of the composite materials for structural applications. Through-thickness reinforcements such as laminate stitching, tufting and z-pinning [30,31] have been extensively studied [32] and demonstrated to significantly improve fracture toughness, impact resistance, damage
tolerance and stiffener pull-off strength [3,33]. However, these through-thickness reinforcements often damage the primary fibre reinforcements thus lowering the pristine in-plane properties of the composites.

Another method to improve the damage tolerance is by toughening the matrix constituent. This route can be achieved by doping the matrix with thermoplastic or elastomer particles [3]. The modified matrix would then potentially possess a higher fracture energy absorption capacity by failing via favourable plastic deformations [3]. However the in-plane properties of the toughened composites are often compromised. An alternative modification to this toughening method is by doping the composites with nanofillers such as nanoclays, nanofibres and CNTs, which possesses enormous strength and stiffness [34]. This technique has been shown to improve the damage tolerance without losses in pristine in-plane properties and will be discussed further in this review.

2.2 Carbon nanotubes, (CNTs)

Since the work and reported properties of CNTs observed by Iijima [35], many studies have investigated the physical, electrical and mechanical properties of this new form of carbon [16,36]. As with all nanostructured materials, the properties of nanostructured composites are highly structure/size dependent [12]. Single-walled carbon nanotubes (SWCNTs) are fullerene based structures which can be considered as a cylinder of carbon graphite (at 1 nanometre diameter), while multi-walled carbon nanotubes (MWCNTs) are similar to SWCNTs but with many layers to the cylindrical structure (5 – 50 nanometre in diameter) [37] (Figure 2-1).

There are several methods to synthesize CNTs. Iijima utilised arc-vaporization to produce the first images of multiwalled CNTs [35]. A similar method is by laser evaporation [38] which is capable of producing single walled CNTs. However both these methods require a huge amount of energy with a low product yield. Therefore the third method, catalytic chemical vapour deposition (CVD), is a much preferred method for industrial scale CNT production [39].
Figure 2-1: Different types of carbon nanotubes, a) schematic view of single walled carbon nanotubes (SWCNT), b) images of a multiwalled carbon nanotube (MWCNT) cap (5 nm scale bar) [40].

CNTs are amongst the stiffest and strongest materials ever made, with a Young’s modulus, in theory, reaching up to 1000-1200 GPa [41,42] and experimental tensile strengths of between 11-63 GPa [39,43,44]. Although the experimental values reported vary significantly, it has been the consensus that CNTs possesses much higher mechanical properties than most metals [41,44]. Furthermore CNTs also possess attractive electrical properties which have been shown to be metallic or semiconducting depending on their structure and diameter [45]. Additionally the CNTs have also been experimentally shown to posses very high thermal conductivities [6,46-48].

2.3 Hierarchical composites (HCs)

The matrix dominated properties in conventional fibre reinforced composites could potentially benefit from the inclusion of CNTs which possess impressive mechanical properties. Such multi-level reinforcements; known as multi-scale, hybrid or hierarchical composites; can be observed to occur in nature such as nacre and Euplectella [49]. These hierarchical biological composites possesses high mechanical performance despite having been formed from fairly weak constituents [50].

2.3.1 Processing methods for HCs

The combination of nanoparticles and conventional polymer composites to produce HCs can be manufactured via three different routes [11,13,51-53]:

28
i) Growing or grafting the nanoparticles onto the primary fibre constituent [14,54-81].

ii) Dispersion of the nanoparticles into the bulk matrix [23,40,46,82-100].

iii) Selective reinforcement on the prepreg interlaminar surfaces [37,101-111].

For this particular study, the focus was on the dispersion of the CNTs into the matrix (method ii). Nonetheless, extensive research has been reported and is still on-going with innovative modifications in all three routes such as chemical modification of the CNTs, surface treatment of the fibre, chemical modification of the matrix and physical optimisation of processing procedures.

Nanocomposites (NCs) are produced after the CNTs have been dispersed into the matrix. A critical issue of the NCs is ensuring a uniform dispersion of the nanoparticles within the matrix and the resulting composites [12]. CNTs tend to form agglomerates because of the van der Waals interaction between the particles and their high surface energy. Methods such as separation in solvents followed by an ultrasonic agitation have yielded good dispersion results [11,12]. However, excessive external work can damage the surfaces of the CNTs resulting in poor mechanical performance. Thostenson et al [12] also recognised the problem of aligning the CNTs in the matrix as the CNTs are very small in diameter but very large in aspect ratio [112].

NCs can be prepared by several production methods. The simplest method would be by mixing the nanotubes in polymer solution and then removing the solvents [39]. Further modification can be done by acid treatment [113], functionalisation of CNTs [114,115] and addition of surfactant to the CNT – polymer solution [116]. A problem with this method is the CNTs tend to agglomerate during processing and therefore prevent good dispersion in the matrix [39]. Furthermore the content of CNTs that can be dispersed in the solvent is limited to avoid the agglomeration. Direct mixing (using mechanical, shear or ultrasonic techniques) is also commonly used to add CNTs into low-viscosity thermosetting resins [11]. Variations of this technique involve using three roll milling [117,118]. However the maximum CNT content are still limited as the CNT inclusions severely increase the processing temperature and viscosity of the NCs [39]. A novel method has been under investigation in which solid thermosetting epoxy/CNT mixture were treated as a highly viscous material and processed via high shear melt mixing route [4]. This method has the possibility of processing high contents of CNTs (up to 25.0 wt%) with a good dispersion.
Once the dispersion of CNTs in the matrix is achieved, the resulting modified matrix was combined with the primary reinforcement constituents. Conventional resin transfer moulding (RTM) [83,85,119,120] and vacuum assisted resin transfer moulding (VARTM) [40,46,86,88,89,93,99,121-123] have been used to infiltrate fibres with the liquid modified resins. However the maximum content of CNTs that can be included into the matrix using liquid modified resins is limited due to the fact that CNTs dramatically increases the viscosity of the resulting matrix [11,120,124] hence most reported work was with less than 2 wt% loading fraction [11]. Another method of producing HCs is by using a filament winding technique to impregnate the fibre with the resin [23,84,125] which is adopted for this present study.

2.3.2 Mechanical properties of HCs

Most of the reported work have shown that the fibre dominated properties such as tensile and flexure properties remain relatively unaffected. The primary interest of the HCs were on the matrix dominated properties such as off-axis tensile, in-plane compression, shear, and interlaminar fracture toughness. The expected improvements provided in compressive and interlaminar toughness after incorporation of the nanofillers in the matrix is demonstrated by Figure 2-2 [126].

![Figure 2-2: Schematic of mechanical property improvement of CFRPs by incorporation of the nanofillers [126].](image)

**Interlaminar shear properties**

Interlaminar shear strength (ILSS) is one property which had demonstrated significant improvements after the inclusion of the nanoparticles within the composite [11,13]. ILSS is a
mechanical property which is often governed by the fibre/matrix interphase performance [1]. Consequently, any improvements in the fibre/matrix interphase would lead to an increase in ILSS. Generally, significant improvements were reported even with the inclusion of a small weight percentage of nanoparticles. However some of the reported work does not include the weight fraction of the nanoparticles [68-72], therefore the direct link between nanofiller content and property improvement cannot be deduced. The reported improvement in the interlaminar shear strength of the HCs is listed in Table 2-1. Short beam shear (SBS) [127] test is the most common test method in which the interlaminar shear is generated indirectly via bending and is often quoted as the ILSS of the composite. Furthermore this test only requires small test pieces compared to other methods with the additional benefit of the test method being fairly simple.

A strengthened interface between the fibres and the nanofillers was proposed as a possible enhancement mechanism contributing to the increased strength [120]. The direct increase of strength and stiffness of the matrix by inclusion of the CNTs had increased the efficiency of stress transfer and reduced the modulus mismatch between the matrix and the fibre. However the interlaminar adhesion properties must be treated with caution as most of the reported results were based on low loadings of nanofillers. With high nanofillers content, agglomeration of the fillers could prevent good adhesion thus reversing the trend in mechanical properties.

To date, very few studies have been conducted on measuring the in-plane shear modulus of the HCs. Upon achieving good dispersion and adhesion with the inclusion of CNTs to the composites, improved shear stiffness property of the HCs would be expected. Qi et al. [79] showed that a 30% increase in shear modulus was achieved with grafted CNTs onto woven glass fibre composite which was attributed to efficient stress transfer within the HCs. However, Godara et al [23] reported an almost 15% reduction of shear modulus in the composites after inclusion of CNTs which was attributed to the probable presence of CNTs agglomerates in the samples.
Table 2-1: The ILSS improvement exhibited by the HCs.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fibre</th>
<th>Nano-filler type</th>
<th>Maximum nano-filler content</th>
<th>Maximum strength improvement over parent</th>
<th>Test method</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>GF</td>
<td>DWCNT</td>
<td>0.1 wt% 0.30 wt%</td>
<td>15.7% 19.8%</td>
<td>SBS</td>
<td>[120]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>GF</td>
<td>DWCNT</td>
<td>0.3 wt%</td>
<td>16%</td>
<td>SBS</td>
<td>[85]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>GF</td>
<td>MWCNT</td>
<td>1 wt%</td>
<td>7.9%</td>
<td>SBS</td>
<td>[86]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>MWCNT</td>
<td>0.5 wt% 1 wt%</td>
<td>3.2% 18.2%</td>
<td>SBS</td>
<td>[40]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>nanofibres</td>
<td>0.1 wt% 1 wt%</td>
<td>23% 8%</td>
<td>SBS</td>
<td>[87]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Carbon fibres</td>
<td>MWCNT</td>
<td>1 wt% 5 wt%</td>
<td>31.2% 45.6</td>
<td>Lap shear</td>
<td>[37]</td>
</tr>
<tr>
<td>Vinyl ester</td>
<td>Woven GF</td>
<td>SWCNT</td>
<td>0.1 wt% 0.2 wt%</td>
<td>18.5% 45%</td>
<td>SBS</td>
<td>[92]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>MWCNT</td>
<td>0.25 wt%</td>
<td>27%</td>
<td>SBS</td>
<td>[65]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven alumina</td>
<td>Grown CNTs</td>
<td>Up to 2.5 wt%</td>
<td>69%</td>
<td>SBS</td>
<td>[66]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>Silica</td>
<td>10 wt% 20 wt%</td>
<td>-3.1% -12.2%</td>
<td>SBS</td>
<td>[96]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>Fabric MWCNT</td>
<td>3 vol%</td>
<td>117%</td>
<td>SBS</td>
<td>[77]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>MWCNT</td>
<td>1 wt%</td>
<td>16%</td>
<td>±45° Tensile</td>
<td>[128]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>MWCNT</td>
<td>14.2 vol%</td>
<td>80%</td>
<td>±45° Tensile</td>
<td>[79]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>MWCNT</td>
<td>10.1 vol%</td>
<td>70%</td>
<td>±45° Tensile</td>
<td>[129]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>CNT–Al₂O₃ hybrids</td>
<td>-</td>
<td>11%</td>
<td>SBS</td>
<td>[130]</td>
</tr>
</tbody>
</table>

*Flexural properties*

The reported flexural property of the HCs is listed in Table 2-2. Fibre dominated properties such as the flexural stiffness were not expected to be greatly influenced by the CNT inclusions [83,93,122,123]. Furthermore, modification on the fibre surface via grafting or CNT growth could damage the pristine fibre resulting to inferior composite compare to the parent composite [63]. Composite under flexural load could exhibit three types of failure modes; tensile fibre failure, compression failure or mid-plane delamination. Compressive failure and mid-plane delamination are matrix dominated properties hence the inclusion of
CNTs is expected to improve the flexural strength if such a failure mode were observed in the HCs [56].

However the improvement is subject to whether a homogeneous CNTs dispersion in the HC was achieved [83,84]. Entanglements of CNTs could create agglomerates acting as flaws which would be detrimental to the flexural strength [83]. The flexural property improvements over the parent composites are attributed to the matrix toughening, CNT bridging [56,122], and mechanical interlocking [63].

In general, the improvements in flexural modulus and strength for uni-directional (UD) systems were not significant, but improvements in flexural properties were more significant in woven fibre systems which often had intrinsically lower flexural properties in comparison to that of the UD system. The result also showed that the surface grown CNTs method had provided the highest flexural improvements whilst the CNTs dispersion in the matrix method offered only slight improvements.

Table 2-2: The flexural properties of HCs.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fibre</th>
<th>Nano-filler type</th>
<th>Maximum nano-filler content</th>
<th>Maximum stiffness improvement</th>
<th>Maximum strength improvement</th>
<th>Test method</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>CSCNT</td>
<td>5 wt% 10 wt%</td>
<td>6.3% 4.0%</td>
<td>13.9% 18.3%</td>
<td>3 pt. bending</td>
<td>[83]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>Forest grown CNT</td>
<td>2 wt%</td>
<td>5.2%</td>
<td>140%</td>
<td>3 pt. bending</td>
<td>[56]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>MWCNT</td>
<td>2 wt%</td>
<td>2%</td>
<td>22.3%</td>
<td>3 pt. bending</td>
<td>[93,123]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>MWCNT</td>
<td>0.3 wt%</td>
<td>4.9%</td>
<td>3.0%</td>
<td>3 pt. bending</td>
<td>[122]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>CSCNT</td>
<td>5 wt% 10 wt%</td>
<td>4.0% 5.3%</td>
<td>4.2% 1.5%</td>
<td>3 pt. bending</td>
<td>[84]</td>
</tr>
<tr>
<td>Phenolic</td>
<td>UD CF</td>
<td>Grown CNT</td>
<td>9.1 wt% 8.3 wt% 18.42 wt%</td>
<td>28% 54% 46%</td>
<td>20% 75% 66%</td>
<td>3 pt. bending</td>
<td>[63]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven GF</td>
<td>CNT–Al₂O₃ hybrids</td>
<td>-</td>
<td>19%</td>
<td>12%</td>
<td>3 pt. bending</td>
<td>[130]</td>
</tr>
</tbody>
</table>
**Delamination fracture toughness**

Another important mechanical property that has shown significant improvements with CNTs inclusion was the delamination resistance and the crack tip arrest [131]. The toughening mechanisms observed in the nanocomposite fractures (as identified in Figure 2-3) [12,132] also manifest themselves in HCs. The reported enhancements in the fracture toughness of the HCs is listed in Table 2-3.

![Fiber Fracture](image)

![Fiber Pullout](image)

![Debonding / Crack Bridging](image)

![Matrix Cracking](image)

Figure 2-3: Key mechanisms of energy dissipation have been identified in the fracture of short as well as continuous fibre-reinforced composites [12].

The HCs manufactured via the CNT growth/grafted methods exhibit significant improvement in fracture toughness (54-358%) whilst the HCs manufactured with nanoparticles dispersed within the matrix have shown only modest results (0-100%). However the fracture toughness improvements in the HCs using the modified interlaminar regions methods must be treated with caution as it was plausible that the modification had increased the resin rich interply thickness, and consequently yielded an increase in the fracture toughness [11,129,133].
Table 2-3: Fracture toughness improvements of HCs over the parent composite.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fibre</th>
<th>Nano filler type</th>
<th>Maximum nano-filler content</th>
<th>Maximum fracture toughness improvement</th>
<th>Test method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>Grown CNT</td>
<td>-</td>
<td>150% 300%</td>
<td>DCB ENF</td>
<td>[102]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>DWCNT MWCNT</td>
<td>0.5 wt%</td>
<td>55% 83%</td>
<td>DCB</td>
<td>[23]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>Grown CNT</td>
<td>-</td>
<td>358% 54%</td>
<td>DCB ENF</td>
<td>[56]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>MWCNT</td>
<td>0.1 wt% 0.3 wt% 0.5 wt% 1 wt%</td>
<td>4% 13% 9% 5%</td>
<td>DCB</td>
<td>[134]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>Grown CNT</td>
<td>-</td>
<td>55%</td>
<td>DCB</td>
<td>[64]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>GF</td>
<td>DWCNT</td>
<td>0.30 wt%</td>
<td>No improvement</td>
<td>DCB/ENF</td>
<td>[85]</td>
</tr>
<tr>
<td>Polyester</td>
<td>GF</td>
<td>CNF</td>
<td>1 wt%</td>
<td>100%</td>
<td>DCB</td>
<td>[135]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>CSCNT</td>
<td>5 wt%</td>
<td>98% 30%</td>
<td>DCB ENF</td>
<td>[84]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>MWCNT</td>
<td>1 wt%</td>
<td>60% 75%</td>
<td>DCB ENF</td>
<td>[89]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>SWCNT</td>
<td>0.1 wt%</td>
<td>13% 28%</td>
<td>DCB ENF</td>
<td>[109]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>MWCNT</td>
<td>-</td>
<td>26% 38%</td>
<td>DCB ENF</td>
<td>[110]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>MWCNT</td>
<td>10.1 vol%</td>
<td>~80%</td>
<td>DCB</td>
<td>[129]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Alumina Fabric</td>
<td>Grown CNT</td>
<td>-</td>
<td>~100%</td>
<td>DCB</td>
<td>[80]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Woven CF</td>
<td>Grown CNT</td>
<td>-</td>
<td>~67% ~60%</td>
<td>DCB ENF</td>
<td>[136]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF</td>
<td>MWCNT</td>
<td>0.3 wt%</td>
<td>143% 127%</td>
<td>DCB ENF</td>
<td>[137]</td>
</tr>
</tbody>
</table>

Several further fracture mechanisms have been proposed to explain the increase in the fracture toughness for HCs. Sadeghian et al [88] and Karapappas et al [89] suggested the improvements were due to rougher fracture surfaces which implies more energy had been required to propagate the crack tip. The CNTs network structures in the HCs were thought to have led to better stress transfer between the matrix and the fibres were also attributed to the improvement in the fracture toughness [138,139]. Furthermore crack bridging by the CNTs could blunt the crack tip during propagation [111]. Interestingly, the inclusion of CNTs can
be used to steer the crack path by adjusting the microfibre orientation creating a tortuous path [80]. However the interactions between the fracture mechanisms are still ambiguous as to whether they were co-existing or competing within a particular fractured sample. Often the increase in the fracture toughness by the inclusion of CNTs would also translate to higher impact performance [100,140].

