Multi-scale Interlaminar Toughening of Fibre Polymer Composites

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy
(Aerospace Engineering)

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed. I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship and the RMIT University School of Engineering Top-up Scholarship Award.

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Summary

Fibre reinforced polymer (FRP) composites are used in aerospace applications due to the increasing demand for lightweight-yet-strong structures. However, a long-standing problem with laminated FRP composites is their susceptibility to delamination damage and matrix cracking when subjected to in-plane loading (e.g. bondline failure of joints) and out-of-plane loading (e.g. hail-stones, bird-strike or in-service damage) scenarios. Due to the poor interlaminar fracture toughness and the brittle nature of the polymer matrix, delamination cracks can grow during service loading, further degrading the well desired structural properties. In improving the delamination resistance, nano-scale or macro-scale reinforcements were used separately to increase the interlaminar fracture toughness of FRP composites. However, natural composites such as bone and nacre contain highly-ordered constituents that span multiple length scales. These multi-scale materials invoke unique toughening mechanisms, exhibiting fracture toughness properties that far exceed the total contribution (i.e. synergistic) of their individual constituents.

The aim of this PhD project was to investigate the effects of incorporating multi-scale toughening approaches to synergistically enhance the fracture toughness, delamination crack growth resistance and other mechanical properties of FRP composites. Multi-scale toughening was achieved by simultaneously adding reinforcements spanning multiple dimensional scales. Reinforcements that were used in this PhD project included nano-scale carbon and metal oxide-based fillers, micron-scale carbon fillers and macro-scale pins. The expected outcome of the project is to identify strategies to generate synergies towards the delamination resistance properties of polymer composites. Systematic investigations were conducted to experimentally measure and numerically predict the fracture toughness properties of the multi-scale reinforced composites with consideration to the volume content, orientation, size, distribution and combination of reinforcements.

The literature review chapter in the PhD thesis is a survey of the techniques reported to improve the fracture toughness properties of polymer composites using reinforcements at multiple dimensional scales. Fracture toughness improvements are dependent on various factors such as the filler geometry, type, size and orientation. The toughening efficacy of fillers can be altered through surface modification or adding functionalities. Earlier reports on multi-scale toughening
demonstrated that a greater-than-expected additive mode I fracture toughening improvement can be achieved by combining randomly orientated nano- and micron-scale fillers in bulk epoxy polymers. The research gap analysis revealed that there is a limited understanding on the synergistic toughening effects of combining nano-, micron- and macro-scale reinforcements on the delamination resistance and the structural properties of composite materials.

The first two research chapters present investigations into the intrinsic fracture toughness properties of bulk epoxy polymers reinforced by aligning and combining carbon nanofibres (CNFs) and micron-scale short carbon fibres (SCFs). The application of an AC electric field was used to simultaneously align the CNFs and SCFs normal to the crack growth direction in the epoxy polymer. On a weight fraction basis, the CNFs were 25-70% effective at improving the mode I fracture toughness of the epoxy polymer than the SCFs. When used in combination, the electric field alignment of the CNFs and SCFs within the epoxy during curing resulted in a fracture toughness improvement of up to 40% when compared to toughening efficacy of the epoxy composite containing both randomly aligned CNFs and SCFs. Toughening mechanisms were identified and an analytical model was developed to successfully predict the improvements to the fracture toughness properties.

The next research chapter presents an experimental investigation into the low-velocity impact damage tolerance of multi-scale reinforced composites. The addition of CNFs or/and SCFs within the epoxy matrix increased both the steady-state mode I and mode II interlaminar fracture toughness properties by up to 120% and 80%, respectively, when compared to the unmodified composite laminated. These improvements translated to the increased delamination resistance (i.e. 3-24% improvement) and post-impact compression strength (i.e. 9-29% improvement) properties of the multi-scale reinforced composites under impact loading.

Investigations were conducted into the synergistic toughening effect induced in the multi-scale reinforced composites by combining carbon nanofibres and carbon z-pins. The modes I and II fracture toughness properties increased with CNF and z-pin contents by up to 1100%, when used separately. Using the CNFs and z-pins in combination lead to a greater-than-additive improvement (i.e. 9-30% synergistic enhancement) in the fracture toughness properties as compared to the sum of the individual toughening effects from the CNFs and z-pins promoted separately. The synergistic improvement was due to the CNFs enhancing the crack bridging toughening efficacy.
of the z-pins. The magnitude of the synergistic toughening was also dependent on the type of carbon nano-filler used (i.e. carbon nanotubes (CNTs) or graphene nanoplatelets (GNPs)). A finite element model was developed to successfully predict the synergistic toughening effect of multi-scale reinforced composites.

A study was conducted into the structural properties of z-pinned composite T-joints toughened by CNTs, CNFs or GNPs. The carbon nanomaterials were 30-70% effective at improving the load at first failure of the z-pinned joints. The ultimate load and total absorbed energy capacity to failure of the T-joints increased by up to 73% and 450%, respectively, with the addition of the carbon nanomaterials and/or z-pins. However, the z-pinned T-joints containing the CNTs or CNFs underwent failure of the skin and flange laminates rather than bond-line failure due to the enhanced mode I and mode II interlaminar fracture toughening effect.

The final research chapter in the PhD thesis is an investigation into the effect of novel nano-dimensional metal oxide platelets on the tensile and fracture toughness properties of bulk epoxy polymers. Aluminium oxide hydroxide (boehmite) platelets were synthesized using a novel liquid metal reaction with aluminium. The addition of boehmite platelets increased the fracture toughness, tensile stiffness and strength of the epoxy polymers by up to 300%, 40% and 14%, respectively. Annealing the boehmite to alumina promoted a 48-55% increase in the toughening efficacy of the aluminium oxide platelets within the epoxy nanocomposites.
Publications

Journal paper publications and conference proceedings arising from this thesis include :-


**dimensional aluminium oxide platelets to reinforce epoxy composites**, Composites Science and Technology, Vol 181, Article 107708. (Impact Factor = 6.309)


Conference proceedings that were published during the PhD project but not included within the main thesis include:


Awards attained during the PhD project:

1. 2nd Place – Airbus Fly Your Ideas Competition – Toulouse, France
2. 1st Place - Academic Research Presentation – Composite Battle World Cup, Xi’an, China.
3. 2nd Place - Young Researcher Award – 11th Asian-Australasian Conference on Composite Materials (ACCM-11), Cairns, Australia.
# Table of Contents

Declaration .......................................................................................................................... 1  
Acknowledgements ............................................................................................................. 3  
Summary ............................................................................................................................... 4  
Publications ........................................................................................................................ 7  

**Chapter 1: Introduction and motivation** ........................................................................ 15  
1.1. Project Background ..................................................................................................... 15  
1.2. Aim and Scope of PhD Project .................................................................................. 17  
1.3. Format of PhD Thesis ............................................................................................... 19  

**Chapter 2: Literature review** ......................................................................................... 22  
2.1 Introduction .................................................................................................................. 22  
2.2 Single-scale toughening of composites ...................................................................... 24  
2.2.1 Toughening of epoxies using nano- and micron-scale fillers .................................. 25  
2.2.1.1 Fracture toughening mechanisms .................................................................... 29  
2.2.1.2 Effect of filler orientation .............................................................................. 32  
2.2.2 Delamination toughening of fibre reinforced epoxy composites using nano- and micron- 
    dimensional scale fillers ....................................................................................... 33  
2.2.2.1 Modification of the epoxy matrix .................................................................. 33  
2.2.2.2 Deposition of nanofillers and interleave toughening ...................................... 37  
2.2.3 Through-the-thickness toughening of fibre reinforced epoxy composites .......... 38  
2.2.3.1 Interlaminar toughening of fibre reinforced epoxy composites using z-pins ..... 39  
2.2.3.2 Comparison of interlaminar toughening techniques .................................... 45  
2.3 Multi-scale toughening of composites ...................................................................... 47  
2.3.1 Multi-scale toughening of epoxy polymers ......................................................... 49  
2.3.2 Multi-scale toughening of fibre reinforced epoxy composites ............................. 51  