*Enhancing fracture toughness of composites*

Enhancing the fracture toughness of conventional fibre reinforced polymer composite is still an active research area. Kim and Mai [24] have published an extensive review regarding the methodologies explored to improve the fracture toughness of polymer reinforced composites. One of the methodologies, intrinsically toughening the matrix with inclusion of thermoplastics or rubber modified thermosets, have already been commercialised such as HexPly® 8552 [141], HexPly® M21 [142] and HexPly® M91 [143]. The modified matrix would promote plastic yielding at the crack tip which would then absorb and arrest the crack propagation [25] as illustrated by Figure 2-4. Some of the mechanisms such as crack deflection and crack pinning had also manifested in CNTs reinforced composites as discussed previously [12]. However toughening the matrix with thermoplastic or rubber particles often compromises the pristine in-plane mechanical and fatigue properties [3].
Figure 2-4: Crack toughening mechanisms in rubber-filled modified polymers: (1) shear band formation near rubber particles; (2) fracture of rubber particles after cavitation; (3) stretching, (4) debonding and (5) tearing of rubber particles; (6) transparticle fracture; (7) debonding of hard particles; (8) crack deflection by hard particles; (9) voided/cavitated rubber particles; (10) crazing; (11) plastic zone at craze tip; (12) diffuse shear yielding; (13) shear band/craze interaction [25].

Toughness improvement via heterogeneity

Another interesting methodology to enhance the global fracture toughness was by generating intermittent regions of weak and strong interfacial bonding between the matrix and the fibres [26], demonstrating an impressive 400% fracture toughness improvement compared to that of unmodified composites. In this approach, interfacial debonding occurs at the weak fibre/matrix interphase and crack blunting as proposed by Cook-Gordon mechanism [144], would take place improving the overall toughness, as illustrated by Figure 2-5.
This intermittent bonding concept was shown to improve the translaminar (105-300%) [27,145,146] and interlaminar (38-180%) [147-150] fracture toughness which suggest that "imperfection" in the composite can be beneficial if correctly engineered. The tortuosity of the crack tip can also be generated by modulating the length and orientation of grafted CNTs onto the fibres [80]. The major characteristics of this intermittent bonding methodology is that the exhibited fracture toughness improvements were attributed to the increased tortuosity and greater interaction of the crack tip with the matrix, fibre and fibre/matrix interphase. Furthermore, this methodology also shows that pursuing perfection in the processing might not be necessary and not cost effective.

Such hierarchical morphologies were often exhibited by nature such as bones, abalone shell and crab exoskeleton [29]. Indeed, homogenous and perfectly arranged structures rarely exist in nature. For example, the microstructure of abalone shells (Figure 2-6) consists of layers of aragonite tiles and further reinforced by nanostructured organic materials between the layers [151]. Mimicking the structures optimised by nature over significant evolutionary time might be beneficial in harnessing untapped potential of the material [50].
However the critical intermittent length required for an optimised hierarchical system is unclear. A key aspect of this critical length is generating sufficient bonding region between the matrix and fibre ensuring adequate stress transfer between the constituents is obtained [26]. Furthermore, the process zone within the material is expected to dictate the stress state at the crack tip [152]. A simple model to estimate the size of the process zone for a brittle material is suggested by Irwin’s modifications [153] (Equation 2-1):

\[
 r_y = \frac{1}{2\pi} \left( \frac{K}{\sigma_{ys}} \right)^2
\]

Equation 2-1

where \( r_y \) is the radius of the process zone, \( K \) is the fracture toughness of the material and \( \sigma_{ys} \) is the yield tensile strength (Figure 2-7).
Figure 2-7: Schematic of the process zone at the crack tip [154].

2.3.3 Physical properties

The incorporation of CNTs have been expected to imbue multifunctionality into the parent composite. Indeed the physical properties such as through-thickness electrical and thermal conductivity are active research areas [11, 52]. However, most of the reported studies have investigated non-conducting fibres such as glass in addition to the non-conducting polymer matrix and hence substantial improvements over the base composite were reported. Nonetheless the conducting mechanisms observed should remain applicable even with conducting fibres such as carbon is employed.

*Through-thickness electrical conductivity*

The in-plane electrical conductivity of conventional carbon fibre reinforced polymer composites are generally high due to the high conductivity of carbon fibres. However the through-thickness electrical conductivity are orders of magnitude lower in comparison to the conductivity in the fibre direction [65]. Improvements in the through-thickness electrical conductivity can be achieved by either modifying the conductivity of the matrix or bridging the fibres by growing/grafting conductive particles on their surfaces [11, 52]. CNTs are
excellent doping material for improving the through-thickness electrical conductivity for both methods (Table 2-4).

Table 2-4: The through-electrical conductivity improvements in the HCs.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fibre</th>
<th>Nano filler type</th>
<th>Through-thickness electrical conductivity improvements</th>
<th>CNTs content</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>CF Fabric</td>
<td>SWCNT</td>
<td>200%</td>
<td>0.25 wt%</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWCNT</td>
<td>~30%</td>
<td>0.25 wt%</td>
<td></td>
</tr>
<tr>
<td>Epoxy</td>
<td>GF Fabric</td>
<td>MWCNT</td>
<td>500%</td>
<td>5 wt%</td>
<td>[79]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>GF</td>
<td>MWCNT</td>
<td>1000%</td>
<td>-</td>
<td>[155]</td>
</tr>
<tr>
<td>Epoxy</td>
<td>CF Fabric</td>
<td>Grown CNT</td>
<td>510%</td>
<td>-</td>
<td>[156]</td>
</tr>
</tbody>
</table>

Comprehensive reviews on the electrical conductivity and percolation threshold within the nanocomposite were reported by Spitalsky *et al* [157] and Bauhofer and Kovacs [158] respectively. The through-thickness electrical conductivity improvement is often attributed to the percolating network generated by the CNTs [65] in the HCs. This percolating network creates conductive paths for the electron transfer [156] thus completing the electrical circuit. The percolating network only requires a small quantity of CNTs to significantly improve the through-thickness electrical conductivity [79]. Since the polymers are often regarded as electrical insulators, the incorporation of conductive particles such as CNTs should always be expected to significantly improve the electrical property regardless of processing method.

**Through-thickness thermal conductivity**

The thermal response from the incorporation of CNTs in the HCs is a much less studied area compared than the mechanical and electrical properties. Nonetheless the inclusion of CNTs into nanocomposite [159] was shown to induce connective thermal network [160] akin to that of the electrical percolating network. Consequently, this network should increase the through-thickness thermal conductivity of the HCs.

Translating the thermal improvements observed in nanocomposites to hierarchical composites would require a more complex analysis as the primary fibre constituents would
affect the thermal response of the composite. Similarly to the electrical conductivity, non-conducting fibres would be preferred to conductive fibres so that improvements from the inclusion of CNTs could be isolated [52]. The coefficient of thermal expansion (CTE) was significantly reduced [161] with the addition CNTs in the matrix which could indicate a reduced thermal mismatched between the primary fibres and the matrix.

2.4 Summary and outlook

Significant progress had been made in the study of hierarchical composites which had demonstrated significant enhancement in the mechanical, electrical and thermal properties. Often the reported improvements were exhibited with the inclusion of a relatively small quantity of CNTs. However, the properties of HCs with extremely high CNT loading (>20 wt%) remained inconclusive.

An approach to this methodology is to promote preferential mechanisms and tailor the morphology to achieve the desired performance. Such methodology could offer the opportunity to increase the potential from nanoparticle inclusion in the system. By placing the mechanisms as the target; the CNTs content, distribution, alignment, dispersion and processing can be engineered to achieve desirable properties.
Chapter 3 : Research Plan

This Chapter draws together the findings from the literature review as described in Chapter 2 and formulates the research plan for this study. The following Section indicates the background of the research and the content of the research plan. Furthermore, the reasoning of the selected property and manufacturing method as optimised in Chapter 4 are detailed.

3.1 Background

This study was envisaged as a continuation from the previous research grant for work conducted by Herceg et al. which was funded via Materials and Structures Technology (MaST) programme under the governance of Defence Science and Technology Laboratory (DSTL), UK [4]. A key objective of the programme was to explore the effects of ultra-high carbon nanotubes loadings up to 25.0 wt%\(_E\). This study [4] had developed key nanocomposite (NC) processing methodology and co-developed the hierarchical processing method used in this present study. The progress unique to the present study is detailed in Section 3.3 and Section 3.4.

3.2 State of the art of HC processing

Conventional processing methods such as resin transfer moulding have been extensively utilised in the studies reported in Section 2.3.1 yielding HCs with good dispersion and exhibiting significant mechanical and physical property improvements over their respective parent composites. However, the loadings of CNTs that could be processed via this production method remained low (<1 wt%) as the inclusion of CNTs severely increase the viscosity of the resin.
Therefore the inclusion of much higher CNT loading would require a different approach. Recently wet powder impregnation was shown to be capable of processing every matrix type provided that the matrix can be powderised [162]. In fact, this wet impregnation route was explored in the prior study by Herceg [4] and further optimised in Chapter 4 in this study. Furthermore, this study also explores a scalable processing method aimed at producing ultra-high CNTs loading up to the processing limit of the equipment, which was predicted to be at 25 wt%\(\text{E}\). A low CNTs content at 2.5 wt%\(\text{E}\) was also manufactured as a comparison to the available literature. Additionally, a series of CNTs loading at 5.0 and 10.0 wt%\(\text{E}\) were also manufactured to generate a spectrum of the CNTs reinforcement behaviour in response to the CNTs content. Therefore, to achieve these objectives, the following research plan was devised:

a) Optimisation of nanocomposites production (Section 4.2.1).
b) Production of HCs via wet impregnation (Section 4.2.2).

### 3.3 Property improvements from the inclusion of CNTs

Significant mechanical and electrical property improvements were observed in the HCs via the inclusions of CNTs. These improvements however were most prevalent in matrix dominated properties such as interlaminar shear strength and fracture toughness as reported in Section 2.3.2. Fibre dominated properties were not expected to be greatly influenced by the inclusion of CNTs unless the processing methods had damaged the primary fibres. In this study, the fracture toughness is the most desirable property improvement. The concept of improving the properties of a cheap matrix to achieve high performance is intriguing.

Herceg [4] noted that a fully homogeneous distribution of CNTs in the HCs was not obtained and the processing method employed has given rise to microstructures which were influenced by the particle size. The CNTs were contained within these microstructures and this study had pursued one of his recommendations which was reducing the particle size of the powder by utilising a jet milling process.

To determine the effects of CNTs inclusion on the mechanical and physical properties of the HCs, the following research plan was devised:

a) Physical characterisation of the HCs (Section 5.1)
b) Mechanical characterisation of the HCs (Section 5.2)
c) Fractography via scanning electron microscopy, SEM (Section 5.3)
3.4 Inducing heterogeneity within the HCs

From previous study [4], the results had suggested that the fracture toughness might have been improved via increased tortuosity of the crack propagation path. This tortuosity was not only induced by the inclusion of CNTs, but was also inferred by the deflection of crack path into the fibre/matrix interface. However, due to the homogeneous CNT distribution that was pursued within the previous study, the crack path was inhibited from propagating into the matrix and persisted within the fibre/matrix interphase. This current study therefore explores a method to further increase the crack path tortuosity during the crack propagation. A weakened matrix region was engineered to redirect the propagation of the crack tip from the fibre/matrix interface into the matrix. Furthermore, the reduced particle size of the NC powder was intended to promote a better CNTs distribution by reducing the separation between the particles and will be discussed further in Section 6.1.1. Hence, an alternative processing modification was proposed to induce cohesive failure in the HCs by mixing the NC powder with control (0 wt%\(_E\)) powder. This control (0 wt%\(_E\)) CNTs powder was expected to promote the cohesive failure and will be discussed in detail in Section 7.5.

Due to the limited quantity of available NC powder, the 25.0 wt%\(_E\) and 10.0 wt%\(_E\) CNTs powder was unavailable for the heterogeneity study. The remaining available powder for this study were the control, 5.0 and 15.0 wt%\(_E\) CNTs powder. The mixture of control and 15 wt%\(_E\) CNTs powder was manufactured with two configurations. The first configuration maximised the heterogeneity by mixing five part of control powder to one part of 15.0 wt%\(_E\) CNTs powder. This mixture had an overall CNTs loading of 2.2 wt%\(_E\) CNTs powder which was comparable to the manufactured homogeneously dispersed 2.5 wt%\(_E\) CNTs HCs. The second configuration was manufactured by mixing the control (0 wt%\(_E\)) and 15.0 wt%\(_E\) CNTs powder at one to one ratio creating a matrix mixture with an overall CNT loading of 7.5 wt%\(_E\) CNTs. Finally the last mixture was produced by mixing the control (0 wt%\(_E\)) and 5.0 wt%\(_E\) CNTs powder at a one to one ratio creating a matrix mixture with an overall CNT loading of 2.5 wt%\(_E\) CNTs. The manufactured heterogeneous mixture is summarised in Table 3-1.
Table 3-1: Heterogeneous mixtures for HCs

<table>
<thead>
<tr>
<th>Matrix type</th>
<th>Constituent powders</th>
<th>Mixing ratio</th>
<th>Overall CNTs content in the matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hetero (1:1, 2.5 wt%$_E$)</td>
<td>Control (0 wt%$_E$ CNT) powder and 5.0 wt%$_E$ CNT powder</td>
<td>1:1</td>
<td>2.5 wt%$_E$</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$_E$)</td>
<td>Control (0 wt%$_E$ CNT) powder and 15.0 wt%$_E$ CNT powder</td>
<td>1:1</td>
<td>7.5 wt%$_E$</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$_E$)</td>
<td>Control (0 wt%$_E$ CNT) powder and 15.0 wt%$_E$ CNT powder</td>
<td>5:1</td>
<td>2.2 wt%$_E$</td>
</tr>
</tbody>
</table>

In summary, the characterisation of the heterogeneity in the HCs was developed as follows:

a) Production of HCs with the largest possible separation between the particles (*Section 4.2.2*).

b) Production of HCs with the smallest separation between the particles (*Section 4.2.2*).

These HCs were manufactured to achieve a similar overall content to that of the lowest homogeneous HC at 2.5 wt%$_E$ CNTs. Another heterogeneous mixture was manufactured to generate the largest possible CNTs average as comparison to the other HCs.

c) Physical and mechanical characterisation of the heterogeneous HCs (*Section 5.1 and Section 5.2*).

d) Fractography of the fractured surface via SEM (*Section 5.3*).

e) Exploring the interactions between the fracture morphologies and mechanical properties (*Section 7.5*)
Chapter 4 : Experimental Details

This chapter describes the optimised experimental methods and techniques used for nanocomposite and hierarchical carbon fibre reinforced composite production during the course of this research. The materials selected are justified and their properties are listed. This Chapter then describes the development of the production method for a thermoset resin system by utilising a widely used thermoplastic processing route, leading to the production of well controlled dispersion of carbon nanotubes (CNTs) in nanocomposite extrudates. The extrudates were milled into powders which were later reinforced with carbon fibres to produce hierarchical composites (HCs). Finally, the productions of hierarchical composites via a wet impregnation filament winding and vacuum assisted hot pressing technique are explained.

4.1 Materials

4.1.1 The thermoset resin

A commercially available thermoset resin, Epikote 1001 (Hexion Specialty Chemicals, UK) supplied by Hexcel, UK, was used as the matrix for this study. Epikote 1001 was chosen as it is solid at room temperature and has a wide processing window hence permitting a robust processing route. This resin was chosen based on the processing parameters expected for HC processing. Firstly, this thermoset system should be insoluble in water as the nanocomposite powder is dispersed with water to create slurry suspensions. Furthermore, the matrix should not swell, therefore maintaining its particle size during the fibre impregnation to ensure consistent matrix uptake.
Table 4-1: Properties of EPIKOTETM resin 1001 [163].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy group content</td>
<td>mmol/kg</td>
<td>2000 – 2220</td>
<td>SMS 2026</td>
</tr>
<tr>
<td>Density at 25°C</td>
<td>g cm⁻³</td>
<td>1.20</td>
<td>ASTM D 792 [164]</td>
</tr>
<tr>
<td>Glass transition temp. (Tg)</td>
<td>°C</td>
<td>26</td>
<td>ASTM D 3418 [165]</td>
</tr>
<tr>
<td>Melting range, Mettler</td>
<td>°C</td>
<td>50 – 62</td>
<td>N/A</td>
</tr>
</tbody>
</table>

4.1.2 Hardener

The hardener was dicyandiamide curing agent (Dyhard® 100S) generously supplied by Hexcel. The hardener reacted with Epikote 1001 epoxy above 140°C, thus initiating the cross linking process [4]. This elevated reaction temperature provided a suitable processing window through extrusion which was historically a predominantly thermoplastic processing route to be applied in this study, whilst still avoiding premature curing in the extruder. Dyhard® 100S has a melting point of 209-212°C and a particle size of 8.0-9.5 µm [166].

4.1.3 Carbon nanotubes (CNTs)

The carbon nanotubes used for this study were Nanocyl™ NC 7000 supplied by Nanocyl (Sambreville, Belgium). These nanotubes are thin, multiwalled CNTs commercially produced via catalytic chemical deposition. The CNTs were used as received without any further modification or purification.

Table 4-2: Properties of Nanocyl™ NC 7000 [167].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Diameter</td>
<td>nm</td>
<td>9.5</td>
<td>TEM</td>
</tr>
<tr>
<td>Average Length</td>
<td>µm</td>
<td>1.5</td>
<td>TEM</td>
</tr>
<tr>
<td>Carbon Purity</td>
<td>%</td>
<td>90</td>
<td>TGA</td>
</tr>
<tr>
<td>Metal Oxide</td>
<td>%</td>
<td>10</td>
<td>TGA</td>
</tr>
<tr>
<td>Surface Area</td>
<td>m²/g</td>
<td>250-300</td>
<td>BET</td>
</tr>
</tbody>
</table>

4.1.4 Carbon fibres

The carbon fibres used for this study were HexTow® AS4C – GP supplied by Hexcel (Cambridgeshire, UK). This carbon fibre was a 12k filament tow, untwisted, continuous, high
strength and high strain polyacrylonitrile (PAN) based carbon fibre sized with epoxy sizing. The choice of fibres was based on the hypothesis that sized fibres would generate better bonding with the epoxy matrix system and a better handle-ability.

Table 4-3: Properties of Hextow® AS4C – GP [168].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>4385</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>GPa</td>
<td>231</td>
</tr>
<tr>
<td>Ultimate Elongation at Failure</td>
<td>%</td>
<td>1.8</td>
</tr>
<tr>
<td>Density</td>
<td>g cm(^{-3})</td>
<td>1.78</td>
</tr>
<tr>
<td>Filament Diameter</td>
<td>µm</td>
<td>6.9</td>
</tr>
</tbody>
</table>

4.2 Manufacturing process

4.2.1 Nanocomposite processing

![Nanocomposite processing diagram](image)

Figure 4-1: The nanocomposite (NC) processing diagram
The nanocomposite processing method stems from an earlier study [4] and was optimised here for better NCs production. Modifications were made to improve the processing such as optimization of the screw speed, temperature, removal of extruder die and manual constituent feeding system in comparison to the auto-feed system previously deployed. With these modifications, less material became airborne during processing in comparison to the agitation of the auto-feed. The nanocomposite processing stages is summarised in Figure 4-1 and explained in details in the next section.

**Nanocomposite (NC) extrusion**

The matrix powder constituents, the CNTs, the epoxy, and the hardener, were dried overnight at room temperature in a vacuum oven to eliminate moisture. Weight percentages (wt%) were calculated relative to the epoxy weight to achieve the desired CNT weight fractions with a constant hardener addition of 4.0 wt%E [4] to epoxy weight. NCs production was optimised for CNT loadings of up to 25.0 wt%E to epoxy weight by shear mixing using a PRISM, TSE 16 TC Series twin screw extruder (Thermo Electron Corporation, Germany) (Figure 4-3). The shear mixing process was identified as the best processing route to achieve a high weight fraction of CNTs whilst obtaining good dispersion of CNTs in the matrix [4].

**Optimisation of nanocomposite production**

The first challenge in this study was to complete the manufacturing process of the nanocomposite via extrusion. Previously, CNTs loadings up to 15.0 wt%E had been successfully extruded via the twin screw extruder. However, the 25.0 wt%E CNTs nanocomposite had remained elusive due to the substantial increase in the viscosity of the nanocomposite mixture at such high CNTs loadings. The twin screw extruder was unable to supply enough power to mix the epoxy and CNTs. One explored route was to elevate the processing temperature during extrusion and hence reduce the viscosity of the mixture. However, this methodology was deemed too risky as the cross-linking process might be initiated thus severely damaging the extruder.

A key step taken to solve this problem was by extruding the mixture without the pelletising die (Figure 4-2). The pelletising die was initially used to physically convert the extrudates into a long 'spaghetti' structure for easier handling. This process however requires the twin screw to generate additional pressure to force the extrudates through a 2 mm diameter die exit. NCs lower than 15.0 wt%E was successfully extruded even with the additional pressure. However, the viscosity of the 25.0 wt%E NC was too high and the twin
screw extruder was not able to produce sufficient pressure to push the material through. Since
the extrudates will undergo milling process afterwards, the pelletising process was redundant
hence removing the pelletising die altogether would reduce the power requirement for the
extrusion of the 25.0 wt%E NC.

Figure 4-2: The extruder a) with the pelletising die, b) without pelletising die.

The NC matrices extruded including the relevant weight and volume percentages are
summarised in Table 4-4. The weight fraction of CNT weight to epoxy weight (wt%E) is
calculated using Equation 4-1;

\[ \text{wt}%_E = \frac{\text{wt}_{\text{CNT}}}{\text{wt}_{\text{epoxy}}} \times 100\% \]  
Equation 4-1

where \( \text{wt}_{\text{CNT}} \) is the weight of the CNTs and \( \text{wt}_{\text{epoxy}} \) is the weight of the epoxy. The weight
fraction of CNT to the whole matrix weight (wt%M) is calculated using Equation 4-2;

\[ \text{wt}%_M = \frac{\text{wt}_{\text{CNT}}}{\text{wt}_{\text{epoxy}} + \text{wt}_{\text{CNT}}} \times 100\% \]  
Equation 4-2

The volume percentage of CNT in the matrix (vol%M) was deduced using Equation 4-3, with
CNT density (\( \rho_{\text{CNT}} \)) and a pure epoxy matrix density (\( \rho_{\text{epoxy}} \)), of 1.90 gcm\(^{-3}\) and 1.20 gcm\(^{-3}\)
respectively as jointly measured alongside Herceg [4], assuming the constituents were
completely dry.

\[ \text{vol}%_M = \frac{\text{wt}%_E}{\text{wt}%_E + \text{wt}%_{\text{epoxy}} \times \frac{\rho_{\text{CNT}}}{\rho_{\text{epoxy}}}} \]  
Equation 4-3

The hierarchical composites (HCs) were manufactured by impregnating carbon fibres with
the nanocomposite matrix. In this study, the desired fibre volume fraction of the HCs was
aimed at 55 %. With this assumption, the matrix volume fraction in the HC will be 45 %.
Therefore the volume percentage of CNT in the hierarchical composite ($vol\%_C$) can be deduced with Equation 4-4. All the matrix content produced in this study is tabulated in Table 4-4. Therefore the content of the nanocomposite as the matrix is 45% without voids.

\[
vol\%_C = 0.45 \times vol\%_M
\]  

Equation 4-4

Table 4-4: Conversion between weight percent and volume percent for CNT loading in the resulting nanocomposites.

<table>
<thead>
<tr>
<th>$wt%_E$</th>
<th>$wt%_M$</th>
<th>$vol%_M$</th>
<th>$vol%_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2.5</td>
<td>2.44</td>
<td>1.55</td>
<td>0.70</td>
</tr>
<tr>
<td>5.0</td>
<td>4.76</td>
<td>3.06</td>
<td>1.38</td>
</tr>
<tr>
<td>7.5</td>
<td>6.98</td>
<td>4.52</td>
<td>2.04</td>
</tr>
<tr>
<td>10.0</td>
<td>9.09</td>
<td>5.94</td>
<td>2.67</td>
</tr>
<tr>
<td>15.0</td>
<td>13.04</td>
<td>8.65</td>
<td>3.89</td>
</tr>
<tr>
<td>25.0</td>
<td>20.00</td>
<td>13.64</td>
<td>6.14</td>
</tr>
</tbody>
</table>

Figure 4-3: Prism co-rotating twin screw extruder.

The extrusion temperature was experimentally chosen for each CNT loading to ensure that only the epoxy was molten without initiating chemical reaction with the hardener, and
such that the NC’s viscosity was compatible with the available extruder torque. The temperature was kept below 140 °C to avoid premature curing. The extrusion process was repeated three times for each batch to ensure a homogeneous mixture of the epoxy, the CNTs, and the hardener as stipulated by Herceg [4].

The twin screw extruder was designed consisting of feed screws, mixing and reverse feed sections as shown by Figure 4-4. The reverse feed feature was included to slightly increase the residence time of the extrudates in the barrel and thus improve the polymer mixing. However this feature would require additional energy at this section which is supplied either through reduction of viscosity by temperature increase or an increase in torque from the power supply. At lower CNT content, the viscosity of the NCs mixtures were sufficiently low to enable extrusion without temperature increase. However, for the highest CNT loadings (25.0 wt%\textsubscript{\text{C}}) which was extruded at maximum torque from the power supply, a slight increase in temperature was required to sufficiently reduce the viscosity of the NCs thus enabling extrusion.

Figure 4-4: The twin screw extruder design [150]
Table 4-5: Extrusion parameters for the nanocomposites

<table>
<thead>
<tr>
<th>CNTs Content (wt.%)</th>
<th>Rear Extruder Temperature (°C)</th>
<th>Front Extruder Temperature (°C)</th>
<th>Screw Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70</td>
<td>70</td>
<td>100-120</td>
</tr>
<tr>
<td>2.5</td>
<td>80</td>
<td>80</td>
<td>100-120</td>
</tr>
<tr>
<td>5.0</td>
<td>85</td>
<td>85</td>
<td>100-120</td>
</tr>
<tr>
<td>10.0</td>
<td>90</td>
<td>90</td>
<td>100-120</td>
</tr>
<tr>
<td>15.0</td>
<td>110</td>
<td>110</td>
<td>100-120</td>
</tr>
<tr>
<td>25.0</td>
<td>122</td>
<td>120</td>
<td>100</td>
</tr>
</tbody>
</table>

**Nanocomposite (NC) powder production**

The nanocomposite powder used as the precursor during powder impregnation was originally produced via cryomilling process as developed by Herceg [4]. However, the nanocomposite powder production was often interrupted by severe machine downtime due to several mechanical and electrical malfunctions. Critically, the particle size distribution from this cryomilling was large as more than 10% of the particles were measured to have particle size larger than 100 µm.

A solid mixing processing route was chosen to achieve high CNTs loading in the matrix. Liquid matrix mixing routes were unsuitable for even a modest weight percentage of CNTs, such as 1.0 wt% of MWCNT in epoxy dramatically increased the viscosity above the rheological percolation threshold [124]. In contrast, extrusion mixing has been demonstrated to be capable of mixing extremely high CNTs loadings above 20 wt% in thermoplastic systems [17,157]. After CNT dispersion in the matrix had been achieved, the HC production using the powder impregnation method was utilised to alleviate the CNT self-filtering that occurs with a liquid processing method [169]. This process also reduced the necessary mobility for the CNTs to disperse in the HCs to the length scale of the particle size.

Upon collaboration with VTT Technical Research Centre of Finland Ltd, a free trial using their jet milling facilities was granted. This trial run has yielded approximately 250 g of nanocomposite powder for all the matrix configurations. A significant portion of this were utilised in nanocomposite study to ensure that the key milestones in the research grant were achieved. The remaining powder was utilised in HCs production and heterogeneity study. However, due to the limited resources, the 25.0 wt% CNTs powder was depleted for the
nanocomposite study and the homogeneous HCs production leaving insufficient amount for heterogeneity study with this matrix.

_Cooled jet milling by VTT Technical Research Centre (Finland)_

The nanocomposite extrudates were pre-grinded using a laboratory blender (Waring blender, Cole-Parmer Instrument, UK) and then dispatched to a collaborating partner, VTT Technical Research Centre of Finland. The NCs were further milled into fine powder form using a cooled jet milling process conducted by with a modified Grinding and Classifying System supplied by Hosokawa Alpine, Germany [170]. The system was a combination of Alpine Fluidised Bed Opposed Jet Mill 100 AFG with Integrated Classifier. The system was modified as such that the grinding air was capable of cooling down to -40°C. The pressurised grinding air was first dried by the membrane dryer at 6 bar pressure and then cooled by the cooling compressor down to -35°C. The NCs was exelerated to high speed at the nozel with this cooled air inducing particle collision which reduces the particle to the desired size. The milled product was separated from the airflow by passing through a prefixed filter before local extraction.

4.2.2 Hierarchical composite (HC) production

The HC production method was summarised in Figure 4-5. The carbon fibre tow was drawn from the creel through a tensiometer which measured and fixed the tension of the fibres. These fibres were then submerged through an impregnation bath which has a series of fixed pin positions which improved the fibre spreading. A dispersed NC powder in the impregnation bath was then collected by the fibres and was then wound up onto a filament winding drum producing the HC composite prepreg ply.

The prepreg ply was then removed from the drum and dried. Each ply was melt-pressed to produce a flat lamina. The laminas were stacked and debulked in a vacuum table. This laminate was then consolidated and cured before final trimming to specimen size with a diamond saw. Further details of the impregnations process in discussed in the next section.
Figure 4-5: The hierarchical composite (HC) processing diagram.

a) Hot pressing – film infusion

A rectangular mould (70mm by 150 mm) was made with several layers of polyamide tape creating a ~150 µm depth walled mould. 2g of NC powder were spread inside the mould and pressed at the extrusion temperature (Table 4-5) with 9 bar pressure to produce thin films. Carbon fibre tow was then wound onto a flat steel plate and the NCs films were hot pressed (P319, Moore Ltd, UK (Figure 4-6)) onto the carbon fibre tows at 27 bar pressure mimicking the prepeging route used to produce conventional composite prepreg [171].
b) Wet impregnation

In the previous study [4], the impregnation suspensions were prepared with the addition of 5.0 wt% surfactant. However, surface tension analysis showed that such a high quantity of surfactant was excessive and could be detrimental to the properties of the resulting composite. Furthermore, the addition of just 0.5 wt% surfactant resulted in the same surface tension of the dispersent as that with 5.0 wt% surfactant. Therefore, the processing method in this study was modified and only 0.5 wt% surfactant was used.

The processing method was optimised by experimentally varying the processing parameters to achieve the desired fibre volume fraction and powder particles distribution. The initial starting (20 wt%) and top-up concentration (30 wt%) as recommended by Ho et al [162] had yielded HCs with low fibre volume fractions (<40 vol%). These concentrations were modified after a few iterations of the starter and top-up suspensions until composites with consistently 55 % fibre volume fraction were achieved. The filament winding process was further optimised by changing from winding onto a plate to filament winding onto a drum (Figure 4-7). The change was made because of variation in the applied tension by the
plate during winding. The fibre tension was maximum when the plate was perpendicular to the fibre tow and minimum when the plate was parallel to the fibre, leading to inconsistent powder uptake within the fibre tow.

Figure 4-7: The a) filament winding plate, b) initial filament winding drum, c) final version of filament winding drum

However, using a drum provided a different challenge: the composites that were wound onto the drum were wavy upon releasing from the drum. This fibre waviness was reduced by doubling the diameter of the drum diameter from 60 mm to 120 mm which was the maximum allowable drum size for the current jig setup. Further reduction in the fibre waviness can be achieved by enlarging the drum size but the waviness could not be perfectly removed. Therefore to achieve an optimised fibre orientation in the HCs, a linear taping processing method as originally proposed by Ho et al [162] should be adapted for future work. The main advantage of the filament winding drum over the linear taping process was that the resulting HCs were 180 mm by 150 mm by size in comparison to that of the tapes which were generally just 20 mm wide. The panels were then easier to handle and to subsequently lay-up.

The prepreg plies released from the filament winding drum were noticeably wavy in the out-of-plane direction. This out-of-plane waviness was removed by melt pressing each individual ply as detailed in the upcoming Single Ply Melt Pressing Section. This process however does not removed the out-of-plane waviness but instead translate this waviness into in-plane waviness. It was noted that the in-plane waviness would affect the fibre dominated properties. However for this study the priority objectives were matrix dominated properties hence further characterisation on the waviness was not undertaken. Nonetheless, for future
work, this waviness should be accounted for composite properties in which the fibre contributions were more profound such as tensile and compression.

Another source of the out-of-plane waviness was due to overlapping fibre tows during winding. In the most extreme case the overlaps were completely on top of the previous tow while on other occasions there were no overlaps. The problem should not occur with a specialised filament winder with displacement control in comparison to the in-house filament winder used in this study. A typical industrial filament winder uses independent lateral control whereas in this in-house winder the lateral movement was coupled to the drum rotation only by means of friction. Occasionally the drum would slip and the lateral travel would be affected. Furthermore during the winding process onto the drum, the fibre tow had adequate space to slide from side to side. This sliding motion was reduced by slotting the roller with a groove as shown in Figure 4-8.

![Figure 4-8: Modified groove in the PTFE roller.](image)

The final filament winding method in this study was a compromise from these cases thus in some places in the lamina had variation in thickness due to variation in fibre content. During laminate consolidation the areas with more fibres would be in contact with the adjacent plies and hence generate the out-of-plane waviness.

**Suspension preparation**

Refrigated distilled water was mixed with 0.5 wt% of surfactant (Triton™ X-100, Sigma-Aldrich): the latter was introduced to improve particle dispersion. The mixture was left stirred in a 500 ml beaker, externally cooled with ice, on a
magnetic stirrer plate for an hour. NC powder was the added to the mixture to create the NC suspension and then stirred for a further hour. The 'starting bath' suspension was prepared to be 10.0 wt% concentration (to the whole suspension weight) with a 'top up' suspension of 15.0 wt% concentration [162]. A typical filament winding run required 350g of suspension for the starting bath and 550 g for the top up, yielding 24 plies of prepregs with dimensions of 180 mm by 150 mm and 0.25 mm thickness per ply. The material mixture for the starting bath and top up is shown in Table 4-6.

Table 4-6: Material weights for NCs sample preparations.