**Chapter 3: Electric field alignment of short carbon fibres to increase the**  
**toughness of epoxy polymers** ...................................................................................... 56  
3.1 Introduction .................................................................................................................. 57  
3.2 Materials and Experimental Methodology .................................................................. 58
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1 Materials</td>
<td>58</td>
</tr>
<tr>
<td>3.2.2 Electric field alignment of short carbon fibres</td>
<td>60</td>
</tr>
<tr>
<td>3.2.3 Composite manufacturing and mode I fracture toughness testing</td>
<td>62</td>
</tr>
<tr>
<td>3.3 Results and Discussion</td>
<td>65</td>
</tr>
<tr>
<td>3.3.1 Electric field alignment of SCFs</td>
<td>65</td>
</tr>
<tr>
<td>3.3.1.1 Effect of SCF aspect ratio and AC electric field strength on SCF orientation</td>
<td>65</td>
</tr>
<tr>
<td>3.3.1.2 In-situ alignment studies of SCFs in liquid epoxy resin</td>
<td>67</td>
</tr>
<tr>
<td>3.3.1.3 Effect of SCF content on fibre orientation distribution in cured epoxy</td>
<td>68</td>
</tr>
<tr>
<td>3.3.1.4 Optimisation of the procedure for orientating the SCFs in the epoxy polymers</td>
<td>70</td>
</tr>
<tr>
<td>3.3.2 Fracture toughness of the epoxy/SCF composites</td>
<td>70</td>
</tr>
<tr>
<td>3.3.2.1 Effect of SCF content and alignment</td>
<td>70</td>
</tr>
<tr>
<td>3.3.2.2 Comparison to literature values</td>
<td>71</td>
</tr>
<tr>
<td>3.3.2.3 Toughening mechanisms</td>
<td>73</td>
</tr>
<tr>
<td>3.3.2.4 Modelling the fracture toughening mechanisms</td>
<td>78</td>
</tr>
<tr>
<td>3.4 Conclusion</td>
<td>84</td>
</tr>
<tr>
<td>Chapter 4: Multi-scale toughening of epoxy polymers via electric field alignment of carbon nanofibres and short carbon fibres</td>
<td>85</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>86</td>
</tr>
<tr>
<td>4.2 Materials and Experimental Details</td>
<td>87</td>
</tr>
<tr>
<td>4.2.1 Materials and electric field alignment</td>
<td>87</td>
</tr>
<tr>
<td>4.2.2 Specimen manufacturing and fracture toughness testing</td>
<td>89</td>
</tr>
<tr>
<td>4.3 Results and Discussion</td>
<td>90</td>
</tr>
<tr>
<td>4.3.1 Electric field alignment of SCF and CNF in epoxy resin</td>
<td>90</td>
</tr>
<tr>
<td>4.3.2 Fracture toughness of epoxy polymers</td>
<td>93</td>
</tr>
<tr>
<td>4.3.2.1 Effect of electric field alignment on the fracture toughness</td>
<td>93</td>
</tr>
<tr>
<td>4.3.2.2 Effect of electric field alignment on the toughening mechanisms</td>
<td>96</td>
</tr>
<tr>
<td>4.3.3 Modelling the fracture toughness of the multi-scale reinforced epoxy polymers</td>
<td>101</td>
</tr>
<tr>
<td>4.4 CONCLUSION</td>
<td>105</td>
</tr>
<tr>
<td>Chapter 5: Multi-scale delamination toughening and low-velocity impact damage resistance of fibre composites using CNFs and SCFs</td>
<td>106</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>106</td>
</tr>
<tr>
<td>5.2 Materials and Experimental Methodology</td>
<td>109</td>
</tr>
<tr>
<td>5.2.1 Composite materials and manufacturing</td>
<td>109</td>
</tr>
</tbody>
</table>
5.2.2 Mode I and mode II interlaminar fracture toughness characterisation .................................. 110
5.2.3 Tensile, flexural and interlaminar shear property characterisation ....................................... 113
5.2.4 Low velocity impact and non-destructive evaluation of impact damage ............................... 115
5.2.5 Compression after impact property characterization .............................................................. 116
5.3 Results and Discussion .............................................................................................................. 117
  5.3.1 Interlaminar fracture toughness properties of multi-scale reinforced laminates ........ 117
    5.3.1.1 Interlaminar toughening mechanisms .............................................................................. 119
  5.3.2 Tensile, flexural and interlaminar shear properties .............................................................. 123
  5.3.3 Impact and post-impact properties of multi-scale reinforced laminates ............................ 124
    5.3.3.1 Load-time response during impact .................................................................................. 124
    5.3.3.2 Impact-induced failure modes and damage area ............................................................ 126
    5.3.3.3 Compression-after impact strength properties ............................................................... 132
5.4 Conclusion ..................................................................................................................................... 133

Chapter 6: Synergistic mode I delamination toughening of carbon fibre composites using carbon nanofibres and z-pins ................................................................. 135
6.1 Introduction .................................................................................................................................. 136
6.2 Materials and Experimental Methodology .................................................................................. 138
  6.2.1 Composite materials and manufacturing .............................................................................. 138
  6.2.2 Mode I interlaminar fracture toughness testing ................................................................. 140
  6.2.3 Z-pin bridging traction and input material property ............................................................. 141
6.3 Finite Element Modelling .......................................................................................................... 143
6.4 Results and Discussion ............................................................................................................... 145
  6.4.1 Effect of CNFs or z-pins on the mode I fracture toughness .................................................. 145
  6.4.2 Effect of hybridising CNFs and z-pins on the mode I fracture toughness ......................... 149
  6.4.3 Comparison of experimental and numerically calculated fracture toughness values ......... 152
6.5 Conclusion ..................................................................................................................................... 156

Chapter 7: Synergistic mode II delamination toughening of carbon fibre composites using carbon nanofibres and z-pins ................................................................. 158
7.1 Introduction .................................................................................................................................. 159
7.2 Materials and Experimental Methodology .................................................................................. 160
  7.2.1 Composite manufacturing .................................................................................................. 160
  7.2.2 Mode II fracture toughness testing .................................................................................... 161
  7.2.3 Material property testing .................................................................................................. 163
7.3 Numerical Modelling of Mode II Delamination Crack Growth .............................. 164
7.4 Results and Discussion .................................................................................... 169
  7.4.1 Effect of CNFs or z-pins on the mode II fracture toughness .......... 169
  7.4.2 Effect of hybridising CNFs and z-pins on the mode II fracture toughness .... 173
  7.4.3 Comparison of experimental and numerically calculated fracture toughness values 177
7.5 Conclusion ..................................................................................................... 181

Chapter 8: Multi-scale delamination toughening of z-pinned composites using 1D and 2D carbon nanofillers .......................................................... 182
  8.1 Introduction .................................................................................................... 183
  8.2 Materials and Experimental Methodology .................................................. 184
    8.2.1 Composite materials and manufacturing ........................................ 184
    8.2.2 Interlaminar fracture toughness testing and fractography assessment .... 186
  8.3 Results and Discussion .............................................................................. 187
    8.3.1 Delamination toughening using nanofillers .................................. 187
    8.3.2 Delamination toughening using z-pins ........................................ 192
    8.3.3 Delamination toughening using both nanofillers and z-pins .......... 194
  8.4 Conclusion .................................................................................................. 200

Chapter 9: Multi-scale strengthening of composite T-joints using carbon nanofillers and z-pins .................................................................................. 201
  9.1 Introduction .................................................................................................. 201
  9.2 Materials and Experimental Methodology .................................................. 205
    9.2.1 Composite T-joint manufacturing and testing ................................ 205
    9.2.2 Composite T-joint pull-off testing .................................................. 208
  9.3 Results and Discussion .............................................................................. 209
    9.3.1 Load-bearing properties of T-joints containing carbon nanofillers .... 209
      9.3.1.1 Strengthening mechanisms from the carbon nanofillers ........ 213
    9.3.2 Load-bearing properties of T-joints containing z-pins ................. 216
      9.3.2.1 Strengthening mechanisms from the z-pins ................. 218
    9.3.3 Load-bearing properties of T-joints containing both nanofillers and z-pins .... 219
      9.3.3.1 Strengthening mechanisms from the nanofillers and z-pins .... 223
    9.3.4 Comparison of interlaminar fracture toughness and structural properties of the T-joints ........................................................... 223
  9.4 Conclusion .................................................................................................. 226
Chapter 10: Liquid metal synthesis of 2D aluminium oxide nanoplatelets in toughening epoxy polymers

10.1 Introduction

10.2 Materials and Experimental Methodology

10.2.1 Liquid metal synthesis of boehmite and alumina platelets

10.2.2 Manufacturing of bulk epoxy polymer composites

10.2.3 Tensile and fracture toughness testing

10.3 Results and Discussion

10.3.1 Tensile properties

10.3.2 Fracture toughness properties

10.4 Conclusion

Chapter 11: Conclusions

11.1 Summary of Major findings

11.2 Future Research Considerations

11.2.1 Electric field alignment of multi-scale carbon reinforcements in epoxy polymers

11.2.2 Multi-scale toughening of carbon fibre reinforced composites using carbon nanofillers and z-pins

Bibliography
Chapter 1: Introduction and motivation

1.1. PROJECT BACKGROUND

For over fourty years, high-performance laminated composites such as continuous fibre reinforced polymers (CFRPs), have been widely used in engineering structures. Consisting of a reinforcement phase (i.e. fibres) and polymer matrix that binds the reinforcements, fibre reinforced polymer composites desirable are their lightweight yet exceptional mechanical properties. Applications of CFRPs include aerospace, civil, medical, automotive and power generation; targeted for minimising fossil fuel emissions, engendering improved performance and safety [1-6]. Carbon fibre reinforced polymer composites exhibit relatively high in-plane specific stiffness and strength compared to many metals (i.e. aluminium). The global demand for composite-end products reached USD 22.2 billion in 2015 [7], and the carbon fibre composite market share is expected to grow to USD 31 billion by 2024 [8]. Fig. 1.1 presents a pie chart on the global carbon usage by industry sector composite, with the aviation, aerospace and defence sector being the largest users [9].

A long-standing problem with laminated carbon fibre composites are the low through-the-thickness mechanical properties due to the weak properties of the polymer matrix and the absence
of reinforcement in the thickness direction [10, 11]. The polymer matrix used within existing fibre reinforced composites include thermoplastics or thermosets. Thermoplastics range from polyetheretherketone (PEEK), polyetherketoneketone (PEKK), polyetherimide to nylon. Thermoplastics exhibit substantial fracture toughness and recyclability [12, 13]. However, some high-performance thermoplastics require high process costs, are soluble with solvents and incompatible with most commercially available carbon fibres that are sized for thermosets [14]. Examples of thermosets include vinyl ester, bismaleimides or phenolics [14]. What make thermosets desirable is the ease of processability (e.g. low viscosity), resistance to solvents and high stiffness. For aircraft applications, the most commonly used thermoset is epoxy [1, 15]. However, epoxies, which is the thermoset of focus for the present thesis, are invariably brittle and exhibit low fracture toughness [1, 15]. Therefore, carbon fibre reinforced composite structures that use epoxies are prone to damage of the matrix parallel to the fibres, such as delamination between the plies and matrix cracking, when subjected to either in-plane or out-of-plane loading [1]. For aircraft structures, examples of delaminations under the in-plane loading conditions include bond-line failure of lap or scarf joints [16], notch (i.e. open-hole or ply terminations) induced delamination development between the plies [17] or compression failure of a structure (i.e. wing spar) [18]. More commonly, out-of-plane loading scenarios such as a bird strike [19], hailstones [20] or tool drop during service [6] can also lead to delaminations within the structure. These events can lead to barely visible impact damage (BVID); where delaminations grow along the ply interfaces and can degrade the in-plane mechanical properties by over 50%. The Federal Aviation Administration (FAA) mandate stringent aviation safety and damage tolerance regulations where an aircraft composite structure containing delamination cracks above a critical size must be repaired or in most cases be replaced [21-24]. Specific FAA regulations permit short delamination to be left unrepaired provided that they do not grow over time under operational loads [21-24].