<table>
<thead>
<tr>
<th>Materials</th>
<th>The Starter Bath Suspension</th>
<th>The Top Up Suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>315 g</td>
<td>467.5 g</td>
</tr>
<tr>
<td>NC powder</td>
<td>35 g</td>
<td>82.5 g</td>
</tr>
<tr>
<td>Surfactant</td>
<td>0.18 g</td>
<td>0.41 g</td>
</tr>
</tbody>
</table>

Filament winding

The schematics of the filament winding process developed and optimized during this study in shown in Figure 4-9. The impregnation bath was further externally cooled to 2°C using cooling jackets (Figure 4-10) to ensure that the NCs particles did not coalesce together. The tension of the carbon fibre tow was set to 500N at the tension controller unit. The suspension was continually stirred with a magnetic stirrer at 700 rpm to prevent the NCs powder from settling on the bottom of the bath. 50 ml of the top up suspension was added into the suspension after each winding to replenish the powder content in the bath. The filament winding speed was 7.0 ± 1.0 ms⁻¹. The transverse axis direction was controlled to ensure a degree of overlap between adjacent tows on the drum and eliminate splitting. The drum winder was run between 27-28 revolution before the tow leading to the drum was cut.

The HC prepreg wound onto the drum was subsequently axial cut across the drum and then unrolled onto a PTFE film on a flat plate. The prepregs were left to dry at ambient laboratory conditions overnight (12 hours) and then in a vacuum oven at room temperature (20 °C) to remove any remaining moisture. This drying regime was in accordance to previous experience with wet impregnation setup [4,150] and was assumed to be sufficiently adequate hence no moisture measurement was undertaken. With hindsight, the moisture removal can
be evaluated by weighing the prepreg over a certain period of intervals until the weight of the prepregs were stabilised.

After drying, the specimens were trimmed and weighed to determine a gravimetric approximation of the fibre volume content using Equation 4-5 [4,150].

\[ v_f = \frac{\rho_m m_f}{\rho_f (m_{\text{prepreg}} - m_f) + \rho_m m_f} \]  

Equation 4-5

where \( m \) and \( \rho \) is the mass and the density and the subscripts \( f \) and \( m \) corresponded to the fibre and the matrix respectively. The mass of the HC prepreg is labelled as \( m_{\text{prepreg}} \) in this equation. The mass of fibre was calculated based on linear density of AS4C – GP carbon fibre which was measured to be 0.8 g/m. The production line of the filament winding process is shown in Figure 4-10.
Figure 4-9: The filament winding schematics for the HCs.
Single ply melt pressing

Removing the HC prepreg from the winding drum had induced out-of-plane fibre waviness in the lamina, which was minimised by hot pressing the HC prepreg at the same temperature as the matrix had been extruded (Table 4-5), at 9 bar pressure for eight minutes. The HCs were pressed between two metal plates wrapped with polyamide film and a layer of peel ply to avoid the HCs from sticking onto the plates. The prepregs were then cooled to room temperature and kept dry and flat in a sample bag. An example of HC prepreg after filament winding and melt pressing is shown by Figure 4-11.
c) **Vacuum assisted hot pressing for HCs**

The HC prepregs were stacked and debulked on a vacuum table with a stacking sequence of \([0^\circ_8, +3^\circ]_{AS}\), which was chosen to reduce the fibre nesting at the central ply interface [172]. This configuration would reduce the fibre bridging contribution during crack propagation hence produce a more stable crack growth. The schematic for the vacuum assisted hot pressing of the HCs is shown in Figure 4-12. Two 3.00 mm thick steel strips were inserted as spacers to ensure constant control of pressure on the laminate and a uniform laminate thickness across different matrix powder combinations. Following lay-up, the sample was vacuum-bagged and kept under constant vacuum.
The curing cycle is summarised in Figure 4-13 which shows the corresponding temperature, pressure and vacuum regimes. The temperature was ramped from room temperature (20 °C) to a soaking temperature of 125 °C at 5 °C/min using a hot press (P319, Moore Ltd, UK) and held for 60 minutes. This soaking process allowed the NC powder particles to melt and any remaining air/moisture in the prepregs to be removed by the vacuum. Pressure was applied to the system until the hot press was in physical contact with the steel spacers; the temperature was then increased to 165°C and the laminate was left to cure under pressure and vacuum for 120 minutes before the vacuum pump was turned off. The laminates were post cured in the hot press overnight (12 hours) at 165°C and cooled down afterwards at 8 °C/min for approximately 180 minutes to room temperature (20 °C). The laminates were then trimmed into test specimens using a wet diamond saw (Diadisc 4200, Mutronic GmbH & Co, Germany).
Figure 4-13: Curing cycle for the HCs with the temperature, pressure and vacuum regimes shown.
This chapter describes the characterisation methods and standards used to assess the physical and mechanical properties of the hierarchical composites (HCs). The quality of the HCs was determined to ensure that the processing method had been optimised. The Mode I fracture toughness, flexural modulus and short beam shear strength were measured to quantify any mechanical enhancement from the inclusion of the CNTs to the parent composite. The through-thickness electrical conductivity and thermal conductivity were also measured to identify any additional multifunctionality imbued by the CNTs on the resulting composites.

5.1 Physical characterisation

5.1.1 Particle size analysis

The particle size of the milled nanocomposite powder was analysed with a Mastersizer 2000 (Malvern Instruments, UK). 0.3 g of nanocomposite powder was dispersed in 10 ml of distilled water by magnetic stirring. 1 wt% to powder weight of Cremaphor A-25 (BASF, Germany) surfactant was added to improve particle dispersion in the suspension. The suspension was circulated in the path of a laser diffraction system to determine the particle size based on the intensity of light scattered at different angle of diffraction as described by the manufacturer [173]. The suspension was prepared in water to mimic the filament winding conditions during the HC production.
5.1.2 The bulk density

The density of the consolidated HC was measured with a pycnometer; Accupyc 1330 (Micromeritics, UK) based on Boyle’s law using two chambers with known volumes, two pressure transducers and helium gas. The pycnometer measured the displaced volume of the samples and calculated the density with the weight input of the sample measured using an analytical balance at a minimum resolution of 0.1 mg. A sample with a minimum size of two thirds of the chamber volume was recommended to ensure sufficient helium displacement for accurate density measurement. These samples were cut from the un-fractured end of the DCB test specimens (15mm x 25 mm x 3 mm) using a diamond saw (Diadisc 4200, Mutronic GmbH & Co, Germany) and subsequently used for the constituent measurements as detailed in Section 5.1.4.

5.1.3 Optical microscopy

The HC microstructure was characterised using bright field imaging on a binocular optical microscope (Axio Imager.M2m, Zeiss, UK) with Ziess Epiplan (Zeiss, UK) objective lenses with objective magnifications of 1.25x, 5x, 20x, and 50x using reflective illumination. The test sample were cut from the un-fractured end of the DCB samples (10 mm x 25 mm x 3 mm) using a diamond saw and then mounted into epoxy and subsequently polished with a Motopol 12 rotary polishing machine (Buehler, UK) as described in the next section. The grinding grid, polishing cloth and diamond polishing suspension were supplied by Buehler, UK.

Polishing procedure

A mixture of EpoxyCure™ epoxy resin (20-8130-128) and EpoxyCure™ epoxy hardener (20-8132-032) from Buehler, UK with a mixing ratio of 5 resin to 1 hardener by weight was used to contain and support the specimens during the polishing process. Mixing was done in a paper cup and was manually stirred until a homogeneous mixture of resin and hardener was achieved. The epoxy mixture was then poured in to a PVC pot coated with release agent. The epoxy was cured at room temperature (20°C) overnight (12 hours).

After curing, the sample was taken out of the pot and the polishing sequence as detailed in Table 5-1 was followed at 5 psi (34.47 kPa) pressure per sample at a base rotational speed of 150 rpm.
Table 5-1: Polishing sequence for the HCs.

<table>
<thead>
<tr>
<th>Grit/Cloth</th>
<th>Medium</th>
<th>Time</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>320 Grit SiC</td>
<td>water</td>
<td>2 minutes</td>
<td>1</td>
</tr>
<tr>
<td>800 Grit SiC</td>
<td>water</td>
<td>2 minutes</td>
<td>1</td>
</tr>
<tr>
<td>2500 Grit SiC</td>
<td>water</td>
<td>2 minutes</td>
<td>1</td>
</tr>
<tr>
<td>Buehler MicroFloc</td>
<td>6 µm MetaDi diamond suspensions</td>
<td>2 minutes</td>
<td>1</td>
</tr>
<tr>
<td>Buehler MicroFloc</td>
<td>3 µm MetaDi diamond suspensions</td>
<td>3 minutes</td>
<td>1</td>
</tr>
<tr>
<td>Buehler MicroFloc</td>
<td>1 µm MetaDi diamond suspensions</td>
<td>3 minutes</td>
<td>2</td>
</tr>
</tbody>
</table>

5.1.4 Fibre volume fraction measurement

The constituents of the HCs (fibres, matrix and voids) were measured in accordance with ASTM standard D 3171 [174] adapted for HCs. Samples (15 mm x 25 mm x 3mm) were cut using diamond saw (Diadisc 4200, Mutronic GmbH & Co, Germany) and dried overnight (12 hours) under vacuum at room temperature (20°C). These were weighed and their densities were measured as described in Section 5.1.2. Each sample was then placed inside a conical flask and 25 ml of sulphuric acid (>97% concentration) was added to fully submerge the sample. The flask was heated to 170 °C until the solvent’s colour stabilised for a minimum of 5 minutes. Hydrogen peroxide (50% concentration) was added drop by drop until the HC sample had been fully digested. The digestion process was deemed to have been completed when either the colour of the solution became clear or the chemical reaction had terminated.

The digested sample was left to cool to room temperature and 100 ml of water was added into the flask. The carbon fibres and CNTs were then vacuum-filtrated with a weighed filter paper and then rinsed with a minimum of 200 ml of water. Final rinsing with acetone was conducted to assist the drying process. The digested sample was then dried in a vacuum oven at room temperature (20°C) overnight (12 hours) and weighed to obtain the fibre weight \(M_f\). The CNTs were not digested during the acid digestion process (Section 7.1) and the weight of the CNTs were estimated and added to the weight of the resin to obtain the weight of the matrix.

The fibre volume content was calculated in accordance with Equation 5-1 [174];

\[ 
\nu_f = \left(\frac{M_f}{M_c}\right) \times 100 \times \left(\frac{\rho_c}{\rho_f}\right) 
\]

Equation 5-1
where $v_f$ is the fibre volume fraction, $M_f$ is the mass of the fibre after digestion, $M_c$ is the mass of the initial composite prior to digestion, $\rho_c$ is the density of the composite and $\rho_f$ is the density of the fibre.

The matrix volume content was calculated in accordance with Equation 5-2 [174]

$$v_m = \left(\frac{M_m}{M_c}\right) \times 100 \times \left(\frac{\rho_c}{\rho_m}\right)$$  

Equation 5-2

where $v_m$ is the matrix volume fraction, $M_m$ is the mass of the matrix after digestion, and $\rho_m$ is the density of the nanocomposite matrix as reported by Herceg [4] (Table 2-1). The density of the heterogeneous mixtures was extrapolated from the density of the homogeneous nanocomposite.

### Table 5-2: The reported homogeneous nanocomposite density

<table>
<thead>
<tr>
<th>Nanocomposite Matrix</th>
<th>Matrix density (gcm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt% E CNTs)</td>
<td>1.196</td>
</tr>
<tr>
<td>Homo (2.5 wt% E CNTs)</td>
<td>1.209</td>
</tr>
<tr>
<td>Homo (5.0 wt% E CNTs)</td>
<td>1.243</td>
</tr>
<tr>
<td>Homo (10.0 wt% E CNTs)</td>
<td>1.270</td>
</tr>
<tr>
<td>Homo (25.0 wt% E CNTs)</td>
<td>1.312</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt% E CNTs)</td>
<td>1.209</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt% E CNTs)</td>
<td>1.257</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt% E CNTs)</td>
<td>1.209</td>
</tr>
</tbody>
</table>

The mass of the matrix was calculated with Equation 5-3;

$$M_m = M_c - M_f$$  

Equation 5-3

The void volume fraction was calculated in accordance with Equation 5-4 [174];

$$v_v = 100 - (V_f + V_m)$$  

Equation 5-4

where $v_v$ is the void volume content in the composite.

### 5.1.5 Dynamic mechanical thermal analysis (DMTA)

The glass transition temperature ($T_g$) of the HCs was investigated using dynamic mechanical thermal analysis (DMTA). DMTA is an analysis of a material’s elastic response...
to cyclic loading whilst temperature is ramped [175]. The dynamic mechanical response of the material from the oscillating force is used to determine the complex modulus \(E^*\);

\[
E^* = E' + iE''
\]  

Equation 5-5

where \(E'\) is the elastic modulus or the in-phase/elastic contribution and \(E''\) is the loss modulus or the out-of-phase/viscous contribution. For a pure elastic solid, the stress and strain response would be fully in-phase (\(\delta = 0^\circ\)) and for a pure viscous liquid the stress and strain response would be fully out-of-phase (\(\delta = 90^\circ\)). The ratio of these effects gives the viscoelastic damping of the material (\(\tan \delta\));

\[
\tan \delta = \frac{E''}{E'}
\]  

Equation 5-6

The glass transition temperature \((T_g)\) is typically taken at the peak of \(\tan(\delta)\) sweep versus temperature [176]. For polymer based material, a dramatic drop of elastic modulus and peak in viscous modulus occurs at the glass transition temperature.

The test samples were prepared by cutting the HC panel (40 mm x 6 mm x 3 mm) with diamond saw (Diadisc 4200, Mutronic GmbH & Co, Germany). The test was performed using a three point bending configuration with a span of 10 mm over a temperature range from room temperature to 200 °C at 2 °C per minute to ensure the whole physical regime of the matrix was characterised at a frequency of 1 Hz.

5.1.6 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the temperature of the sample of interest and a reference sample are varied while the amount of heat flow required to heat or cool the samples is compared. DSC was used to determine the degree of cure and the heat capacity of the HCs.

DSC was conducted using a Q2000 DSC (TA Instruments, UK) using two different methods. Samples weighing between 10-20 mg were cut from the HC panels. To determine the degree of curing, a dynamic scan was performed at 10°C/min from -50°C to 220°C followed by cooling rate of 20 °C/min to -50 °C before another dynamic temperature sweep at 10 °C/min to 220 °C.

The heat capacity of the HCs was determined from a dynamic scan at 5 °C/min from 5°C to 35°C. This temperature scan was conducted at a higher rate to reduce the experiment time as the heat capacity was required to be taken at a specific temperature (25 °C) over a full
temperature envelope, to be used an input parameter to evaluate the through-thickness thermal conductivity.

5.1.7 Through-thickness electrical conductivity

![Image of electrical resistivity jig]

Figure 5-1: The electrical resistivity jig.

The through-thickness electrical resistivity of the HCs was measured using an in-house built contact assessment method (Figure 5-1). The contact jig consisted of two flat aluminium stubs bolted onto acrylic block and then connected to a low voltage ohmmeter via insulated copper cables. The top and bottom surfaces of the samples (10 mm x 10 mm x 3 mm) were polished with 800 Grit SiC polishing paper to obtain flat and smooth surfaces. The polished surfaces were then coated with conductive silver paint (Agar Scientific, UK) and dried for one hour at room temperature. The top and bottom surfaces of the samples were clamped between the two metal stubs and the resistance was measured by the low voltage ohmmeter. The through-thickness resistivity was calculated taking into consideration the thickness \( t \) and cross sectional area \( A \) with Equation 5-7 [177]. The through-thickness electrical conductivity was taken as the inverse of the through-thickness electrical resistivity.

\[
\rho_{\text{electrical}} = \frac{R A}{t}
\]

where \( R \) is the resistance as measured by the ohmmeter and \( \rho_{\text{electrical}} \) is the through-thickness electrical resistivity.

5.1.8 Through-thickness thermal conductivity

The thermal diffusivity of the HCs samples (8 mm x 8 mm x 3 mm) was measured using a Xenon light flash system (LFA 447, Netzsch Instruments, UK). The test was
calibrated using Pyroceram 9606 as supplied by the manufacturer [178]. The calibration and test was conducted at 25 °C. The samples were spray-coated with graphite paint to ensure optimised diffusion of energy from the heat source into the HCs.

The thermal diffusivity was measured by rapidly heating the specimen on one side via a known heat source (Xenon flash light) and measuring the temperature rise curve on the opposing side. The time undertaken for the heat to travel through the sample was measured with respect to the specimen thickness. The graphite coating was sufficiently thin (unmeasured) and the contribution from the coating was assumed to be negligible in comparison to the diffusion rate of the composites. The through-thickness thermal conductivity was then calculated using Equation 5-8:

$$K_{zz}^\text{thermal} = \rho C_p \alpha_{thermal}$$  \hspace{1cm} \text{Equation 5-8}

where $K_{zz}^\text{thermal}$ is the through-thickness thermal conductivity, $\rho$ is the density of the HC as measured by pycnometer, $C_p$ is the heat capacity of the HC measured by DSC and $\alpha_{thermal}$ is the through-thickness thermal diffusivity [179]. A minimum of six samples was tested for each HCs configurations.

![Figure 5-2: The LFA 447 Nanoflash for thermal diffusivity measurements.](image)

5.2 Mechanical characterisation

Three mechanical properties of the HCs were characterised in this study comprising of fracture toughness, interlaminar shear strength and flexure stiffness. The fracture toughness and flexure stiffness were obtained with the double cantilever beam test (Section
5.2.1) while the interlaminar shear strength was obtained with the short shear test (Section 5.2.2). A minimum of five test samples were tested for each HC configuration.