Another recurring problem with modular/discontinuous composites structures, such as bonded composite lap joints [25] or T-joints [26], is that they often exhibit inferior mechanical properties compared to their continuous counterparts. During both in-plane or out-of-plane loading, these discontinuities (i.e. ply terminations and resin-rich regions) are zones of high-stress concentrations which may initiate matrix cracking between the plies [27]. Failure mechanisms are often dominated by delamination within the bond-lines between the ply adherends. Hence there is
a need for new design methodologies for high-performance composites to meet delamination resistance and damage tolerance requirements.

Various toughening methods have been developed to improve the delamination resistance. More recently, a popular technique to enhance the interlaminar fracture toughness properties of carbon fibre composite is addition of high strength nanofillers, such as carbon nanotubes (CNTs), to toughen the epoxy matrix [28-30]. The use of toughened interleaves containing nano- or micron-dimensional scale reinforcement between the plies has also attracted much attention due to the simplicity of incorporating within the manufacturing process of a composite [31-34]. Conventional techniques to enhance the delamination resistance include the incorporation of a macro-scale through-the-thickness (i.e. 3D) reinforcement phase in a composite preform. Examples include 3D weaving, stitching, 3D braiding and tufting [35]. Z-pinning is another cost-effective technique used in aerospace structures which follows the process of inserting thin metal or composite macro-scale rods along the thickness direction of a composite before curing [36]. Z-pinning is not only effective at improving the delamination resistance, but also enhances the damage tolerance of composites when subjected to impact loads and the structural properties of composite joints [26, 37-45].

Until very recently, nano-scale and macro-scale reinforcements were used separately to increase the fracture toughness and delamination resistance of composites through various toughening mechanisms. However, natural materials such as bone, wood and nacre are hierarchically or multi-scale reinforced, meaning that they contain highly-ordered constituents that spans multiple length scales [46]. These multi-scaled toughened natural materials exhibit toughness properties that are far greater than the sum of the contribution of their constituents [46]. The multi-scale toughening design motifs, by combining fillers at multiple dimension scales, have been reported to promote additive or greater-than-additive (i.e. synergistic) improvements to the fracture toughness of polymers [47-49]. However, the effect of hybridising two or more toughening methods to enhance the delamination resistance and structural properties of fibre reinforced composite materials and structures is not well understood.

1.2. AIM AND SCOPE OF PhD PROJECT

The aim of this PhD project is to develop multi-scale toughening approaches for carbon fibre reinforced epoxy composites. By assimilating reinforcements at multiple length scales, the
objective is to identify new methodologies to synergistically enhance the interlaminar fracture toughness and structural properties. As shown in Fig. 1.2, multi-scale toughening is achieved by combining various toughening methods, in-situ, to invoke additional toughening processes at multiple structural hierarchies.

This PhD project builds upon the current body of literature on methods of interlaminar toughening [49-54] of carbon fibre reinforced epoxy composite. Toughening methods investigated within this PhD project include (a) toughening of the epoxy matrix using various types of nano- and micron-scale fillers, and (b) the use of macro-scale 3D reinforcements such as z-pins. In achieving the aim of the PhD project, the research work will address the following specific objectives:

- Investigate and quantify the effect of nano-scale and micron-scale filler contents, combinations and orientations on the fracture toughness of bulk epoxy polymers (with no continuous reinforcement phase) and fibre reinforced epoxy composites (containing the continuous reinforcement phase).
- Develop analytical and numerical models to predict the fracture toughness contribution generated by the individual fillers in bulk polymers.
Identify strategies to generate synergies between nano-scale fillers, micron-scale fillers and macro-scale z-pins on the interlaminar fracture toughness and crack growth resistance behaviour of fibre reinforced epoxy composites.

Assess the effect of multi-scale toughening on the impact damage resistance and compression-after-impact strength of carbon fibre reinforced epoxy composites.

Investigate the effect of multi-scale toughening on the load-at-first failure, ultimate load and extension-to-failure properties of carbon fibre reinforced epoxy composite T-joints.

Upon successful completion of the above objectives, this PhD project will provide new insights into the understanding and development of a new class of damage tolerant engineered composites. The outcome and significance of this project will advance the knowledge base on the comparison and interactions between nano-, micron- and macro-scale toughening approaches has on the fracture toughness, damage tolerance and structural properties of carbon fibre reinforced epoxy composites.

1.3. FORMAT OF PhD THESIS

Chapter 2 presents an overview of the methods reported to enhance the mechanical properties of bulk epoxy polymers and fibre reinforced epoxy composites. The first part of this literature review presents a progress report on the recent strategies to enhance the fracture toughness properties. A comparative assessment between the individual toughening methods is conducted with consideration to factors such as the reinforcement type, geometry, morphology, orientation relative to the crack propagation plane, volume content and interfacial properties between the reinforcement and polymer matrix. As a foundation for this thesis, the second part of Chapter 2 presents a detailed survey of multi-scale toughening methods used to synergistically strengthen and toughen composite materials by combing two or more existing toughening strategies. Key gaps within the current research literature are highlighted.

Chapter 3 presents an investigation into the mode I fracture toughness properties of epoxy polymers containing short carbon fibres (SCFs) arranged in various orientations. The SCFs were aligned using an externally applied alternating current (AC) electric field. The effects of SCF length, SCF content and AC electric field strength on the rotation rate of the SCFs suspended in
liquid (i.e. uncured) epoxy resin was investigated. The fracture toughness of the epoxy polymers containing SCFs, that were or were not exposed to an electric field, were measured. Chapter 4 extends on this research by reporting on the effect of hybridising carbon nanofibres (CNFs) and SCFs on the mode I fracture toughness of epoxy polymers. An assessment on the toughening efficiency of CNFs and SCFs, when used separately or together, was conducted. In addition, the effects of aligning the CNFs and SCFs normal to the crack growth plane using an applied AC electric field on the fracture toughness properties was experimentally studied. Based on the identified intrinsic and extrinsic toughening mechanisms, an analytical model is presented in Chapters 3 and 4 to predict the improvement to the fracture toughness or epoxy polymers due to electric field alignment of the CNFs and SCFs.

Chapter 5 presents an experimental study into the delamination resistance and impact damage tolerance properties of multi-scale toughened carbon fibre reinforced epoxy composites containing SCFs and CNFs, used together or separately. The composite materials, containing various combinations of fillers, were subjected to a low-velocity projective impact at incident energies up to 50J. The impact response and damage to the composites was investigated. To correlate the variation in delamination area, the mode I and II interlaminar fracture toughness and crack growth (i.e. R-curve) response of the composites containing CNFs and SCFs were characterised. Mechanical properties such as the tensile modulus, tensile strength, flexural modulus, flexural strength and the interlaminar shear strength of the composite laminates were measured. Lastly, the residual compression strength of the impacted samples were also measured.

Chapters 6, 7 and 8 present studies into the potential synergistic delamination toughening of multi-scale reinforced carbon fibre reinforced epoxy composite laminates containing carbon nanofillers and carbon fibre z-pins. Chapter 6 reports on the mode I delamination toughness properties of the multi-scale reinforced composites containing both CNFs and carbon fibre/bismaleimide z-pins. A parametric experimental analysis was conducted into the effects of CNF and z-pin content, used separately or together, on the mode I interlaminar fracture toughness of the composites. The mode I traction properties of z-pins in the presence of CNFs in the epoxy matrix was measured. Using the traction properties of the z-pins and the interlaminar properties of the unpinned laminate, a finite element model was developed to successfully predict the interlaminar fracture energy and the synergistic toughening effect. Chapter 7 follows on the
research work presented in Chapter 6 to assess the mode II interlaminar fracture toughness properties of composites containing both CNFs and z-pins. Chapters 8 expands on the previous two chapters with an experimental investigation into the effect of combining different types of 1D or 2D carbon nanofillers (e.g. CNTs, CNFs and GNP) with z-pins on the mode I and mode II interlaminar fracture toughness properties of composite materials.

By adapting the toughening approach of hybridising carbon nanofiller toughening of the epoxy matrix and z-pinning, Chapter 9 presents an experimental study on the structural properties of multi-scale toughened carbon fibre reinforced epoxy composite T-joints. Carbon nanofillers that were used to toughen the epoxy matrix of the T-joints include CNTs, CNFs and GNPs. An out-of-plane load was applied to the stiffener laminate section of the T-joint. The load-at-first failure, ultimate load, extension-to-failure and absorbed energy capacity of the different T-joints were measured. The structural properties were correlated to interlaminar toughness properties reported for the composite materials within Chapters 6, 7 and 8.