5.2.1 Double cantilever beam (DCB) testing

Mode I fracture toughness of the HCs laminates was assessed using the ASTM D5528 double cantilever beam (DCB) test [180]. A 25 μm thick PTFE film (Aerovac Systems, UK) was inserted at one end of the specimen prior to cure at a length of 60 mm from the edge of the stacked laminate at the mid plane during lay-up to act as the crack initiation point. Two aluminium loading blocks (12 mm x 19 mm x 10 mm) were bonded onto the HC samples (150 mm x 20 mm x 3 mm) with Araldite 2011 (Huntsman Advanced Materials Ltd, UK) epoxy adhesive (Figure 5-3) and then cured overnight at room temperature. A thin layer of silver paint was sprayed onto one side of the sample and increments at 1 mm intervals were drawn on the paint starting from the middle of aluminium blocks as stipulated by the standard [180].

![DCB sample after fracture toughness testing.](image)

The samples were loaded in an Instron 5900 universal testing machine with 50 kN load cell. The samples were pre-cracked in Mode I at a rate of 5 mm/min. After pre-cracking, the samples were unloaded to the initial position at a rate of 5 mm/min and afterwards the testing was resumed at 1 mm/min test speed until 25 mm crack length had been generated. The applied load (P), cross head displacement (δ) and crack length (a) were recorded to determine the critical strain energy release rate (G_{ic}) for the HC samples.
Corrected beam theory (CBT) [181] was used to deduce the Mode I fracture toughness ($G_{ic}$) values with the formulae given in Equation 5-9, Equation 5-10 and Equation 5-11.

\[
G_{ic} = \frac{3P\delta}{2B(a + |\Delta|)} \quad \text{Equation 5-9}
\]
\[
C = \frac{8(a + \Delta)^3}{E_f bh^3} \quad \text{Equation 5-10}
\]
\[
C = \frac{\delta}{P} \quad \text{Equation 5-11}
\]

where $C$ is the compliance, $P$ is the load, $\delta$ is the displacement, $b$ is the specimen width, $a$ is the crack length, $h$ is the arm thickness (i.e. half the laminate thickness) and $\Delta$ is the correction for beam rotation at the crack tip determined from the x axis intercept of the $C^{1/3}$ against crack length plot.

The initiation fracture toughness was taken as the critical strain energy release rate for initial (1 mm) crack growth beyond the pre-crack which was found to be comparable to the values calculated from the maximum load as stipulated by the standard [180]. The propagation fracture toughness was the average critical strain energy release rate after the crack front had grown 25 mm from the initial pre-crack. The fracture toughness was
separated to partition the fibre bridging contribution from the carbon fibre to the delamination toughness.

The arm stiffness for the DCB samples was determined from the slope of the compliance ($C$) versus crack length ($a$). The flexural modulus ($E_f$) of the arms were calculated using Equation 5-12;

$$E_f = \frac{8}{m^3bh^3}$$

Equation 5-12

where $m$ is the gradient of the $C^{1/3}$ plotted against crack length ($a$).

5.2.2 Short beam shear (SBS) testing

The interlaminar shear strength of the composite laminates were measured using the short beam strength (SBS) test using ASTM standard D 2344 [127]. The test pieces (20 mm x 5 mm x 3 mm) were cut using a wet diamond saw. The SBS test was conducted with a test span of 12 mm at a crosshead speed of 1 mm/min with the test setup as show in Figure 5-5. Equation 5-13 was used to calculate the short beam strength ($F_{SBS}$).

$$F_{SBS} = 0.75 \frac{P_m}{bt}$$

Equation 5-13

where $P_m$ is the maximum load, $b$ is the specimen width and $t$ is the specimen thickness.

![Figure 5-5: Schematics of the three point bending short beam shear test jig setup.](image)

5.3 Fractography

The fractured surfaces were analysed using a scanning electron microscope (SEM) to investigate the fracture morphology and mechanisms. High resolution SEM micrographs were taken using a LEO Gemini 1525 field emission gun SEM. Low resolution micrographs
were taken using a Hitachi S-3700N analytical SEM. The SEM samples were coated with chromium for high resolution SEM and sputter coated with gold for low resolution SEM. The acceleration voltage used for both microscopes was 5.0 kV. Two different types of objective detectors were available for the LEO Gemini 1525 field emission gun SEM. The detectors were SE2 for higher resolution of the fracture surfaces and the in-lens detector was used to maximise contrast of the CNTs patches, as shown in Figure 5-6.

Two types of fracture surfaces were examined. The fracture surface of the bulk NCs were produced via testing 'dog-bone' test samples under tensile load as previously conducted by Herceg [4]. The fracture surfaces of the HCs were produced by mode I DCB test as detailed in Section 5.2.1.
Figure 5-6: Micrographs of Hetero (5:1, 2.2 wt% E CNTs) taken using (a) typical secondary electron detector (SE2), and (b) In-lens detector taken at identical site. Crack growth was from left to right.
Chapter 6: Experimental Results

This Chapter presents the results of the characterisation methods on the hierarchical composites (HCs) as described in Chapter 5. Critical findings on the exhibited physical and mechanical properties by the hierarchical composites (HCs) were highlighted. The quality of composite production in comparison to the previous production methods [4] were assessed. Dynamic scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to determine the extent of the curing and consolidation. The mechanical properties characterised included Mode I fracture toughness, short beam shear strength, and flexure modulus. Other properties such as through-thickness electrical and thermal conductivity were also measured to determine the multifunctionality imbued upon the composites by the inclusion of CNTs. Detailed fractography using optical and scanning electron microscopy highlighted notable morphologies which were used to interpret the observed mechanical behaviour.

6.1 Manufacturing quality of the composite

This study had utilised a powder impregnation route to produce the HCs as detailed in Section 4.2.2. The slurry suspensions for the powder impregnation were produced by dispersing nanocomposite powder into water. This nanocomposite was manufactured via extrusion mixing followed by jet milling into powder form as detailed in Section 4.2.1.

6.1.1 The particle size analysis

After jet-milling, the powder particle size distribution (Figure 6-3) showed that 90% of the particles had a diameter ($D_{90}$) of less than 26 µm; which is significantly smaller than
the D$_{90}$ value of 100 µm obtained previously via cryomilling. The average particle size (D$_{50}$) for the jet milled powder was 10.8 ± 0.5 µm in comparison to the 26.8 ± 1.7 µm from the cryomilling process [4]. The distribution of the particle size have a lead-in due to the usage of a filter during milling process ensuring only particles with certain size (~ 20 µm) passing through prior to collection.

As discussed in the literature review, the inclusion of CNTs would significantly increase the viscosity of the nanocomposites even at CNTs loading as low as 5 wt% [182]. Therefore if was proposed [4] that instead of homogeneous matrix flow (Figure 6-1, the top two images), the compressive load during consolidation had actually forced the resin out of the particle into the interstitial space between particles (Figure 6-1, the bottom two images). This behaviour then generates CNTs rich regions which was highly influence by the particle size of the nanocomposite powder surrounded by resin rich areas as shown in Figure 6-2 [4].

![Diagram for mechanism that gave rise to quasi-grain boundary morphology due to relative nanotube density.](image)

Figure 6-1: Diagram for mechanism that gave rise to quasi-grain boundary morphology due to relative nanotube density.
Therefore the smaller particle size powder from the jet milling process was expected to facilitate a better CNTs distribution within the composites. The ideal powder size and distribution is discussed in the upcoming Section 7.2.
6.1.2 Fibre volume fraction via gravimetric estimation

The fibre volume fractions of the uncured, melt-pressed HC laminas were estimated prior to laminating, as detailed in Section 4.2.2. The fibre volume fraction was between 50 to 57% for all the laminas. The laminas with 55 ± 1% fibre volume fraction were laid up close to the mid plane while laminas with lower fibre volume fraction were used in the outer plies during laminate stacking. This layup allowed any excess resin to be bled out and kept the overall fibre volume fraction consistent between the laminates.

6.1.3 Curing of the HCs

6.1.3.1 Differential scanning calorimetry (DSC)

The curing cycle of the NC was investigated to ensure that the HC laminates were fully cured after vacuum assisted hot pressing. The previous study [4] had cured the laminates at 150°C overnight, however DSC results from the current study using the same thermoset system showed that the exothermic cross-linking reaction between the epoxy and the hardener particles initiated at a temperature above 160 °C as shown by Figure 6-4.

![Figure 6-4: A representative image of the exothermic reaction from the nanocomposite powder during the DSC cycle.](image-url)
Therefore, the curing temperature for the HCs in this study was elevated to 165°C from 150°C [4] as a precautionary action to ensure fully cured HCs were manufactured. Further investigation regarding the curing and consolidation of the HCs was conducted via dynamic mechanical thermal analysis (Section 6.1.3.2).

6.1.3.2 Dynamic mechanical thermal analysis (DMTA)

A representative DMTA result from the HCs is shown in Figure 6-5. The tan δ plot versus temperature sweep exhibited a single peak showing that a fully cured composite was manufactured during processing in comparison to the previous processing method [4] which had exhibited multiple peaks and broadening due to inadequate curing.

![Figure 6-5: Comparison of the tan delta curves derived from DMTA measurements, between the HCs cured with the revised curing cycle and the previous curing cycle [4].](image)

The inclusion of CNTs did not influence the glass transition temperature of the HCs (Figure 6-6). The glass transition temperature determined as the peak of tan delta remained within the margin of error of the control (0 wt%\text{E}) composites at 126 ± 1.2°C.
6.2 Physical characterisation

The physical properties measured were comprised of the constituent volume fractions, bulk densities, through-thickness electrical conductivity and through-thickness thermal conductivity. The constituents of the HCs were separated into three sections, the fibre volume fraction which is comprised of solely carbon fibres, the matrix volume fraction which is comprised of the epoxy, hardener and CNTs, and the void volume fractions which are the areas devoid of materials. Furthermore, the through-thickness thermal diffusivity and the heat capacity of the HCs was measured and then used to determine the through-thickness thermal conductivity.

6.2.1 The constituent volume fractions

As shown in Table 6-1, the HCs had fibre volume fractions of between 50 - 55% and the matrix volume fraction of between 42 to 49% while the void content was determined to have been less than 2.0%. However, the HC manufactured from homogeneous (25.0 wt% E CNT) powder had contained a void content of 3.75%.
Table 6-1: The fibre, matrix and void volume fractions for the HCs (with standard deviations shown).

<table>
<thead>
<tr>
<th>Matrix type for HCs</th>
<th>Fibre volume, $v_f$ (%)</th>
<th>Matrix volume, $v_m$ (%)</th>
<th>Void content, $v_v$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt%$_E$ CNTs)</td>
<td>54.3 ± 0.4</td>
<td>45.5 ± 0.5</td>
<td>0.2 ± 0.2</td>
</tr>
<tr>
<td>Homo (2.5 wt%$_E$ CNTs)</td>
<td>51.1 ± 0.2</td>
<td>48.8 ± 0.3</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Homo (5.0 wt%$_E$ CNTs)</td>
<td>52.7 ± 0.2</td>
<td>45.6 ± 0.4</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>Homo (10.0 wt%$_E$ CNTs)</td>
<td>55.2 ± 0.2</td>
<td>42.8 ± 0.3</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td>Homo (25.0 wt%$_E$ CNTs)</td>
<td>49.6 ± 0.1</td>
<td>46.7 ± 0.2</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt%$_E$ CNTs)</td>
<td>52.4 ± 0.3</td>
<td>47.1 ± 0.5</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$_E$ CNTs)</td>
<td>53.0 ± 0.2</td>
<td>45.2 ± 0.2</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$_E$ CNTs)</td>
<td>52.4 ± 0.3</td>
<td>46.7 ± 0.4</td>
<td>0.9 ± 0.1</td>
</tr>
</tbody>
</table>

6.2.2 Bulk densities of the HCs

The densities as measured by the pycnometer as described in Section 4.1.2 are summarised in Table 6-2. The results showed that there was no significant change to the bulk density with the addition of CNTs. However, since there was a significant variation to the fibre content as shown in Table 6-1, the true contribution from the CNTs to the HC densities were not established.

Table 6-2: The densities of the HCs

<table>
<thead>
<tr>
<th>Matrix type for the HCs</th>
<th>Measured density, $\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt%$_E$ CNTs)</td>
<td>1.510 ± 0.002</td>
</tr>
<tr>
<td>Homo (2.5 wt%$_E$ CNTs)</td>
<td>1.498 ± 0.002</td>
</tr>
<tr>
<td>Homo (5.0 wt%$_E$ CNTs)</td>
<td>1.504 ± 0.001</td>
</tr>
<tr>
<td>Homo (10.0 wt%$_E$ CNTs)</td>
<td>1.525 ± 0.001</td>
</tr>
<tr>
<td>Homo (25.0 wt%$_E$ CNTs)</td>
<td>1.495 ± 0.001</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt%$_E$ CNTs)</td>
<td>1.501 ± 0.001</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$_E$ CNTs)</td>
<td>1.511 ± 0.001</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$_E$ CNTs)</td>
<td>1.498 ± 0.001</td>
</tr>
</tbody>
</table>
6.2.3 Through-thickness electrical conductivity

All HCs had exhibited improved through-thickness electrical conductivity (Figure 6-7) over the control (0 wt%\( E \) CNTs) composite and a substantial conductivity improvement (356%) was achieved with the inclusion of 10.0 wt%\( E \) (2.67 vol%\( E \)) CNTs. Hetero (5:1, 2.2 wt%\( E \)) HCs however, exhibited a slightly lower through thickness electrical conductivity improvement in comparison to the other HCs. Interestingly, both the hetero 1:1 species had exhibited similar through-thickness electrical conductivity which suggest that the particle content within the sample had influenced the formation of conducting network. Further interpretation of the result is discussed in Section 7.6.

![Figure 6-7: The through-thickness electrical conductivity of the HCs.](image)

6.2.4 Through-thickness thermal conductivity

Through-thickness thermal diffusivity

The through-thickness thermal conductivity is a direct product of the through-thickness thermal diffusivity, heat capacity and density. The through-thickness thermal diffusivity, as measured using the method described in Section 4.1.8, had increased with the inclusion of CNTs within the matrix (Table 6-3). Further increase in the CNTs content had further increased the diffusivity. However, the diffusivity dropped with the inclusion of 25.0 wt%\( E \) CNTs which was attributed to the voidage in this HC. The distribution of the CNTs in
the HCs, either homogeneously or heterogeneously dispersed, did not appear to influence the through-thickness thermal diffusivity.

Table 6-3: Through-thickness thermal diffusivity of the HCs

<table>
<thead>
<tr>
<th>Matrix type for the HCs</th>
<th>Through-thickness thermal diffusivity, $\alpha_{\text{thermal}}$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt%$E$ CNTs)</td>
<td>0.46 ± 0.005</td>
</tr>
<tr>
<td>Homo (2.5 wt%$E$ CNTs)</td>
<td>0.52 ± 0.011</td>
</tr>
<tr>
<td>Homo (5.0 wt%$E$ CNTs)</td>
<td>0.52 ± 0.008</td>
</tr>
<tr>
<td>Homo (10.0 wt%$E$ CNTs)</td>
<td>0.63 ± 0.013</td>
</tr>
<tr>
<td>Homo (25.0 wt%$E$ CNTs)</td>
<td>0.53 ± 0.011</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt%$E$ CNTs)</td>
<td>0.53 ± 0.011</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$E$ CNTs)</td>
<td>0.59 ± 0.014</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$E$ CNTs)</td>
<td>0.53 ± 0.010</td>
</tr>
</tbody>
</table>

Heat Capacity (Cp) at 25°C

The heat capacity of the composites (Table 6-4) remained consistent within the margin of error at 1.57 ± 0.12 J/°C. Heterogeneity in the HCs did not measurably affect the heat capacity of the HCs.

Table 6-4: Heat Capacity (Cp) at 25 °C of the HCs

<table>
<thead>
<tr>
<th>Matrix type for the HCs</th>
<th>Heat Capacity (Cp) at 25 °C (J/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt%$E$ CNTs)</td>
<td>1.59 ± 0.064</td>
</tr>
<tr>
<td>Homo (2.5 wt%$E$ CNTs)</td>
<td>1.64 ± 0.087</td>
</tr>
<tr>
<td>Homo (5.0 wt%$E$ CNTs)</td>
<td>1.67 ± 0.154</td>
</tr>
<tr>
<td>Homo (10.0 wt%$E$ CNTs)</td>
<td>1.36 ± 0.129</td>
</tr>
<tr>
<td>Homo (25.0 wt%$E$ CNTs)</td>
<td>1.68 ± 0.065</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt%$E$ CNTs)</td>
<td>1.46 ± 0.176</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$E$ CNTs)</td>
<td>1.47 ± 0.143</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$E$ CNTs)</td>
<td>1.69 ± 0.103</td>
</tr>
</tbody>
</table>
Through-thickness thermal conductivity

All HCs exhibited increased in through-thickness thermal conductivity (Table 6-5 and Figure 6-8) over the control (0 wt% \( \text{E} \) CNT). No significant further change was observed with increased CNT content or heterogeneity, due to the scatter in the results. Furthermore, the conductivity was highly influenced by the fibre content in the specimen. The Hetero (1:1, 2.5 wt% \( \text{E} \) CNTs) had a slightly lower conductivity although still within the scatter which can be attributed to the lower fibre volume fraction of this sample as shown in Section 6.2.1. Further interpretation of the result is discussed in Section 7.7.