Chapter 10 presents an investigation into the effect of novel low-dimensional thick metal oxide platelets on the tensile and fracture toughness properties of epoxy polymers. Aluminium oxide hydroxide (boehmite) or AlO(OH) platelets were synthesised using a liquid metal reaction with aluminium. The boehmite particles were annealed to form alumina (Al$_2$O$_3$). The boehmite and alumina particles were then used separately to reinforce an epoxy polymer. The tensile modulus, tensile strength and mode I fracture toughness was measured. Lastly, Chapter 11 summarises the significant findings and conclusions. Considerations for future work of the PhD thesis are listed.
Chapter 2: Literature review

Abstract

This chapter presents a comprehensive literature survey of the techniques reported to improve the fracture toughness properties of polymers and delamination resistance of fibre reinforced polymer composites using fillers or reinforcements, separately, at nano-, micron- and macro-dimensional scales. Fracture toughness improvements are dependent on various factors such as the filler geometry, type, size and orientation. The fracture toughness improvements stem from multiple intrinsic and extrinsic toughening mechanisms. The toughening efficacy of the reinforcements can be altered through surface modification or adding functionalities. Earlier reports on multi-scale toughening demonstrated that a greater-than-expected additive (i.e. synergistic) fracture toughening improvement can be achieved by combining randomly orientated nano- and micron-scale fillers in epoxy polymers. The research gap analysis revealed that there is a limited understanding on the synergistic toughening effects of combining nano-, micron- and macro-scale reinforcements on the delamination resistance and the structural properties of fibre reinforced composite materials.

2.1 INTRODUCTION

A long-standing problem of fibre reinforced polymer composites is their susceptibility to delamination damage. These delamination damages or cracks can grow during service, consequently degrading the structural properties. Crack propagation in either bulk epoxies or between the plies of laminated fibre reinforced composites can occur under various modes exclusively or in combination. Delamination cracks within engineering composite structures during loading can propagate under the opening (mode I), shear sliding (mode II) and tearing (mode III) modes, as illustrated in Fig. 2.1.
Since composite laminates exhibit high mechanical properties along the in-plane (or fibre) direction, the low delamination resistance stems from the (a) weak mechanical properties of the polymer matrix, (b) low interlaminar fracture resistance along the ply-to-ply interface and (c) lack of a fibre reinforcement phase in the thickness direction. The material property well correlated to the delamination resistance of composites is the fracture toughness ($G_c$), which is also known as the strain energy release rate. Fracture toughness is defined as the energy required to propagate a delamination crack for a given flaw/damage area. Therefore, there is an interest in improving the fracture toughness properties of polymers and fibre reinforced polymer composites.

This chapter presents a comprehensive review into methods used to enhance the fracture toughness properties of polymers and composites. Epoxies are the polymers frequently described throughout the thesis as they are widely used in aerospace composite structures, as briefly described in Section 1.1. Firstly, a review is presented on the effect of different types of nano-, micron- or macro-scale reinforcement, when used separately, on the fracture toughness of epoxy polymers and fibre reinforced epoxy polymer composites. The fundamental toughening mechanisms imparted by the reinforcements at various length scales are described. Secondly, a survey is presented on multi-scale toughening techniques using nano- and micron-scale reinforcements in combination towards the fracture toughness properties of epoxy polymers and fibre composites. Synergistic toughening enhancements in the reported multi-scale reinforced composites are identified. Lastly, the review concludes with a gap analysis from the literature survey, which are addressed in the subsequent research chapters.

Fig. 2.1. Crack propagation under (a) opening mode, (b) sliding mode and (c) tearing mode [55].
2.2 SINGLE-SCALE TOUGHENING OF COMPOSITES

Various methods have been developed to improve the delamination resistance of composite using the addition of reinforcements or phases at multiple dimensional scales. Examples of these methods include the addition of nano-dimensional (i.e. <100 nm) or micron-dimensional (i.e. 1 µm - 100 µm) scale fillers within the polymer matrix or ply interlayer. Another method is the inclusion of macro/micro-dimensional scale (i.e. 100 µm – 2 mm) reinforcements along the through-the-thickness direction of the composite preform [49, 50, 52, 54, 56-60].

While being different, fundamentally, these methods improve the crack growth resistance by two classes of toughening mechanisms simultaneously, which include mechanisms that occur behind (i.e. extrinsic toughening) and ahead (i.e. intrinsic toughening) of the main crack tip, as illustrated in Fig. 2.2. The current and subsequent chapters contain a detailed description of the individual extrinsic and intrinsic toughening mechanisms invoked by the reinforcements.

![Fig. 2.2. Schematic of the extrinsic and intrinsic toughening mechanisms observed in structural materials [47].](image-url)
2.2.1 Toughening of epoxies using nano- and micron-scale fillers

Epoxies exhibit desirable property which includes good electrical insulating properties, the adhesion to substrates, flexibility to be processed for various conditions, high chemical and corrosion resistance [61]. Epoxies, either used in bulk or as matrices to bind the reinforcements, are intrinsically brittle. The brittle nature of epoxy stems from the high cross-link density of the polymer chains, thereby promoting to the low crack initiation and growth resistance when a flaw or notch is present [62]. A conventional method used improve the fracture toughness of epoxies and other brittle polymers is the inclusion of separate toughening phase. These phases or fillers are available in various morphologies and sizes.

The reinforcing fillers are dispersed into the liquid epoxy resin, at a random orientation, before adding the catalyst, further curing the epoxy. Fillers are commonly dispersed into the epoxy via manual mixing, shear mixing (or speed mixing), three-roll milling (or calendaring), ball milling, ultrasonication and extrusion (i.e. twin-screw extrusion) [63-69]. As shown in Fig. 2.3, fillers can be produced with various morphologies which include spherical particulates (i.e. zero-dimensional or 0D) [62, 70, 71], fibrous (i.e. one-dimensional)[72-74] or platelets (i.e. two-dimensional or 2D)[75-77]. Over the years, many different types of fillers have been used to toughen epoxies, some of which include rubber particles [78], silicates [79], thermoplastics [62, 65], and metal oxides [80-82].

![Fig. 2.3. Morphology of fillers used to toughen polymers and composites.](image)
Spherical silica (SiO$_2$) nanoparticles and microparticles (as shown in Fig. 2.4a) are widely used to improve the fracture toughness properties of polymer composites [78, 83-85]. The use of SiO$_2$ nanoparticles has attracted potential application in aircraft structures, windmill blades and composite storage tanks [61]. Liu et al. [86] reported that SiO$_2$ nanoparticles at 20 wt% in the epoxy can promote 310% improvements on the mode I fracture toughness ($G_{Ic}$) of epoxy polymers/composites when compared to the unmodified epoxy. Metal oxide spherical particles and platelets, as well, have been reported to enhance the fracture toughness and multi-functional properties of polymers and composites. Aluminium oxide [87] and titanium dioxide (TiO$_2$) [88], that possess near transparent optical properties (i.e. low-wideband gap), are used as additives for epoxy encapsulants and coatings. Alumina (Al$_2$O$_3$) has attracted much attention due to its high stiffness, strength and abrasive properties. Spherical or platelet-shaped Al$_2$O$_3$ nanofillers to increase the tensile and fracture toughness properties of bulk epoxies [71, 81, 89-91]. Fu et al. [84] reported that the toughening efficacy of these particles is critically dependent on the epoxy/filler interfacial properties, filler content, particle size and the filler type.

![SEM images of silica nanoparticles, carbon nanotubes (CNTs), carbon nanofibres (CNFs) and graphene nanoplatelets (GNPs).](image)

*Fig. 2.4* Scanning electron microscope (SEM) images of (a) silica nanoparticles [92], (b) carbon nanotubes (CNTs), (c) carbon nanofibres (CNFs) and (d) graphene nanoplatelets (GNPs). (Note: SEM images of CNTs, CNFs and GNPs in Figs. 6b, 6c and 6d were taken by the PhD Student (Anil) using FEI Nova SEM.)
**Table 2.1. Mode I fracture toughness of epoxy polymers containing various types of nanofillers.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Filler Type</th>
<th>Nanofiller Content (wt%)</th>
<th>Mode I Fracture Toughness, G&lt;sub&gt;Ic&lt;/sub&gt; (J/m&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu et al. [86]</td>
<td>Nanosilica - SiO&lt;sub&gt;2&lt;/sub&gt; (0D, 20nm dia)</td>
<td>0</td>
<td>277</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>390</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>560</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>791</td>
<td>185</td>
</tr>
<tr>
<td>Zhang et al. [81]</td>
<td>Alumina - Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (0D, 20-200 nm dia)</td>
<td>0</td>
<td>124</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>143</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>160</td>
<td>29.0</td>
</tr>
<tr>
<td>Rubab et al. [80]</td>
<td>Titanium Dioxide – TiO&lt;sub&gt;2&lt;/sub&gt; (0D, 35-60 nm dia)</td>
<td>0</td>
<td>1020</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>1080</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>1190</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>1380</td>
<td>35.3</td>
</tr>
<tr>
<td>Tang et al. [93]</td>
<td>Multi-walled carbon nanotubes-MWCNT (1D, 1.08 μm length and 15 nm dia)</td>
<td>0</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>135</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>145</td>
<td>34.2</td>
</tr>
<tr>
<td>Hsieh et al. [94]</td>
<td>MWCNT (1D, 120 μm length and 120 nm dia)</td>
<td>0</td>
<td>133</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>162</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>188</td>
<td>41.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>223</td>
<td>67.7</td>
</tr>
<tr>
<td>Liu et al. [95]</td>
<td>Carbon Nanofibres - CNF (1D, 30 μm length and 20-80 nm dia)</td>
<td>0</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>55</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>95</td>
<td>90.0</td>
</tr>
<tr>
<td>Zhang et al. [96]</td>
<td>CNF (1D, 50-200 μm length and 70 - 200 nm dia)</td>
<td>0</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.73</td>
<td>180</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1</td>
<td>170</td>
<td>42.0</td>
</tr>
<tr>
<td>Ladani et al. [58]</td>
<td>CNF (1D, ~20 μm length and 70 - 200 nm dia)</td>
<td>0</td>
<td>136</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>2160</td>
<td>1490</td>
</tr>
<tr>
<td>Zaman et al. [97]</td>
<td>Graphene Nanoplatelet - GNP (2D, 0.7 μm dia)</td>
<td>0</td>
<td>204</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>278</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>417</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>400</td>
<td>96</td>
</tr>
<tr>
<td>Ladani et al. [98]</td>
<td>GNP (2D, 25 μm dia and 15 nm thick)</td>
<td>0</td>
<td>136</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>380</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>790</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>980</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>1050</td>
<td>670</td>
</tr>
</tbody>
</table>

Silicates, metal oxides, thermoplastic and thermoset additives are effective at improving the fracture toughness properties of epoxy polymers. However, these materials are intrinsically dielectric, and have low electrical conductivity. Hence, there is a need for improving the electrical and other multi-functional properties of polymers. For the past decade, carbon nanomaterials such as carbon nanotubes (CNTs) and graphene has garnered significant attention primarily due to their superior stiffness, strength, electrical and thermal properties [72, 74, 99-101]. Applications of
carbon CNTs and graphene include biomedical [102], electronics [103], computation, sensing [63], power storage and reinforcing engineering structures [75, 104-106]. **Fig. 2.4b** presents a scanning electron microscope image of multiwalled carbon nanotube (MWCNT). MWCNTs have a tensile strength between 10 and 63 GPa and tensile modulus in the range of 270 to 950 GPa [107]. The mechanical properties of a monolayer (~0.3 nm) of graphene is higher with a tensile strength and modulus of ~130.5 GPa and ~1 TPa, respectively [108]. Carbon nanofibres (CNFs) is another popular nano-reinforcement that has garnered much interest due to the wide availability and low cost [57, 109]. The morphology of CNFs is represented as a helically stacked cup of sheets of carbon atoms with an outer fullerene wall [110], as shown in **Fig. 2.4c**. These type of nanofillers can be produced with high length-to-thickness or aspect ratios, making them desirable for reinforcing polymers.

**Table 2.1** presents a comparison of the effect SiO$_2$, Al$_2$O$_3$ and TiO$_2$, CNTs, CNFs and graphene (see **Fig. 2.4d**) nanoparticles have on the fracture toughness properties of epoxy polymers. The relative toughening improvement, with respect to fracture toughness of the epoxy polymer from the corresponding study, is dependent on the type of nanofiller, the dimensions and geometry of the nanofiller. Ladani et al. [98] reported substantial fracture toughness improvements of 1490% and 670% for an epoxy polymer containing 2 wt% of CNFs or 2 wt% of graphene nanoplatelets (GNPs), respectively. However, considering that different epoxy systems and dispersion techniques are used in various studies [66], it is difficult to make a clear distinction on the toughening efficacy of the various filler types. Factors such as the interfacial adhesion and the presence of functional groups on the fillers influence the improvements to the fracture toughness [111, 112]. Also, the dispersion of the nanofiller has a major role in improving the toughness of polymers and their composites. The van der Waals forces between carbon-based nanomaterials leads to agglomeration and poor dispersion within polymers. Tang et al. [93] reported on the effect of introducing hydroxide (OH) and carboxyl (COOH) groups on the surface of MWCNTs via ozone functionalization on the dispersion and mechanical properties of epoxy polymers. The presence of the polar OH and COOH groups not only minimises agglomeration but also promotes a stronger bond between the MWCNTs and epoxy, thereby resulting in a greater toughening efficacy when compared to the filler without functionalized groups [93]. However, there are process-structure effects arising from adding nanofillers within epoxies [113-115]. For instance, the addition of carbon nanofillers (i.e. CNTs) can, in most cases, increase viscosity of the epoxy
resin, which can negatively affect the processability when impregnated within a fibre reinforced composite [116, 117]. More importantly, the cure kinetics (i.e. curing reaction or degree of cure) and resin shrinkage can be altered when adding nanomaterials [116-118]. While findings from the literature are mixed, the presence of amine or hydroxide groups within carbon-based nanomaterials has been reported to catalyse the cure reaction in epoxies [116]. The addition of graphene oxide and CNTs has also been reported to increase the Vicker’s hardness of epoxies [119].

Fillers at the micron dimensional scale such as short carbon fibres (SCFs), as shown in Fig. 2.5a, are used to enhance the fracture toughness and other properties of epoxy polymers and composites [96]. The benefits of using SCFs is their relatively low material and processing costs combined with their high stiffness and strength. Studies have shown that SCFs extracted from waste material, such as off-cuts from dry carbon fabrics and carbon fibre-polymer laminates, can be used as a low-cost reinforcement (i.e. fillers, interleaves or veils) to improve the fracture toughness of bulk epoxy resin and composites [60, 96, 120]. For example, Cholake et al. [60] demonstrated that blending randomly oriented 10 wt% SCF into an epoxy yielded a 690% increase to the mode I fracture toughness, as shown in Fig. 2.5b.

![SEM image of short carbon fibres](image1)

**Fig. 2.5.** (a) SEM image of short carbon fibres [121] and (b) effect of short carbon content on the mode I fracture toughness of an epoxy polymer [60].

2.2.1.1 Fracture toughening mechanisms

The improvement in the fracture toughness properties of bulk epoxy polymers invoked by the nano- or micron-dimensional fillers, as described previously, are governed by the intrinsic and
extrinsic toughening mechanisms. These mechanisms are also present within laminated composites, metals, ceramics, and other engineering materials, which is further emphasised within this thesis.

The intrinsic toughening process occurs ahead of the main crack tip. When the crack tip is subjected to an external load at various modes (e.g. crack opening or shear sliding), tri-axial or hydrostatic stresses occur in the process zone, as shown in Fig. 2.6. Mechanisms that may occur in composite materials include interfacial debonding, shear yielding and plastic void growth within the polymer matrix phase [6, 78, 84, 86, 122-126]. During the interfacial debonding process, the filler is subjected to the tri-axial stress within the process zone [127]. The filler debonds when the local stress within the epoxy matrix exceeds the interfacial shear stresses, thereby dissipating some of the stored elastic strain energy. As shown in Fig. 2.6a, interfacial debonding is usually followed by shear banding or yielding of the epoxy matrix surrounding the fillers [126].

![Fig. 2.6. (a) Schematic of the intrinsic toughening mechanisms within a polymer [70]. SEM images of plastic void growth in (b) rubber-toughened [125] and (c) CNF reinforced [98] epoxy polymers. (d) SEM image of crack branching and microcracking in an epoxy containing GNP's [50].](image-url)
Voids can initiate next to the debonded fillers grow due to the tri-axial stresses and localised plastic flow of the epoxy matrix adjacent to the fillers. This mechanism is known as plastic void growth (also called cavitation). Examples of plastic void growth in epoxy polymers containing 0D rubber particles and CNFs are presented in Figs. 2.6b and 2.6c. The shear yielding and void growth mechanism involving plastic deformation of the epoxy further dissipates some of the stored strain energy [122]. From the SEM images of the fracture surface (see Figs. 2.6b and 2.6c), evidence of stress-whitening or shear bands of the epoxy surrounding the voids is indicative of plastic void growth process [122]. The mechanism of microcracking, as shown in Fig. 2.6d, is another intrinsic toughening mechanism where microcracks initiate ahead of the main crack which promote further crack propagation. These intrinsic toughening mechanisms promote improvements to the fracture toughness via crack tip plasticity mechanisms [47, 48, 128, 129].

Extrinsic toughening mechanism increases the fracture energy through crack-tip shielding that occurs behind the advancing crack front. Extrinsic toughening include bridging, snubbing and pull-out of the fillers, as illustrated in Fig. 2.7a. Examples of these processes reported for CNT, CNF and GNP reinforced epoxy polymers are presented in Figs 2.7b, 2.7c and 2.7d, respectively. The dominant extrinsic toughening mechanism is usually pull-out of the reinforcement from the matrix. [61]. Under the crack opening mode, the fillers are more likely to pull-out when aligned near normal to the crack plane. However, it is not reflective of most reports into the fracture toughness properties of 1D, or 2D particulate reinforced composites since the fillers are expected to be randomly orientated when dispersed within the polymer matrix. Fillers aligned near the crack growth direction are likely to rupture or not intersect with the advancing crack front. Therefore, in maximising the efficacy of the extrinsic toughening process, there is a desire to tailor the orientation of the fillers.
Fig. 2.7. (a) Schematic of intrinsic and extrinsic toughening mechanisms for epoxy polymers containing CNF and GNP [98]. SEM images of the fracture surface of epoxy polymers showing the bridging and pull-out mechanisms of (b) CNTs [130], (c) CNFs [98] and (d) GNP [98].

2.2.1.2 Effect of filler orientation

The fracture toughness of epoxy polymers is dependent on the orientation of the fillers used [15, 131, 132]. Fu et al. [133] demonstrated that the in-plane fracture toughness of an injection moulded SCF/polypropylene (PP) composite containing fibres that were normal to the crack plane was ~30% greater than the material containing fibres that were parallel to the crack plane. Externally assisted control of filler orientation has been reported using mechanical-assisted alignment [134, 135] and ultrasonic-assisted alignment [136]. The use of magnetic field to orient CNTs, CNFs and GNP along the direction of the applied field to tailor the mechanical properties of epoxy polymers have been reported in [137-140]. Recent studies have shown that CNTs [141-
143], CNFs [57] or GNP s [50, 58] can be rapidly aligned in a liquid epoxy resin using an alternating current (AC) [50, 57, 58] or direct current (DC) electric field [143].