Table 6-5: Through-thickness thermal conductivity of the HCs

<table>
<thead>
<tr>
<th>Matrix type for the HCs</th>
<th>Through-thickness thermal conductivity, ( K^s_{22} ) (Wm(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt% ( \text{E} ) CNTs)</td>
<td>1.10 ± 0.046</td>
</tr>
<tr>
<td>Homo (2.5 wt% ( \text{E} ) CNTs)</td>
<td>1.28 ± 0.073</td>
</tr>
<tr>
<td>Homo (5.0 wt% ( \text{E} ) CNTs)</td>
<td>1.30 ± 0.121</td>
</tr>
<tr>
<td>Homo (10.0 wt% ( \text{E} ) CNTs)</td>
<td>1.30 ± 0.127</td>
</tr>
<tr>
<td>Homo (25.0 wt% ( \text{E} ) CNTs)</td>
<td>1.34 ± 0.059</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt% ( \text{E} ) CNTs)</td>
<td>1.17 ± 0.142</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt% ( \text{E} ) CNTs)</td>
<td>1.31 ± 0.131</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt% ( \text{E} ) CNTs)</td>
<td>1.34 ± 0.086</td>
</tr>
</tbody>
</table>

Figure 6-8: The through-thickness thermal conductivity of the HCs.
6.3 Mechanical characterisation

The fracture toughness of the HCs was characterised with DCB tests. The result of this test was analysed by plotting the load-displacement curves and the toughness against crack propagation curves (R-curves). These curves would characterise the fracture behaviour of the HCs such as stable propagation with localised slip stick behaviour. The flexural modulus obtained from this DCB test was also presented to ensure that the fibre dominated properties had remained undisturbed and comparable to that reviewed in the literature. The interlaminar shear strength (ILSS) of the HCs was represented by the short beam shear test characterising the fibre/matrix interphase property of the HCs.

6.3.1 Double cantilever beam (DCB) test

Fracture toughnesses measured from the DCB tests were partitioned into two parameters, the initiation fracture toughness and the propagation fracture toughness, as described in Section 5.2.1. The fracture toughness for an absolute crack length at 64 mm amongst the various matrices were also presented as a comparison to the propagation fracture toughness [183].

6.3.1.1 Load versus displacement curves

Representative load versus displacement curves for the DCB tests in which the crack front had progressed 25 mm from the pre-crack is shown in Figure 6-9 (homogenous HCs) and Figure 6-10 (heterogeneous HCs). The heterogeneous HCs had exhibited relatively longer displacements and higher load to grow the same crack length in comparison to the homogeneous HCs and the control (0 wt% E) composites. The crack tip also initiated earlier in the control (0 wt% E) composite in comparison to the HCs. However the initiation for the homogeneous 25 wt% E HC was lower compared to that of the other HCs configurations.
Figure 6-9: Load versus displacement curves for the DCB tests for representative homogeneous HC specimens.

Figure 6-10: Load versus displacement curves for the DCB test for representative heterogeneous HC specimens.

The load and displacement curves for representative HC specimens with similar CNTs loadings showing the variability of test results between nominally identical specimens.
is shown by Figure 6-11 and Figure 6-12. The load versus displacement for specimens with a homogeneous CNTs distribution of 2.5 wt%\(E\) CNTs loading is presented in Figure 6-11 while the response for a heterogeneous CNT distribution with a gross CNT loading of 2.2 wt%\(E\) is presented in Figure 6-12. Comparing the curves of the samples, the responses exhibited by the samples were consistent in shape and features in both cases for homogeneously and heterogeneously dispersed CNTs in the HCs. Some of the samples exhibited sharp drops in the load during crack propagation which is a characteristic of slip-stick growth as noted in the figures. However this slip-stick growth is not representative of the intermittent bonding via the heterogeneity due to the difference in the observable length scale. The heterogeneity was engineered at the length scale of the powder size which had a maximum length of typically less than 40 µm (Hetero (5:1, 2.2 wt%\(E\) CNTs)).

Both the R-curves in Figure 6-11 and Figure 6-12 had exhibited slight variation in the compliance of the elastic region. These variations were attributed to the localised in-plane fibre waviness from the wet filament winding method utilised as the production method. Furthermore, the transition of load after initiation was smooth on both homogenous and heterogeneous distribution of CNTs.

Figure 6-11: DCB load versus displacement curves for Homo (2.5 wt%\(E\) CNTs) HCs.
6.3.1.2 Mode I Fracture Toughness

The typical fracture toughness against crack length response (R-curves) for all the matrix configurations are shown in Figure 6-13 (homogeneous), Figure 6-14 (heterogeneous) and the results were tabulated in Table 6-6. These plots mostly demonstrated stable crack propagation with some degree of fibre bridging apart from the control (0 wt%\textsubscript{E} CNTs) composite which exhibited unstable crack growth. The stability of crack growth was determined by the gradient of the R-curves from the initial crack initiation until the crack had propagated. Most of the R-curves are almost level however the R-curves for the control (0 wt%\textsubscript{E} CNTs) composite and Homo (25.0 wt%\textsubscript{E} CNTs) composite continuously increased over the crack length.
Figure 6-13: Mode I fracture toughness against crack length from representative DCB tests with homogeneous CNT distributions.

Figure 6-14: Mode I fracture toughness against crack length from representative DCB tests with heterogeneous CNT distributions.
Table 6-6: Mode I fracture toughness of the HC specimens (with standard deviation shown).

<table>
<thead>
<tr>
<th>Matrix type for HCs</th>
<th>Mode I fracture toughness</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initiation fracture toughness, $G_{Ic}$ (Jm$^2$)</td>
<td>Difference from control (%)</td>
</tr>
<tr>
<td>Control (0 wt%$_E$ CNTs)</td>
<td>601 ± 23</td>
<td>-</td>
</tr>
<tr>
<td>Homo (2.5 wt%$_E$ CNTs)</td>
<td>634 ± 9</td>
<td>6</td>
</tr>
<tr>
<td>Homo (5.0 wt%$_E$ CNTs)</td>
<td>674 ± 7</td>
<td>12</td>
</tr>
<tr>
<td>Homo (10.0 wt%$_E$ CNTs)</td>
<td>623 ± 10</td>
<td>4</td>
</tr>
<tr>
<td>Homo (25.0 wt%$_E$ CNTs)</td>
<td>376 ± 57</td>
<td>-38</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt%$_E$ CNTs)</td>
<td>636 ± 27</td>
<td>6</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt%$_E$ CNTs)</td>
<td>721 ± 22</td>
<td>20</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt%$_E$ CNTs)</td>
<td>817 ± 6</td>
<td>36</td>
</tr>
</tbody>
</table>

**Mode I fracture toughness (initiation)**

The control (0 wt%$_E$ CNTs) composite exhibited an initiation fracture toughness of 601 ± 23 Jm$^2$. The inclusion of CNTs into the composites had improved the initiation fracture toughness for all types of HCs with the exclusion of those manufactured from 25.0 wt%$_E$ CNT powder. The homogeneous matrix HCs displayed a maximum increase in initiation fracture toughness at 5.0 wt%$_E$ CNTs content (+12%) but at higher loadings, the initiation fracture toughness declined (Figure 6-15).

The Hetero (5:1, 2.2 wt%$_E$ CNTs) composite exhibited a significant 36% (817 ± 6 Jm$^2$) enhancement in initiation fracture toughness (Figure 6-15 and Figure 6-16 ) in comparison to the control (0 wt%$_E$ CNTs) composite. Comparatively, the homogeneous HCs with 2.5 wt%$_E$ exhibited a fracture toughness of 634 ± 9 Jm$^2$. Hence the heterogeneously dispersed CNTs HCs were 29% higher in toughness compared to that of homogeneously dispersed CNTs HCs.

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Figure 6-15: Mode I initiation fracture toughness for the HCs.

Figure 6-16: Comparison of the initiation fracture toughness for different HCs.
However, using the matrix components (0 wt% and 5 wt% CNTs) at a 1:1 ratio to produce a similar average loading of 2.5 wt% CNTs [Hetero (1:1; 2.5 wt%)] yielded the same initiation fracture toughness as that of the homogeneous 2.5 wt% matrix. A detailed discussion regarding these trends of fracture toughness in light of the fractography is presented in Section 6.2.

**Mode I fracture toughness (propagation)**

All the HCs exhibited increased propagation fracture toughness in comparison to the initiation fracture toughness (Table 6-6) with the exception of the Hetero (5:1; 2.2wt%) HCs for which it remained unchanged (Figure 6-17). In comparison, the control (0 wt% CNTs) HC exhibited a 21% increase in propagation fracture toughness (726 ± 45 Jm⁻²) as compared to the initiation fracture toughness. Although the propagation fracture toughness for Hetero (5:1; 2.2 wt%) had not increased, the values were still higher than that of the control (0 wt% CNTs) HC and Hetero (1:1; 2.5 wt%) HC as shown in Figure 6-18.

![Figure 6-17](image)

Figure 6-17: Mode I propagation fracture toughness for the HCs averaged over 25 mm of crack propagation beyond the initial pre-crack length.
Figure 6-18: Comparison between the averaged propagation fracture toughness for different HCs.

\textit{Mode I fracture toughness (propagation) at crack length of 64 mm}

Displacements of the insert film during laminate lay-up generated a slight variation of insert length between HC samples. Furthermore, the unstable nature of the HCs pre-cracking generated slight variation to the absolute pre-crack length. An absolute crack length of 64 mm was chosen as the reference point since this point was commonly shared between all the samples and the crack front had sufficiently propagated through the laminate to have reached a steady state condition.
Figure 6-19: Mode I fracture toughness of the HCs at 64 mm crack length.

The Mode I fracture at an absolute crack length of 64 mm is shown by Figure 6-19 and Figure 6-20. In comparison to the averaged propagation fracture toughness as detailed previously, the fracture toughness at the absolute crack length of 64 mm provided an indication as to which composites possessed a weak fibre/matrix interphase, since these toughnesses constituted a larger contribution from the fibre bridging. This higher degree of fibre bridging was exemplified by the control (0 wt% CNTs) composite which has exhibited propagation fracture toughness at 64 mm crack length of $807 \pm 67 \text{ Jm}^{-2}$ which was a 34% increase in fracture toughness in comparison to the initiation values. Other HCs exhibited only a minor increase in the fracture toughness over the same change in crack length.
6.3.1.3 Flexural Modulus

The flexural modulus of the arms from the DCB test were obtained using Equation 5-12 as detailed in Section 4.1.7 and are tabulated in Table 6-7. The flexural modulus of the HCs was unaffected by the inclusion of homogeneously dispersed CNTs within the matrix. Surprisingly, the flexural modulus for Hetero (1:1, 2.5 wt%\textsubscript{E} CNTs) and Hetero (1:1, 7.5 wt%\textsubscript{E} CNTs) was superior to that of the control (0 wt%\textsubscript{E} CNTs) composite with 16% and 14% increases, respectively, as shown in Figure 6-21.

Both of these heterogeneous mixtures of HCs were manufactured as the last batch of samples, where the handling process of the plies was slightly altered. In earlier batches, the prepreg plies that were wound on the filament winding drum were axially cut and then scrape onto a metal plate. This process had required two people to either hold the plate or scrape the plies. On the last two batches, modifications were made to allow the process being run by a single person. This modification was done by removing the drum completely from the filament winder and then unrolling the plies onto the plate. The slight pressure during the unrolling process might have induced better fibre alignment in the prepreg which then
translated to superior flexural. The flexural moduli were normalised to 60% fibre volume fraction to permit direct comparison between the HCs.

Figure 6-21: Flexural moduli for the DCB specimens normalised to 60% fibre volume fraction.

Table 6-7: Flexural moduli for the arms of DCB specimens.

<table>
<thead>
<tr>
<th>Matrix type for HCs</th>
<th>$E_f$(GPa)</th>
<th>$E_f$(GPa) normalised to 60% $v_f$ (\frac{E_f}{v_f} \times 60%)</th>
<th>Improvement over control (0 wt% E CNTs) composite(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (0 wt% E CNTs)</td>
<td>100.4 ± 6.2</td>
<td>111.1 ± 6.9</td>
<td>-</td>
</tr>
<tr>
<td>Homo (2.5 wt% E CNTs)</td>
<td>95.4 ± 5.1</td>
<td>112.1 ± 6.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Homo (5.0 wt% E CNTs)</td>
<td>96.4 ± 1.8</td>
<td>109.8 ± 2.0</td>
<td>-1.1</td>
</tr>
<tr>
<td>Homo (10.0 wt% E CNTs)</td>
<td>104.4 ± 4.2</td>
<td>113.6 ± 5.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Homo (25.0 wt% E CNTs)</td>
<td>91.5 ± 9.4</td>
<td>110.7 ± 11.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>Hetero (1:1, 2.5 wt% E CNTs)</td>
<td>112.4 ± 5.4</td>
<td>128.8 ± 6.2</td>
<td>15.9</td>
</tr>
<tr>
<td>Hetero (1:1, 7.5 wt% E CNTs)</td>
<td>111.4 ± 10.8</td>
<td>126.1 ± 12.2</td>
<td>13.6</td>
</tr>
<tr>
<td>Hetero (5:1, 2.2 wt% E CNTs)</td>
<td>92.0 ± 2.1</td>
<td>105.3 ± 2.4</td>
<td>-5.2</td>
</tr>
</tbody>
</table>
6.3.2 Short Beam Shear Strength

The control (0 wt% CNTs) composite exhibited an interlaminar shear strength (ILSS) of 62 ± 1 MPa which was low in comparison to the commercially available toughened prepregs system such as Hexcel HexPly M21 (110 MPa) [142] and Hexcel HexPly M91 (105 MPa) [143]. These commercial prepregs exhibited a higher ILSS due to the interply resin layer toughening from the inclusion of the toughening agents within the prepregs. The HCs failure modes were inspected to be either at the mid-plane or at the edge of the samples via delamination as shown by Figure 6-22. Samples which had exhibited compression or flexural failure were discarded from the test results.

![Figure 6-22: The short beam shear test failure modes exhibited by valid samples [127].](image)

As can be seen in Figure 6-23, the highest improvement in ILSS over the control (0 wt% CNTs) composite was exhibited by the homogeneous matrix HC with 5.0 wt% CNTs at 32% (81 ± 1 MPa) but the ILSS was reduced subsequently with the further addition of CNTs. Homo (2.5 wt% CNTs) HC exhibited ILSS of 77 MPa and the heterogeneity within the matrix had not influenced the ILSS as shown by both Hetero (5:1; 2.2 wt%) and Hetero (1:1; 2.5 wt%) mixtures which contained similar CNTs loading and had ILSS, of 77 ± 1 MPa and 74 ± 1 MPa respectively.
Figure 6-23: Interlaminar shear strengths (ILSS) of the HCs.

Figure 6-24: ILSS for different HCs.
6.4 Fractography

The polished cross section and fracture surface morphology of the composites were investigated via optical microscopy and scanning electron microscopy (SEM) respectively. The optical microscopy was utilised to examine the interply interface, void distributions and ply waviness of the composite whilst the SEM fractography was utilised to examine the fracture mechanisms associated with the inclusion of CNTs.

6.4.1 Optical Microscopy

Micrographs from polished cross sections of the HCs (Figure 6-25, Figure 6-26 and Figure 6-27) show that the resin interply rich zones between plies were not present in comparison to conventional industrial prepregs. The adjacent plies were observed to have nested with each other despite the layup of [+3°, -3°] at the mid-plane, thus resulting in fibres bridging across the ply interface. The micrographs of Homo (25.0 wt%$_E$ CNTs) (6.14 vol%$_C$) HC demonstrated significant voidage at the critical mid-plane interface. Control (0 wt%$_E$) composite and Homo (2.5 wt%$_E$ CNTs) (0.70 vol%$_C$) HC also contained voids, although they were distributed away from the critical mid-plane interfaces.
Figure 6-25: Polished cross sections of the HCs. [1.25x]
Figure 6-26: Polished cross sections of the HCs. [20x]
Figure 6-27: Polished cross sections of the HCs. [50x]
6.4.2 Scanning Electron Microscopy

Electron microscopy was utilised to study the fracture morphology of the nanocomposites and the HCs. It also provides a qualitative indication of the CNT distribution. The samples were sputter coated with 5-10 nm thick layer of chromium to improve the electron conductivity. The imaging was conducted at 5kV voltage and between 5-6 mm working distance. The fracture surface for the ILSS samples could not be obtained due to the excessive fibre bridging which prevented a complete delamination of the laminates after testing.

*Micrograph of the extruded nanocomposite (NC)*

Good CNT dispersions had been achieved at low CNT content using a conventional liquid sonification route however a good dispersion was obtained at much higher CNT loadings using high shear extrusion. All the CNT loadings had dispersed uniformly in the matrix without any CNTs agglomerates of CNTs apparent (Figure 6-28 to Figure 6-32); in collaboration with Herceg [4]. These micrographs were taken from fractured nanocomposite ‘dog-bone’ tensile specimens.