Khan et al. [141] reported that aligning CNTs normal to the crack propagation plane using a DC electric field further increased the mode I fracture toughness by ~30-40% when compared to CNTs at a random orientation, as shown in Fig. 2.8. This enhancement was due to the increased proportion of CNTs participating in the bridging toughening process. Wu et al. [50] found a similar toughening effect for GNP s aligned in epoxy polymers using a low AC electric field (of ~30V/mm). Magnetophoretic techniques have been reported to align SCFs within liquid thermosetting and elastomeric resins [144, 145]. However, the electric field alignment of SCFs in an epoxy resin and its effect on the fracture toughness of epoxy polymers has not been reported.

![Fig. 2.8. Effect of DC electric field alignment on the mode I fracture toughness of epoxy nanocomposites containing various contents of CNTs [141].](image)

**2.2.2 Delamination toughening of fibre reinforced epoxy composites using nano- and micron-dimensional scale fillers**

**2.2.2.1 Modification of the epoxy matrix**

Recent studies have shown that the addition of nano- or micron-dimensional scale fillers within the epoxy matrix phase are effective at increasing the delamination resistance of fibre reinforced epoxy composites. The methods of blending nano-fillers into the liquid resin are similar to those reported for bulk epoxies, as mentioned in Section 2.2.1. The toughened epoxy resin is
introduced into a dry fibre preform by wet-hand layup [146], resin infusion [117], resin transfer moulding [147], liquid compression moulding [49], resin film infusion (with limitations) [148] and pre-impregnation of partially (or B-stage) cure resin into a dry preform (i.e. pre-preg) [67]. Arai et al. [149] reported the delamination resistance properties of carbon fibre composites containing MWCNTs at various areal densities within the epoxy interlayer, where Fig. 2.9 presents the mode I interlaminar fracture toughness ($G_{IC}$) with crack extension ($\Delta a$). The mode I interlaminar fracture toughness increases with crack extension (i.e. R-curve effect) due to the cross-fibre bridging between plies [150]. The fracture toughness then plateaus to a steady-state value due to the development of a fully bridged zone. The addition of MWCNTs enhances both the initiation and steady-state mode I interlaminar fracture toughness of the composite [151]. Wu et al.[152] reported a similar effect with the addition of 0.73 wt% CNFs within the epoxy matrix of glass fibre reinforced epoxy composites, as shown in Fig. 2.10. The improvement in the initiation toughness was due to plastic void growth. With crack propagation, the rapid increase in fracture toughness was attributed to the extrinsic toughening mechanisms of bridging and pull-out of CNFs between the crack faces [152]. The steady-state mode I toughness ($G_{IC,ss}$) was enhanced by aligning the CNFs near normal to the delamination plane.

![Mode I crack growth resistance curve (R-curve) of carbon fibre reinforced epoxy composites containing different areal densities (g/m²) of MWCNTs](image)

**Fig. 2.9.** Mode I crack growth resistance curve (R-curve) of carbon fibre reinforced epoxy composites containing different areal densities (g/m²) of MWCNTs [151].
Fig. 2.10. Effect of electric field alignment on the (a) mode I crack growth resistance curves and (b) fracture toughness of glass fibre reinforced epoxy composites containing CNFs [152].

Table 2.2 presents a comparison of the reported improvements to the mode I fracture toughness of carbon fibre reinforced epoxy composites using CNTs, CNFs or GNPs. The mode I delamination toughening increases with the nanofiller content. The addition of carbon-based nanofillers, particularly CNFs and GNPs, at contents lower than ~3 wt% results in improvements to the steady-state mode I fracture toughness of between 10% to 150%. Toughening mechanisms are identical to intrinsic and extrinsic toughening mechanism reported for epoxy polymers, as detailed in Section 2.2.1. However, these improvements to the delamination toughness are lower than the mode I fracture toughness improvement observed for the epoxy polymers containing CNFs or GNPs (see Table 2.1).

Table 2.2. Steady-state mode I interlaminar fracture toughness of carbon fibre reinforced epoxy composites containing CNTs, CNFs or GNPs.

<table>
<thead>
<tr>
<th>Source</th>
<th>Nanofiller doped within the epoxy matrix</th>
<th>Nanofiller Content (wt%)</th>
<th>Steady-State Mode I Interlaminar Fracture Toughness, $G_{Ic,ss}$ (J/m²)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quan et al. [153]</td>
<td>MWCNT</td>
<td>0</td>
<td>428</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>462</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>537</td>
<td>25.0</td>
</tr>
<tr>
<td>Mirjalili et al. [154]</td>
<td>MWCNT</td>
<td>0</td>
<td>424</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>630</td>
<td>48.0</td>
</tr>
<tr>
<td>Abdin et al. [155]</td>
<td>MWCNT</td>
<td>0</td>
<td>570</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>639</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>658</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>MWCNT</td>
<td>0</td>
<td>550</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>G_{IIc-ss} (J/m²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------</td>
<td>--------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Kostagiannakopoulou et al. [67]</td>
<td>0.5</td>
<td>720</td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>750</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>Hsiao et al. [156]</td>
<td>CNF</td>
<td>0</td>
<td>305</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>393</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>371</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>Palmeri et al. [157]</td>
<td>CNF</td>
<td>0</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>174</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>159</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Kostopoulos et al. [158]</td>
<td>CNF</td>
<td>0</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.37</td>
<td>910</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Srivastava et al. [159]</td>
<td>GNP</td>
<td>0</td>
<td>843</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2130</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Du et al. [33]</td>
<td>GO (Graphene Oxide)</td>
<td>0</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>995</td>
<td>91.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1260</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Moghadam et al. [76]</td>
<td>GNP</td>
<td>0</td>
<td>339</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>379</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>Roy et al. [160]</td>
<td>GNP</td>
<td>0</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>756</td>
<td>65.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>917</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

High resistance to mode II delamination crack growth is critical to low-velocity impact damage tolerance [161, 162] and the load-carrying capacity of structural composite joints [163], as further reviewed in Chapters 5 and 9. Table 2.3 presents a comparison of the mode II interlaminar fracture toughness ($G_{IIc}$) values for carbon fibre reinforced epoxy composites toughened using CNTs, CNFs or GNPs. The improvement in the $G_{IIc}$ is due to the extrinsic and intrinsic toughening mechanisms such as the frictional shear sliding resistance and crack bridging and pull-out of the nanofillers, together with microcracking [67, 164-167], as detailed in Chapters 5, 6, 7 and 8. CNTs promote a much greater relative mode II toughening improvement (i.e. 70 - 170%) than CNFs or GNPs. However, considering that different epoxy systems, dispersion techniques and composite manufacturing methodology are used in various studies [66], it is difficult to make a clear comparison on the modes I and II toughening efficacy of different nanofiller types.
Table 2.3. Steady-state mode II interlaminar fracture toughness of carbon fibre reinforced epoxy composites containing CNTs, CNFs or GPNs.

<table>
<thead>
<tr>
<th>Source</th>
<th>Nanofiller doped within the epoxy matrix</th>
<th>Nanofiller Content (wt%)</th>
<th>Steady-State Mode II Interlaminar Fracture Toughness, ( G_{IIc} ) (J/m²)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quan et al. [153]</td>
<td>MWCNT</td>
<td>0</td>
<td>2030</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>3410</td>
<td>68.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>5500</td>
<td>170</td>
</tr>
<tr>
<td>Srivastava et al. [159]</td>
<td>MWCNT</td>
<td>0</td>
<td>161</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>346</td>
<td>115</td>
</tr>
<tr>
<td>Mirjalili et al. [154]</td>
<td>MWCNT</td>
<td>0</td>
<td>542</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>614</td>
<td>13.0</td>
</tr>
<tr>
<td>Ma et al. [168]</td>
<td>CNF</td>
<td>0</td>
<td>440</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>550</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>565</td>
<td>28.0</td>
</tr>
<tr>
<td>Yokozeki et al. [169]</td>
<td>CNF</td>
<td>0</td>
<td>605</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>786</td>
<td>30.0</td>
</tr>
<tr>
<td>Srivastava et al. [159]</td>
<td>GNP</td>
<td>0</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>229</td>
<td>43.0</td>
</tr>
<tr>
<td>Kostagiannakopoulou et al. [67]</td>
<td>GNP</td>
<td>0</td>
<td>1570</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>1860</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>1680</td>
<td>7.0</td>
</tr>
</tbody>
</table>

2.2.2.2 Deposition of nanofillers and interleave toughening

Alternative approaches to improve the interlaminar fracture toughness through the deposition of carbon-based nanofillers onto continuous fibres, tows or plies have been investigated. For example, Zhang et al. [170] recently reported a 50% improvement in the mode I fracture toughness of carbon fibre laminates by spray coating a very low loading of CNTs (~ 0.047 wt%) between the prepreg plies. Electrophoretic deposition of carbon nanofillers on fibre reinforcement can also improve the interlaminar properties [30]. Growing CNTs directly onto carbon fibres, via chemical vapour deposition (CVD) has attracted much interest in optimising dispersion and increasing the fibre-matrix interfacial properties [100, 120]. For examples, Kim et al. [171] found that growing carbon nanotubes on the surface of carbon fibre ply/fabric yielded up to 80% improvement in the \( G_{IIc,ss} \) value when compared to the baseline composite material.