Therefore locally homogenised CNTs distribution was achieved within the extruded nanocomposite. Furthermore, even after the nanocomposites were powderised by the milling process, the distribution of CNTs within each of the powder particles was expected to be well dispersed hence the heterogeneity observed in the HCs afterwards was a product of the engineered powder mixtures.
Figure 6-28: The dispersion of CNTs in the homogeneous 2.5 \textit{wt}\% \textit{Fe} nanocomposite. (50k x)

Figure 6-29: The dispersion of CNTs in the homogeneous 5.0 \textit{wt}\% \textit{Fe} nanocomposite. (50k x)
Figure 6-30: The dispersion of CNTs in the homogeneous 10.0 wt%\(_E\) nanocomposite. (50k x)

Figure 6-31: The dispersion of CNTs in the homogeneous 15.0 wt%\(_E\) nanocomposite. (50k x)
Figure 6-32: The dispersion of CNTs in the homogeneous 25.0 wt% _E_ nanocomposite.(50k x)

**Micrographs of DCB samples**

Micrographs of the control (0 wt% _E_ CNTs) matrix which had fully wetted the fibres are shown in Figure 6-33; i.e. there were no interfacial voids apparent. The presence of riverlines (Figure 6-33 to Figure 6-36) after crack propagation shows that the crack had initiated at the fibre/matrix interphase and subsequently propagated into the matrix. However, in places the fracture surface had exhibited clean carbon fibre surfaces and smooth fibre tracks (Figure 6-37 and Figure 6-38). Further examination of the interfacial debonding on the fibre/matrix interphase, as highlighted by Figure 6-40a, suggests that the interphase strength was poor. However, this figure also shows that the crack tip was driven into the matrix from the interphase. At the end of crack propagation during DCB test (i.e after 25 mm crack propagation) there were significant broken fibres which were attributed to the nesting of the tows at the mid-plane of the sample for all of composite specimens regardless of CNTs content (Figure 6-41a).
Figure 6-33: Riverlines exhibited by the control (0 wt%\textsubscript{E} CNTs) composite during crack propagation. Crack growth was from left to right. (5000x)

Figure 6-34: Riverlines exhibited by the 2.5 wt%\textsubscript{E} CNTs HC during crack propagation. Crack growth was from left to right. (5000x)
Figure 6-35: Riverlines exhibited by the 5.0 wt% CNTs HC during crack propagation. Crack growth was from left to right. (5000x)

Figure 6-36: Riverlines exhibited by the 10.0 wt% CNTs HC during crack propagation. Crack growth was from left to right. (5000x)
Introduction of homogeneous CNT reinforcement (Figure 6-39b, Figure 6-40b) at 2.5 wt% CNT presented a similar fracture morphology to that of the control (0 wt% CNTs). Clean carbon fibre surfaces, smooth fibre tracks and interfacial debonding (Figure 6-40b) indicated that the crack had mainly propagated through the fibre/matrix interphase. However the matrix surface exhibited a rougher surface than the control (0 wt% CNTs) which indicated a more tortuous fracture path. Similarly to the control (0 wt% CNTs) composite, significant broken fibres were observed after 25 mm crack propagation indicating fibre bridging mechanisms had dominated.

However, engineered heterogeneity within the distribution of the CNTs presents a different fracture morphology to that of the control (0 wt% CNTs) composite and homogeneous HCs. The fracture surface (Figure 6-39c, Figure 6-40c) was almost exclusively covered in matrix indicating the crack front had mainly propagated cohesively within the matrix. Figure 6-40c showed that the crack front was driven into the matrix from the surface of the fibres which resulted in a higher tortuosity in the fracture surface. Images at lower magnification (Figure 6-42) further emphasize the different topography of the fracture surface between the control (0 wt% CNTs) and homogeneous HCs to that of heterogeneous HCs. Despite the gross content of CNTs being almost identical, the homogeneous HCs exhibited a largely interfacial failure while the heterogeneous matrix exhibited predominantly cohesive failure in the matrix.
Figure 6-37: Fracture surface showing clean carbon fibre for homogenous 2.5 wt%$_E$ CNTs HC. Crack growth was from left to right. (10k x)

Figure 6-38: Fracture surface showing smooth fibre tracks for Homogenous 10.0 wt%$_E$ CNTs HC. Crack growth was from left to right. (10k x)

The microstructural fracture mechanism exhibited by the Hetero (5:1, 2.2 wt%$_E$ CNTs) HC is shown by Figure 6-43(a) and (b). The presences of the parabolas indicate that
the crack front was deflected during crack propagation and the textured microflow (Figure 6-43b) further increased the tortuosity of the fracture surface. Homo (25.0 wt% _E_ CNTs) HC had exceeded the processing limit of the processing method as exhibited by Figure 6-43c. The re-agglomeration of CNTs within the matrix resulted in a poor consolidation of the HC. Furthermore the excessive visco-elasticity of the matrix had prevented the resin to flow thus resulting in morphology of merged matrix globules. The stitched images of multiple SEM micrographs of the fractured surface after DCB testing for different CNT configurations are shown in Figure 6-44. These stitched images show that the fracture morphologies were representative throughout the cross-sections of the samples as discussed previously.

### 6.5 Summary

This Chapter has presented the experimental results of the HCs from the characterisation methods described in Chapter 5. Improvements over the control (0 wt% _E_ CNTs) composite were generally exhibited by the HCs in both physical and mechanical properties. The heterogeneous distribution of CNTs in the HCs had no detrimental effects on the properties of the HCs. Furthermore, the engineered heterogeneity on the HCs has further improved the fracture toughness of the HCs. Fractography of these fractured surfaces showed that the morphology was transformed from interfacial failure in the homogeneous HCs to cohesive failure in the heterogeneous HCs. Detailed discussion regarding the property improvements are contrasted with the findings in the literature review is presented in Chapter 7.
Figure 6-39: Micrographs of the HCs following 1 mm of crack growth. Crack growth was from left to right. (1000x)
Figure 6-40: Micrographs of the HCs following 1 mm of crack growth (initiation). Crack growth was from left to right. (5000x)
Figure 6-41: Micrographs of the HCs following 25 mm of crack growth. Crack growth was from left to right. (1000x)
Figure 6-42: Low resolution micrograph of the fracture surfaces of: (a) Control (0 wt%\textsubscript{E} CNTs) composite, (b) Homo (2.5 wt%\textsubscript{E} CNTs) HCs, (c) Hetero (5:1, 2.2 wt%\textsubscript{E} CNTs) HCs, following 1 mm of crack growth. Crack growth was from left to right. (100x)
Figure 6-43: Different fracture mechanisms from the (a), (b) Hetero (5:1, 2.2 wt%$_E$ CNTs) HCs, (c) Homo (2.5 wt%$_E$ CNTs) HCs and (d) Homo (25.0 wt%$_E$ CNTs) HCs. Crack growth was from left to right.
Figure 6-44: Stitched micrographs of fracture surfaces after DCB test; a) Control (0.0 wt%<sub>E</sub> CNTs) composite, b) Homo (2.5 wt%<sub>E</sub> CNTs) HC, c) Hetero (5:1, 2.2 wt%<sub>E</sub> CNTs) HC.

Crack growth was from left to right.
Chapter 7 : Discussion

This Chapter discusses and interprets the test results as detailed in Chapter 6 in light of the background literature and draws inferences from these results. Optimisation of the processing method was achieved and the quality of the composites obtained from this processing method were compared to those from previous studies. The effects of the inclusion of the CNTs on the mechanical, electrical and thermal properties were considered and interpreted. The fracture mechanisms presented by the fracture surfaces of the DCB samples were investigated and linked to the observed mechanical performance.

7.1 Acid digestion and the composite constituents

The acid digestion method used to evaluate the constituent volume fractions of the HCs demonstrated that the CNTs were not digested during composite digestion (Figure 7-1). The CNTs therefore remained with the undigested fibres and were then filtered together. The content of the CNTs were estimated with the assumption of negligible CNTs loss during processing. These were added to the digested resin weight to obtain the total weight of the nanocomposite matrix (the CNTs were considered part of the matrix in this study). Following process optimisation, the fibre volume fraction of the HCs was consistently between 50-55% with void contents less that 2 % apart from the Homo (25.0 wt%$_E$ CNTs) HC, which contained 3.8 % void content.

Attempts were made to directly measure the CNTs content within the HCs after a complete processing cycle. A Raman spectra analysis as used by Qian et al [75] was explored as a possible technique but this method encountered a problem in which the Raman spectrum
of the CNTs was identical to the Raman spectrum of the carbon fibres. A direct measurement using thermogravimetric analysis (TGA) was proposed in accordance with the methodology explored in nanocomposites research in the previous study [4]. However the CNT content was at the limit of the TGA analyser (~0.1 µg). The iron content in the CNTs was marked as a possible signature for the CNTs as stipulated by the manufacturer in Section 4.1.3. Attempts were made to completely dissolve the HCs in strong acid and then de-couple the iron from the CNTs into the acid solution. After neutralising the acid, the solution was analysed using inductively coupled plasma mass spectrometry (ICP-MS) [184] which measured the iron content. However a complete de-coupling of the iron from the CNTs was not achieved even with piranha solution or aqua regia and furthermore, the acid neutralising process diluted the solution close to the resolution of the ICP-MS equipment (~1 ppm). A possible method to conclusively measure this CNT content is by using a larger TGA which can accommodate larger samples with higher resolution.

![Image](image_url)

Figure 7-1: Acid digested composite from control (0 wt% CNTs) composite (left) and Homo (2.5 wt% CNTs) HC (right) in 500 ml conical flasks.

7.2 The mobility of the CNTs during processing

The mobility of the CNTs in the HC processing method was assessed via SEM microscopy. The CNTs were contained within regions matching the particle size as demonstrated by Figure 7-2. The cryomilled particles in the previous study [4] exhibited CNTs patches of approximately 30 µm in diameter while the jet milled particles in this study exhibited CNTs patches of approximately 10 µm in diameter. In both cases, the size of CNTs patches was dictated by the NC particle size. This observation shows the lack of mobility from the CNTs within the NCs during HC processing even with the introduction of a
relaxation period during the curing cycle. Therefore, to obtain a homogeneous distribution of CNTs within the HC, the particle size of the NC powder should be as small as possible and just limited by the carbon fibre pickup during filament winding (>5 µm) [162].

a) Cryomilled particle

![Cryomilled particle](image1)

b) Jet milled particle

![Jet milled particle](image2)

Figure 7-2: CNTs distribution within HCs from a) cryomilled particle, b) jet milled particle from 10 wt%$_{\text{E}}$ CNTs HCs composite.

Due to the lack of mobility of the CNTs, the pure resin was pressed out of the particles and filled the gaps between particles as shown by the illustration in Figure 7-3. However, the HCs with extremely high CNTs content, particularly the Homo (25.0 wt%$_{\text{E}}$ CNT) HC, were highly visco-elastic. The resin did not flow leading to HCs with globules of merged particles and voids as illustrated by Figure 6-43(d). The CNTs had inhibited the resin flow by forming percolated networks in the resin and re-agglomerating during HC processing.
Figure 7-3: Schematics of the resin flow from the nanocomposite particles during consolidation. (Not to scale)

**Engineering the CNT distribution**

The distributions of the CNTs were engineered to achieve either a homogeneous or heterogeneous distribution within the HCs. The engineered heterogeneity was achieved via a novel method by mixing the control (0 wt% CNTs) powder with NCs with varying CNT content. This mixture allowed a larger separation between CNTs rich patches as shown in Figure 7-4(d) which increased separation between patches of CNTs from the particle size (~11 µm) to approximately 40 µm. The regions between the CNTs rich patches were filled with pure resin which engineered brittle regions within the HCs.

Homo (2.5 wt% CNTs) HCs exhibited a largely homogeneous distribution of CNTs (Figure 7-4b). The relatively low quantity of CNTs within the powder particles allowed the flow of CNTs throughout the HCs with minimal visco-elasticity. However with the increased content of CNTs to 10.0 wt% , as shown in Figure 7-4(c), a slight heterogeneous distribution was observed at the length scale of the particle size. This showed that the CNTs were immobilised during processing due to the increased visco-elasticity and remained within the particles as the pure resin was forced out from the local particles. The optimum heterogeneity for the system is discussed in Section 7.5.
7.3 The CNTs filtration by the carbon fibres

CNTs filtration had occurred with the film infusion method (Section 4.2.2 (a)) regardless of the CNTs loading. The CNTs were optically observed to reside on the film surface while the pure resin had penetrated through the fibre tows. This process resulted in a composite surface where the CNTs reinforcement were abundant but lacked the presence of CNTs within the fibre tows and the opposite surface. This result was as predicted by the literature as the lowest CNTs content in the nanocomposite for this study was 2.5 wt%\textsubscript{g}. Nanoparticles filtration by the parent fibres is well documented in several studies \cite{88,169,185} in which filtration occurred at nanoparticles content as low as 0.3 wt\%\textsubscript{g} (for multiwalled CNTs), depending on the size and shape of the nanoparticles.

The presences of CNTs within the fibre tows were essential to support the fibres under compressive stress and also create a percolating conductive network between the carbon fibres for the through-thickness electrical and thermal conductivity improvement, thus imbuining multifunctionality in the HCs. Therefore the film infusion technique was discarded in favour of the wet powder impregnation in which the powder particles penetrated within the fibre tow thus dispersing the CNTs throughout the HCs and hence enhancing the intralaminar properties.

7.4 Degree of cure

The degree of cure of the HCs investigated using DSC and DMTA showed that fully cured HCs were obtained after processing. The complete curing of HCs were imperative for ensuring that the mechanical, electrical, and thermal properties measured would quantitatively represent the properties of the HCs. The fracture toughness improvement of the previous study \cite{4} was suspect due to under-curing which might have led to matrix ductility and hence not fully characterised the contribution of the CNTs.

DMT and DSC analysis also showed that the glass transition temperature of the HCs remained constant despite the inclusion of the CNTs. This unchanged glass transition temperature of the HCs suggests that the degree of cross-linking in the epoxy matrix remained constant and the mechanical, thermal and electrical improvement exhibited by the HCs could be attributed purely to the inclusion of CNTs.
Figure 7-4: The distribution of CNTs in the fibre reinforced composites. Crack growth was from left to right.
7.5 The effect of the inclusion of CNTs on mechanical properties

Significant improvements in the interlaminar shear strength (ILSS) indicate that the inclusion of CNTs had improved the interphase property between the fibre and matrix. These improvements were in line with previously reported studies as reviewed in Section 2.3.2 [65,85,86,92,120]. Coincidently, the Mode I initiation fracture toughness ($G_{IC}$) for the homogeneous HCs followed a similar trend to that of the ILSS as shown in Figure 7-5. This trend would imply that the crack path was immediately propagating on the fibre/matrix interphase after the pre-crack and therefore by improving the fibre/matrix interphase, direct improvement would be exhibited by the interlaminar fracture toughness.

![Figure 7-5: Comparative behaviour for the homogeneous HC between ILSS and initiation fracture toughness ($G_{IC}$).](image)

Fractography (Section 6.4.2) illustrated that the crack propagation within the homogeneous matrix HCs was driven along the fibre/matrix interphase which verified that the initiation fracture toughness was influenced by the interfacial performance of the HCs. With the crack front propagating within the interphase which lacked CNTs, the incorporated CNTs had not fully contributed to the fracture toughness of the HCs. For the heterogeneous HC, Hetero (5:1, 2.2 wt%$_E$), in contrast, a significant increase in the initiation fracture
toughness was exhibited without any changes to the ILSS as shown in Figure 7-6 despite the gross CNTs content having been very similar to that of the homogeneous HC.

Figure 7-6: Comparative behaviour for the HC between ILSS and initiation fracture toughness (\(G_{IC}\)). The hollow legends indicates the heterogeneous HCs.

Fractography had shown that the failure mechanism was predominantly cohesive particularly for the Hetero (5:1, 2.2 wt%\(_E\)). This HC had the highest degree of heterogeneity where the regions of CNTs rich patches were approximately 40 µm apart. The cohesive failure ensured that more CNTs within the matrix contributed to the fracture toughness of the HCs since the crack front was constrained within the matrix and not just driven to the fibre-matrix interphase. Furthermore the generated tortuosity of the crack path subsequently would have imposed local interlaminar shear loading to the crack propagation when under global Mode I loading as illustrated by Figure 7-7 and Figure 7-8. This shear loading would have provided Mode II toughening process and hence increased the overall fracture toughness.

Comparison among heterogeneous HCs shows that similar propagation fracture toughness were obtained with both Hetero (5:1, 2.2 wt%\(_E\)) and Hetero (1:1, 7.5 wt%\(_E\)) despite the latter containing a greater CNTs content. These fracture toughnesses suggests that
maximizing heterogeneity by increasing the separation of the CNTs rich regions could achieve similar propagation toughness as HCs manufactured with a higher CNTs average content. However, the internal fracture mechanics of both species were expected to be different. The Hetero (5:1, 2.2 \( \text{wt}\%_E \)) had exhibited mostly cohesive failure whilst the Hetero (1:1, 7.5 \( \text{wt}\%_E \)) had achieved a similar propagation toughness via a combination of cohesive failure and elements of fibre bridging.

a) Homogeneous HCs

![Homogeneous HCs](image)

b) Hetero (5:1, 2.2 \( \text{wt}\%_E \))

![Hetero (5:1, 2.2 \( \text{wt}\%_E \))](image)

a) Hetero (1:1, 7.5 \( \text{wt}\%_E \))

![Hetero (1:1, 7.5 \( \text{wt}\%_E \))](image)

Figure 7-7: Illustration of the fracture mechanism for the HCs. (Not to scale)

The fracture mechanisms were consistent with the intermittent debonding mechanism as reported by Atkins [26] and Favre [27]. Furthermore, the crack path tortuosity and interaction with the adjacent fibres would promote the Cook-Gordon mechanism [144] under global interlaminar Mode I fracture loading. Further interest within the study would be in predicting the optimised heterogeneity to achieve the maximum toughening potential of the
CNTs. The schematics (Figure 7-7c) illustrated that insufficient heterogeneity were generated with the CNTs patches closely packed.

Figure 7-8: Crack path deflection in Hetero (5:1, 2.2 wt%e) HCs

An estimation with Irwin’s modifications [153] (Equation 7-1) yielded an approximation of the process zone size with a radius of 39 µm in an idealised nanocomposite;

\[
r_y = \frac{1}{2\pi} \left( \frac{K}{\sigma_{ys}} \right)^2
\]

Equation 7-1

where \( r_y \) is the radius of the process zone, \( K \) is the fracture toughness of the nanocomposite under Mode I which is 1.3 MPa.m\(^{1/2} \) [4] and \( \sigma_{ys} \) is the tensile yield strength of the nanocomposite (83 MPa [4]). Although the process zones in the HCs are more complex due to the presence of the fibres, this approximation concurred with the heterogeneity distribution in Hetero (5:1, 2.2 wt%e) which had CNT rich regions spaced at about 40 µm apart (Figure 7-4(d)). The actual process zone in the hierarchical system would be expected to be smaller due to the pinning effect by the adjacent fibres. Nonetheless, the estimated value can be taken as the minimum heterogeneity distribution length to generate the tortuosity.
Crack deflection and textured microflow [1] were amongst the fracture mechanisms found on the fracture surfaces, albeit these fracture mechanisms were not limited just to CNT reinforcements. The CNTs had contributed to the toughness by pull-out, debonding and pinning mechanisms as seen in the nanocomposite study [4]. However, upon reduction of the separation distance between CNTs patches in Hetero (1:1, 2.5 wt% CNTs) which had a heterogeneity region at the length scale of the particle size, the mechanical properties appear to be similar to that of Homo (2.5 wt% CNTs) HC (Figure 7-9). One particular sample with heterogeneous HC (Figure 6-12) exhibited significant stick-slip behaviour. This was attributed to the severe fibre bridging within that particular sample and the formation of secondary delamination planes. At the point of slipping, these crack planes had converged after breaking the bridging fibres, thus releasing the load.