The insertion of interleaves made of thermoplastic, nano- or micron-scale reinforcements between the plies is effective technique to enhance the delamination resistance [34, 165, 172-175]. Beckermann and Pickering [176] found that electrospun nanofibre veils interleaved within a
carbon-epoxy laminate increased the $G_{IC-SS}$ and $G_{IIc-SS}$ values by up to ~160% and 70%, respectively. Veils made of chopped SCFs are also effective [32, 60]. Garcia et al. [28] developed a novel method to join prepreg composite layers using vertically aligned carbon nanotube (VACNT) forests, as shown in Fig. 2.11. By incorporating a ~20 μm thick interlayer of VACNT (1 vol%) between the plies, it increases the modes I and II fracture toughness by 250% and 300%, respectively.

Fig. 2.11. Schematic of aligned carbon nanotube forest, and (b and c) SEM images of CNT forest [171].

### 2.2.3 Through-the-thickness toughening of fibre reinforced epoxy composites

Conventional fibre reinforced polymer composites lack a fibre reinforcement phase along the thickness direction, making them prone to delamination. Well-established techniques in improving the through-the-thickness and interlaminar properties of composites is the incorporation of through-the-thickness fibres, pins or other reinforcements [5, 35], as illustrated in Fig. 2.12a. 3D fibre reinforced composites are produced by 3D weaving [35, 54, 177, 178], stitching [177, 179-182], tufting [56, 183, 184], braiding [35, 185-187], z-anchoring [35] and z-binding [54].
For example, Dransfield et al. [181] investigated the effect of through-thickness stitching of carbon-epoxy composite using T900 carbon fibre tows (3.33 mm long and ~164 μm in diameter), on the delamination toughness properties. An improvement of up to 1470% in the $G_{IC,s}$ value was reported, at a stitch density of 8/cm². These large-scale improvements at typically measured for 3D composites under mode I and II interlaminar loading [54, 177, 189-191], which is attributed due to the large-scale bridging of the through-thickness reinforcement behind the crack tip. Figs. 2.12b to 2.12d, presents an example of the large-scale bridging process of z-binders within a 3D reinforced composite under mode I loading [188]. Reported demonstrator component made with 3D reinforced composites include wind turbine blades, leading edges to wings, stiffeners and T-sections/joints for fuselage frame structures [4, 5].

2.2.3.1 Interlaminar toughening of fibre reinforced epoxy composites using z-pins

Z-pinning is another technique to transversely toughen composite laminates [36]. Z-pinning is a simple process of inserting thin metallic or pultruded fibrous rods along the through-thickness direction of fibre preforms or prepregs via an ultrasonically assisted insertion (UAZ) process [36], as shown in Fig. 2.13.
Z-pins are used currently in structural joints and stiffened panels to aircrafts such as the F/A-18 E/F Superhornet [193] and C-17 Globemaster II [43]. Partridge and colleagues estimated that the automated insertion process of z-pins in an aircraft structure would minimise the assembly cost by 70% compared to using metal fasteners [37]. Many studies have demonstrated the use of z-pins to improve the delamination toughness [39, 194-203], impact damage tolerance [40, 204-206] and joint strength [26, 43, 45, 207-209] of composites [36]. For example, Pingkarawat et al. [53] assessed the effect of carbon fibre/bismaleimide (BMI) z-pins on the mode I interlaminar fracture toughness and fatigue delamination properties of carbon fibre reinforced epoxy composites. They found that the toughness improved up to 15.5 fold in comparison to the unpinned composite laminate [53], as shown in Fig. 2.14. Factors such as z-pin volume content, diameter and embedded length influence the interlaminar properties, as shown in Figs. 2.14b, 2.14c and 2.14d. [52, 53, 192]. The toughness improvement increases proportionally with the increase in z-pin volume fraction, in increase in z-pin embedded length and decrease in z-pin diameter (a a fixed volume fraction). The mode I fracture toughness improvement is due to the large-scale extrinsic toughening via elastic deformation, interfacial debonding and pull-out of the pins. The toughening process occurs along the thickness of the composite rather between the ply-to-ply interlayer bondline [11, 36, 52]. The traction loads carried by the bridging of z-pins minimises the stress intensity at the crack tip [36]. The fracture energy due to pin pull-out, under mode I loading condition, is
the most dominant toughening mechanism contributing to the large fracture toughness enhancement.

![Image](image-url)

**Fig. 2.14.** (a) Mode I crack growth resistance curve of carbon fibre composites containing z-pins. Effect of z-pin (b) volume content, (c) diameter and (d) embedded length on the $G_{Ic}$ value. Results are adapted from [53].

Considering the relationship between the toughening efficacy and the geometrical parameters of the z-pins, increasing the embedded length can promote significant increases in the apparent mode I interlaminar fracture toughness [210]. However, past a critical pull-out length, the pins are likely to rupture due the interfacial shear stress exceeding the failure strength of the pins, thereby decreasing the toughening efficacy [211]. From a practical standpoint, increasing the thickness of laminate to accommodate for the long pins may lead to overdesigning and increased weight of the structural composite. A long-standing problem associated with z-pinned, as well as
3D woven or stitched, composites is that these macro-scale through-thickness reinforcements and interleaves inevitably imparts defects such as fibre crimp (e.g. local misalignment), fibre damage and localised resin rich regions [35, 36, 41, 44, 178, 212-214]. As a tradeoff in improving the through-the-thickness properties, these geometric defects can degrade the in-plane properties under both quasi-static and cyclic loading. For example, fibre reinforced composites containing a relatively high volume content of z-pins (~ 4 vol%) exhibit lower in-plane tensile and compression properties (i.e. stiffness and strength) up to 11% when compared to their un-pinned counterpart [36, 178, 213, 214].

To enhance the toughening efficacy of z-pins at lower contents, several studies have investigated modifying the interfacial shear properties between the z-pin and epoxy interface or changing the z-pin type. For example, Hoffmann et al. [215] found that introducing circumferential notches on the surface of carbon fibre z-pins (see Fig. 2.15) increased the mode I interfacial shear friction stress and pull-out traction energy (measured via pin pull-out tests) by up to 150% and 14%, respectively, when compared to unnotched z-pins. Pingkarawat et al. [11] investigated the effect of z-pin material type, and found that carbon fibre/BMI z-pins were much effective at improving the mode I delamination resistance compared to stainless-steel, titanium and copper pins. The use of rectangular z-pins has been reported increase the $G_{\text{IC}}$ value of carbon-epoxy composites by 42.8-fold, which is significantly greater than the 38.6-fold improvement using circular z-pins [215]. Wang et al. [216] recently demonstrated that coating carbon fibre/BMI z-pins with SCFs or CNTs (see Figs. 2.16a, 2.16b and 2.16c) can further enhance the z-pin pull-out traction energy generated by the z-pins. Coating the z-pins with carbon fillers can increase the interfacial shear friction stress at during pullout by up to ~200%, as shown in Fig. 2.16d. As a result, the z-pin coated with nano- and micron- scale fillers were effective at increasing the steady-state mode I fracture toughness and crack-growth toughness in comparison to the composite containing uncoated z-pins by up to ~43%, as shown in Fig. 2.16e [216].
Fig. 2.15. Circumferentially notched carbon fibre z-pins [215].

Fig. 2.16. SEM images of (a) uncoated, (b) SCF coated and (c) CNT coated carbon fibre/BMI z-pins. Mode I (d) pull-out response of single z-pins and (e) crack growth resistance of carbon fibre composite laminates containing particulate coated z-pins [216].
While the toughening mechanisms of z-pinned composites under mode I loading is primarily dominated by pull-out of the pins, different toughening mechanisms are presented for mode II growth. Pegorin et al. [51] reported that the addition of 2.0 vol.% z-pins improve the $G_{IIc}$ value by up to 10.6 fold. The mode II toughness increases with the volume content of z-pins, as shown in Fig. 2.17a.

**Fig. 2.17.** (a) Mode II crack growth resistance curve of carbon fibre epoxy composites containing z-pins at various contents [51]. (b) Illustration and SEM images of the z-pin bridging process behind the crack tip under the mode II crack propagation mode [51].
The improvements to the mode II is due to elastic deformation followed by longitudinal splitting, snubbing, partial pull-out and shear rupture of the z-pins with increasing crack sliding displacement [10, 51, 52], as shown in Fig. 2.17b. Z-pins with a shorter embedded length [192] and larger diameter [51] for a given volume fraction have been reported to enhance the mode II toughening efficacy of z-pins. M’membe et al. [10] demonstrated that inserting carbon fibre/BMI z-pins diagonally (i.e. +45°) rather than orthogonally promotes a ~90% improvement to the mode II fracture energy. Inclining the z-pins diagonally towards the nap or along the shearing direction engenders higher snubbing and pull-out, thereby increasing the mode II toughness [10, 217]. However, there are little or no reports directly correlating the effect of the interfacial shear friction stress properties or the geometrical modification of the pin on the mode II or even mixed mode I/II delamination toughness of z-pinned composites.