ILSS is known to be dictated by the fibre-matrix interface performance [1]. For example, moisture and temperature are known to reduce interfacial strength and this is
reflected in depression of ILSS. Composites with a low ILSS are more susceptible to fibre bridging as the crack propagates in Mode I thus affecting the propagation fracture toughness [183]. Fibre bridging in Mode I is associated with the process zone ahead of the crack tip extending into the plies adjacent to the interface [186,187]. Hence, the weaker the fibre-matrix interface, the greater the susceptibility to fibre bridging in Mode I. This presents an inverse relationship between severity of fibre bridging (i.e increase in $G_{IC}$ with crack length) and ILSS. This was previously demonstrated by Greenhalgh [183], and is utilised to interpret these results. The initiation fracture toughness, averaged propagation fracture toughness and ILSS can be related by normalising the fracture toughness values to each initiation value [183]. The $R_{IN}$ versus ILSS [183] was plotted in Figure 7-10;

$$R_{IN} = \frac{G_{IC,P} - G_{IC,I}}{G_{IC,I}} \times 100\%$$

where $R_{IN}$ is the normalised propagation fracture toughness to initiation fracture toughness.

This figure shows that with increased ILSS, the disparity between initiation and propagation fracture toughness was reduced. The composite manufactured with base control powder exhibited the highest normalised toughness percentage suggesting that the composite had lowest interphase properties thus promoting higher degree of fibre bridging. The composite manufactured with homogeneous 25.0 wt%$_E$ CNTs also exhibited a high normalized toughness ratio but was attributed to the presence of a high void content.
The effect of CNTs on electrical properties

The composite manufactured from the production method reported here had exhibited through-thickness electrical conductivity which was generally higher than that reported in the literature as discussed in Chapter 2. Even the control (0 wt% E CNTs) composite exhibited through-thickness electrical conductivity of 13 Sm$^{-1}$ which was an order of magnitude higher than conventional prepreg. This increase was attributed to the fibre-to-fibre contact and fibre bridging which would have significantly contributed to the conductivity (Figure 7-11). Investigation using a conventional prepreg, Hexply 914C-TS, using the same jig setup yielded a through-thickness electrical conductivity of 0.14 ± 0.02 Sm$^{-1}$ which is comparable to that reported in the literature.

This high conductivity has been observed previously [188] where it was also attributed to the high consolidation pressure during laminate production. The conductivity was further increased with the inclusion of CNTs which generated conductive electrical networks between adjacent fibres. Furthermore, the inclusion of high CNT content had offset the voidage effect for the Homo (25.0 wt% E CNTs, 6.12 vol% C) HC. The increment in CNTs content had generated higher conductive paths thus further increasing the conductivity of the HC which peaked at 10.0 wt% E CNTs (2.67 vol% C). Nonetheless, without the high
voidage content in the homo (25.0 wt% CNTs) HC, this HC could have potentially exhibited higher through-thickness electrical conductivity.

Figure 7-11: Optically imaged polished cross-section of a random sample showing the potential conductive through-thickness networks by direct contact between fibres.

The heterogeneity within the composite had slightly affected the conductivity of the composite. The density of the CNTs conductive network per unit area would have been reduced by the heterogeneity thus reducing the overall conductivity of the HCs. This density was observed to correspond to the volume of particle per area. In hetero 1:1 species, the number of particles generating the conductive path per specimen was expected to be similar regardless of overall CNT content. As a result, the through-thickness electrical conductivity for both had also remained similar. However in the hetero 5:1 specimens, the particles per unit area were less, which had translated in a slight reduction of the through-thickness electrical conductivity.

With further optimisation of the HCs processing, the through-thickness electrical conductivity could be improved further. This conductivity improvement would provide beneficial application for lightning strike protection and electro-magnetic shielding.

7.7 The effect of CNTs on thermal properties

The inclusion of CNTs into the composite had improved the through-thickness thermal conductivity. However the through-thickness thermal conductivity had remained almost constant even with varying CNT content. The inclusion of CNTs had improved the through-thickness thermal diffusivity without changing the heat capacity and just slightly increasing the density. Equation 7-3 [189] was used to estimate the through-thickness thermal conductivity for the HCs;
where $K_{\xi_2}^t$ is the through-thickness thermal conductivity, $B$ is the through-thickness matrix volume fraction which was set to 45% due to the processing method which was optimised to produce composite with 55% fibre volume fraction, $K^f_\perp$ is the transverse conductivity of the carbon fibre and $K_m$ is the conductivity of the matrix [4]. Figure 7-12 shows the plotted estimation in comparison to the measured through-thickness thermal conductivity. A slight drop in the estimated through-thickness thermal conductivity of the homogeneous samples can be attributed to the slightly lower fibre volume content in the specimen compared to the other species. Due to lack of source as stated in the literature review, comparison to the open literature could not be performed.

The measured through-thickness thermal conductivity was slightly higher than the estimated values which was attributed to the conductive thermal networks generated by the CNTs. High consolidation pressure had been shown to increase the through-thickness thermal conductivity [190] which had also influenced the HCs in this study. Furthermore, the contacting fibres, as show in the electrical conductivity (Figure 7-11) would have also increased the thermal conductivity of the composite.

*Figure 7-12: Through-thickness thermal conductivity compared to the estimated values*
Chapter 8 : Conclusions and Outlook

This chapter concludes the thesis and summarises the findings from Chapter 6 and the discussion in Chapter 7. The general trends exhibited by the hierarchical composite in the mechanical, electrical and thermal properties are highlighted. Suggestions for potential future work are presented in line with the reported findings.

8.1 Concluding remarks

The HCs manufacturing process was optimised using jet milled particles rather than by cryomilling the particles. This jet milling process has produced particles with an average diameter of 10.8 ± 0.5 µm, which was 59.7% smaller than that of the cryomilled particles (26.8 ± 1.7 µm). These smaller particles had consequently generated better CNTs distribution within the HCs. Furthermore, improvements in the processing method such as external cooling during impregnation, hot-melt of HCs plies prior to stacking and use of displacement spacers during consolidation had yielded HCs with consistent dimensions, low void content and reproducible samples. However 25.0 wt% CNTs content was above the processing limit of this production system, resulting in poor consolidation and re-agglomeration of the CNTs in the HC.

This work presents a new methodology to harness the toughening potential of CNTs within the HCs. A perfectly homogeneous CNTs distribution within the matrix has been the goal for many researchers. However, this study has shown that such homogeneously toughened system does not fully utilise the toughening potential of the CNTs. The homogenised system had inhibited crack path propagation within the matrix hence deflecting
the crack path onto the fibre/matrix interphase which lacked CNTs. Therefore the CNTs had not fully contributed to the HC toughening. To exploit the full potential of the CNTs, the preferential crack path should be tailored to propagate within the matrix.

Heterogeneity within the matrix was a viable engineering approach to tailor the crack path by promoting cohesive failure. The best fracture toughness was exhibited by the HC when regions of CNT rich patches were separated by the length of the matrix process zone. This separation had promoted cohesive failure which is essential for CNT toughening in the HCs. The initiation fracture toughness ($G_{IC}$) of this HC was $817 \pm 6$ Jm$^{-2}$ which was 29% higher than the counterpart homogeneous mixture ($634 \pm 9$ Jm$^{-2}$). The engineered heterogeneity microstructure however did not change the interfacial properties as shown by the short beam shear result.

The CNTs distribution can be engineered and micro-structurally optimised to harness improved mechanical properties, whilst imbuing multifunctionality via thermal and electrical properties. High through-thickness electrical conductivity was obtained with the inclusion of CNTs. At 10.0 wt%$_E$ CNTs content the conductivity was $57.4 \pm 4.3$ Sm$^{-1}$ which is more than a 350% improvement over the control 0 wt%$_E$ composite. The through-thickness electrical and thermal conductivity was unaffected by the heterogeneity of CNT distribution in the HCs. Unfortunately the highly conductive carbon fibres had bridged the laminate thus generating conductive paths even without the inclusion of CNTs. Nonetheless, significant improvements were still observed although the contribution of carbon fibres architecture cannot be separated.

In conclusion, this study shows that the inclusion of CNTs is beneficial in improving the fracture toughness and ILSS over the parent composite. In comparison to the thermoplastic or rubber toughened epoxy system, the fracture toughness improvement from the inclusion of CNTs is expected to be non-detrimental to the pristine inplane properties of the HCs. Furthermore, the heterogeneity in the HC was shown to be a viable route in tailoring the fracture morphology to achieve a better fracture toughness in comparison to that of the homogeneous mixture. In addition, the inclusion of CNTs also had imbued multifunctionality via improved electrical and thermal properties.
8.2 **Recommendations for future work**

8.2.1 **Processing scaling up**

The HC manufacturing method in this study was developed with possible scalability throughout all the processing stages. All the key processing steps such as CNTs dispersion via matrix extrusion, resin uptake by wet powder impregnation and hot press consolidation can be upscaled to produce larger laminates. Furthermore, the quality of the filament winding process can be improved with a larger drum which will reduce the in-plane waviness of the fibres. Subsequently, this waviness reduction should greatly increase the fibre dominated properties such as flexural and tensile stiffness and strength.

8.2.2 **Optimisation of CNTs heterogeneity**

The highest fracture toughness improvements were exhibited when the CNTs patches were engineered to be the same length of the process zone. However, due to the very limited materials available, only three iterations of matrix combinations were produced and tested. Further experimental work by varying the particle separation could shed more light of the effect of heterogeneity within the HCs. In this study, only two types of separations were investigated:

a) **1 to 1 ratio of mixture**

This mixture was manufactured by mixing the control (0 \text{wt}\%_E) CNTs powder with the 5.0 \text{wt}\%_E CNTs powder and also mixing control CNTs powder with the 15.0 \text{wt}\%_E CNTs powder at a 1/1 weight ratio.

b) **5 to 1 ratio of mixture**

This mixture was manufactured by mixing the control (0 \text{wt}\%_E) CNTs powder with the 15.0 \text{wt}\%_E CNTs powder at a 5/1 weight ratio.

By using other matrix powders such as 10.0 \text{wt}\%_E and 25.0 \text{wt}\%_E CNT nanocomposite powder as the precursors to the mixture, more permutations of heterogeneity could be engineered. Furthermore, mixing different type of nanocomposites together offers limitless possibilities to explore the effect of heterogeneity although their contribution to the mechanical and physical properties remained to be studied.

Moving forward, a key mixture to be investigated is by mixing the control (0 \text{wt}\%_E) CNTs powder with the 25.0 \text{wt}\%_E CNTs powder at a 10/1 weight ratio. This mixture would
generate a larger separation between the CNT patches and the separation will be larger than
the process zone. This investigation could reveal whether the optimum heterogeneity was
exactly at the length scale of the process zone for the matrix or larger.

8.2.3 Mechanical characterisation

In this study, the mechanical properties characterised were Mode I fracture toughness
and interlaminar shear strength. These were matrix dominated properties and the specimen
preparation for the test samples was relatively simple. Furthermore, the DCB test for Mode I
fracture toughness also yielded the flexural stiffness of the HCs.

Other important matrix dominated test could be employed to explore the effect of
heterogeneity and the inclusion of CNTs in the composite. In-plane compression were
expected to benefit from the CNTs inclusion although the effect of heterogeneity remained to
be proven. In the case of fracture toughness of the HCs, additional tests such as Mode II via
end notched flexure (ENF) or end loaded split (ELS) could show further interaction between
the inclusion of CNTs and heterogeneity to the fibre/matrix interphase. Finally, by combining
Mode I and Mode II, the characteristics of HCs under mixed mode loading is yet to be
conclusively discovered.

Beyond quasi-static loading, characterisation could also delve into dynamic loading
such as fatigue. The inclusion of CNTs however is not expected to significantly improve the
fatigue property. Furthermore the CNT inclusion could indeed promote localised stress
concentration which could initiate failures. Although conventional carbon fibre reinforced
composites often already possesses good fatigue properties [191,192], damage resistance (i.e.
after damage had initiated) under cyclic loading is often poor hence the CNTs could be
gineered to address this performance.

8.2.4 Physical characterisations

With successful impregnation and CNT distribution in the HCs other physical
properties such as fire retardant and resistance would be expected to improve. However, the
effect of heterogeneity on these properties is unclear. Further effects on physical properties
such as solvent/chemical resistance and moisture uptake can be studied to ensure the
inclusion of CNTs could be beneficial in comparison to the parent composite. Furthermore,
the inclusion of CNTs could also be beneficial in reducing the heat or radar signature, for
military applications.
8.2.5 Finite element modelling

The experimental work during this study was expensive and consumed a substantial amount of time. Therefore, the property prediction and constituent optimisation through finite element (FE) modelling could save considerable resources prior to extensive experimental work. The FE modelling could be utilised to predict the optimised heterogeneity configuration i.e. the separation distance between CNTs rich regions and different heterogeneous mixture.

8.2.6 Structural elements

The current state of research of HCs [13,51,61] has been mainly focussed on processing and testing at coupon level (refer Figure 8-1). Delamination resistance of HCs are characterized mostly by using double cantilever beam (DCB) tests for mode I and end notch flexure (ENF) tests for mode II [11,23,89,90,101,135,193]. Figure 8-1 illustrates the conceptual design building block for typical aerostructure development. The design certification process for typical fixed wing structures [194] manufactured with composite materials consist of investigation from coupon level up to complete full scale component. However, the relationship between toughness at coupon level and structural damage tolerance is poorly understood [3]. Therefore, the data from damage resistance tests at the coupon test level should not simply be extrapolated to represent damage tolerance at structural level.

Figure 8-1: Schematic diagram of building block tests (Rouchon Pyramid) for a fixed wing aircraft [194]
Figure 8-2: The suggested placement of HCs on the critical surfaces in a) four point bending test, b) T-peel test [3].

Structural test represents multiple degradation mechanism subjected simultaneously on the test specimens [51]. Unlike coupon test methods, there are no test standards at the structural levels. Numerous element tests have been developed [195] in order to examine the characteristics of composite materials at structural level. Manufacturing full scale stiffened panels are relatively expensive therefore conducting smaller but representative tests on stiffened elements are preferable. Representative elements can vary in size (from 25 mm up to 450 mm in width) [196-199] depending on test methods and loading conditions. Some of the suggested structural element test are bending; including three [196-198] and four point test [200,201], stiffener pull-off or T-peel test [3,195,202,203], lateral tension [195,200], and combined axial tension and bending test [196]. Other possible engineering tests are open-hole compression (OHC)[204] and compression after impact (CAI)[205].

Depending on the desired properties, the structural elements can be manufactured either entirely from HCs or placing the HCs on the critical surfaces. In cases where
multifunctionality of the composite is the upmost desired outcome, the elements should be wholly manufactured from HC. However, due to the often limited and expensive resources to manufacture these HCs, structural elements could be manufactured by placing the HCs at critical load bearing areas such as the joint surfaces between the skin and flange (Figure 8-2). This manufacturing method is suitable when the desired property was interface dominated such as fracture toughness.
References


150. Riaz, S., Carbon fibre reinforced pvdf and peek nanocomposites, PhD thesis, in Department of Chemical Engineering. 2012, Imperial College London: Imperial College London.


Appendix A: Load vs Displacement Curves

Figure A - 1: DCB load versus displacement curves for control composite.

Figure A - 2: DCB load versus displacement curves for Homo (2.5 wt%$_E$ CNTs) HCs.
Figure A - 3: DCB load versus displacement curves for Homo (5.0 wt%\textsubscript{E} CNTs) HCs.

Figure A - 4: DCB load versus displacement curves for Homo (10.0 wt%\textsubscript{E} CNTs) HCs.
Figure A - 5: DCB load versus displacement curves for Homo (25.0 wt%$_E$ CNTs) HCs.

Figure A - 6: DCB load versus displacement curves for Hetero (1:1, 2.5 wt%$_E$) HCs.
Figure A - 7: DCB load versus displacement curves for Hetero (1:1, 7.5 wt%\(_E\)) HCs.

Figure A - 8: DCB load versus displacement curves for Hetero (1:1, 2.2 wt%\(_E\)) HCs.
Appendix B: R-Curves

Figure B - 1: The R-curves for the control (0 wt%\textsubscript{E} CNTs) composite.

Figure B - 2: The R-curves for the Homo (2.5 wt%\textsubscript{E} CNTs) HCs.
Figure B - 3: The R-curves for the Homo (5.0 wt%\textsubscript{E} CNTs) HCs.

Figure B - 4: The R-curves for the Homo (10.0 wt%\textsubscript{E} CNTs) HCs.
Figure B - 5: The R-curves for the Homo (25.0 wt% CNTs) HCs.

Figure B - 6: The R-curves for the for Hetero (1:1, 2.5 wt% CNTs) HCs.
Figure B - 7: The R-curves for the Hetero (1:1, 7.5 wt%\(E\)) HCs.

Figure B - 8: The R-curves for the Hetero (5:1, 2.2 wt%\(E\)) HCs.