2.2.3.2 Comparison of interlaminar toughening techniques

Table 2.4 presents a comparative overview of the improvements to the interlaminar fracture toughness of composites using reinforcements with different dimensional scales. Macro-scale reinforcements (e.g. z-pins) promote a much greater delamination toughening effect than carbon nano-fillers. This is attributed to the larger-scale extrinsic toughening mechanism that occurs at long crack propagation lengths (i.e. 20-30mm), using z-pins, stitches or 3D woven yarns. Nanofillers create a much shorter bridging zones (i.e. <20 μm) along the delamination cracks. However, carbon-based nanofillers can improve the initiation fracture toughness due to the intrinsic toughening mechanisms and the functional enhancement in the properties of the epoxy matrix [49, 91, 155, 218-220], which does not occur using macro-scale reinforcements.
**Table 2.4. Modes I and II interlaminar fracture toughness of carbon fibre reinforced epoxy composites toughened by reinforcement with different length scales**

<table>
<thead>
<tr>
<th>Dimensional Scale</th>
<th>Reinforcement Type</th>
<th>Content of reinforcements</th>
<th>Interlaminar fracture toughness</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro length scale through-the-thickness reinforcements (300µm - 2mm)</td>
<td>3D stitching (T900 Carbon Fibre 164 µm dia)</td>
<td>Unstitched -</td>
<td>1280</td>
<td>[177]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T900 carbon 4 stitch /cm² -</td>
<td>3850 (201%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>T900 carbon 8 stitch /cm² -</td>
<td>4240 (230%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3D stitching (24K Tenax ST240) z-binder</td>
<td>0 vol.% 800</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8 vol.% -2300 (190%)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.2 vol.% -6100 (660%)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z-pins (4mm long, 280 µm dia, Carbon Fibre/BMI)</td>
<td>0 vol.% 970</td>
<td>1100</td>
<td>[51, 53]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 vol.% 2700 (180%)</td>
<td>3700 (240%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0 vol.% 15030 (1450%)</td>
<td>5200 (370%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0 vol.% -</td>
<td>11700 (960%)</td>
<td></td>
</tr>
<tr>
<td>Micron (7 µm - 100 µm)</td>
<td>Milled SCF (7µm dia)</td>
<td>0 280</td>
<td>-</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 wt.% (6.0vol%) 460 (64%)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SCF interleaves (7µm dia)</td>
<td>0 mg/cm² 520</td>
<td>-</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 mg/cm² 920 (73%)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nano (1µm-2nm)</td>
<td>MWCNT (Multiwalled carbon nanotubes) (10-15nm dia)</td>
<td>0 wt% 300</td>
<td>1000</td>
<td>[164]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 wt% 420 (40%)</td>
<td>1750 (75%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 wt% 480 (60%)</td>
<td>1450 (45%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nanosilica (20nm)</td>
<td>0 wt% 995</td>
<td>968</td>
<td>[221]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 wt% 1007 (1.2%)</td>
<td>929 (-4.0%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 wt.0% 1203 (21%)</td>
<td>750 (-22%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF interleaves (carbon nanofibre with 70-200nm dia)</td>
<td>0 g/m² 500</td>
<td>1250</td>
<td>[167]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 g/m² 520 (4%)</td>
<td>1900 (52%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 g/m² 700 (40%)</td>
<td>2000 (60%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF (70-200nm dia)</td>
<td>0 wt% -</td>
<td>450</td>
<td>[168]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 wt% -</td>
<td>550 (22%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0 wt% -</td>
<td>850 (90%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNF (70-200nm dia)</td>
<td>0 wt% 670</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 wt% 1120 (70%)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Note: Numbers in bracket along the "Interlaminar Fracture toughness" column indicates the percentage improvement in the properties of fibre reinforcement comparison to their unmodified counterpart.
2.3 MULTI-SCALE TOUGHENING OF COMPOSITES

Nano-dimensional scale fillers, toughened interleaves and macro-scale through-the-thickness reinforcements are almost always used separately to increase the fracture toughness of bulk epoxy composites/polymers and fibre reinforced polymer composites. There is interest in combining various reinforcing approaches via hierarchical or multi-scale toughening with the aim to synergistically increase the toughness properties. Synergistic toughening is achieved when the materials exhibit a property (e.g. toughness) far exceeds the sum contribution of their constituents (i.e. greater than additive effect).

Bone, wood and nacre (i.e. abalone shell), are examples of natural materials that have relatively high toughness values via multi-scale or hierarchically reinforcements. Natural composite-like materials consist of highly-ordered constituent materials spanning the nano- to macro-length scales that induce stiffening, strengthening and toughening mechanisms not achieved when the constituents are used separately [222-225]. As shown in Fig. 2.18a, human cortical bone is an example of a multi-scale reinforced material. The fracture resistance of cortical bone can be separated into intrinsic mechanisms that promote ductility and extrinsic toughening mechanisms that act to resist crack growth [224, 226, 227]. The intrinsic toughness of bone originates at the nanometer length scale through multiple processes, which include uncoiling of mineralised collagen and fibrillary sliding (1.5nm) [149]. These mechanisms promote plasticity near the crack tip at the nano- and micron-length scales resulting in a high fracture toughness [149]. An even more significant contribution to the fracture resistance in bone occurs via large-scale extrinsic toughening behind the crack tip [224, 228, 229]. During the crack growth process, large-scale reinforcements (10-100 µm) such as the osteons bridge the crack and promote substantial toughness [228]. Nacre is another multi-scale reinforced structure has garnered significant interest particularly in exhibiting high stiffness, toughness and ductility which consists of brittle constituents (e.g. calcium carbonate) [222, 223]. Nacre has a “brick and mortar” architecture (see Fig. 2.18b), which is essential for high toughness [224]. Interestingly, these processes are analogous to the extrinsic toughening mechanisms exhibited by fibre reinforced composite containing carbon nanofillers or z-pins, as described in Section 2.2 [49].
Using brittle building blocks, natural composite-like materials are claimed to possess toughness properties (i.e. $\Delta G_{1+2+3+...}$) that are far greater than the additive contribution their individual components (i.e. $\Delta G_1 + \Delta G_2 + \Delta G_3 + ...$) [46, 48, 224, 229]; thereby inducing a synergistic toughening effect which can expressed below [49, 230]:

$$\Delta G_{1+2+3+...} \geq \Delta G_1 + \Delta G_2 + \Delta G_3 + ...$$ (2)

The interactions between the constituents at the nano- and micron-scale levels invoke additional toughening mechanisms that promote the synergistic toughening effect [47, 128, 231]. Synergy is also referred to as the joint action of reinforcements, that each increases the effectiveness of the others when combined. In this case, the synergistic or greater-than-expected additive improvement can be expressed as [49, 230, 232]:

$$Synergy\,\% = \left( \frac{\Delta G_{1+2+3+...}}{\Delta G_1 + \Delta G_2 + \Delta G_3 + ...} - 1 \right) \times 100\%$$ (3)
The magnitude of the toughening effect in natural composites depends on the relative concentrations, material type, architecture and orientation of the constituent materials [227, 233, 234].

Inspired by this effect, there is a growing interest in adapting hierarchical or multi-scale toughening approaches to synergistically improve the fracture toughness properties of engineered composites [47-49].

### 2.3.1 Multi-scale toughening of epoxy polymers

Many studies have investigated the effect of hybridising two or more fillers types via a multi-scale toughening approach to synergistically enhance various properties of bulk polymers. For examples, synergistic improvements to the electrical conductivity of polymers has been achieved using two types of carbon-based nanofillers (63, 232, 235-239). Yang et al. [240] reported a synergistic of enhancement on the tensile strength (~1.6%) and thermal conductivity (~10.6%) of an epoxy polymer containing 0.1 wt% MWCNTs and 0.9 wt% GNPs, when compared to a epoxy polymer containing either 1 wt% MWCNTs or 1 wt% GNPs.

Several studies hybridised nano- and micron- scale reinforcements to synergistically improve the fracture toughness properties of bulk polymers. For example, Kinloch et al. [83] showed that hybridising spherical carboxyl-terminated butadiene-acrylonitrile (CTBN) micron-sized rubber particles with SiO$_2$ nanoparticles can promote synergistic toughening of epoxy polymers. The mode I fracture toughness for the multi-scale reinforced polymers containing 9 wt% CTBN rubber particles and SiO$_2$ nanoparticles far exceeds the expected additive enhancement when the two filler types are used separately [83], as shown in Fig. 2.19. The greater-than-expected additive enhancement in fracture energy increased with SiO$_2$ content, with a synergistic improvement of up to ~95% [83].
Fig. 2.19. Mode I fracture toughness of unmodified and CTBN rubber particle reinforced epoxy polymers/composites at various concentration of SiO$_2$ nanofillers [83]. (Note: data was gathered from [83] and the dashed line added represents the expected additive improvement when taking the separate toughening contribution from the epoxy polymer containing 9 wt% CTBN rubber particles and SiO$_2$ nanoparticles at various contents.)

Fu et al. [133] found a synergistic improvement of up to 8% to the mode I fracture toughness of multi-scale toughened polypropylene containing short carbon and glass fibres. However, hybridising two fillers does not necessarily yield any synergistic enhancement in most cases. For instance, Chatterjee et al. [65] investigated the fracture toughness properties of an epoxy polymers containing both CNTs and GNPs. Toughening the epoxy both with CNTs and GNPs at various hybridisation ratios did not induce a synergistic toughening effect, and instead the toughness was lower than the expected additive effect [65]. A more recent study on the hybridisation effects of GNPs and CNF on the mode I fracture toughness of epoxy polymer also reported an additive enhancement due to the absence of any additional toughening mechanisms [98].

As another example, Zhang et al. [96] found that combining randomly oriented milled CNFs (0.73 – 1.1 wt%) with SCFs (14.3 wt%) in epoxy polymers resulted in synergistic improvements to the $G_{Ic}$ values, as shown in Fig. 2.20a. The synergistic toughening improvement is measured to be 69% to 80% greater than the expected additive enhancement [96]. As shown in Figs. 2.20b and 2.20c, the addition of CNFs imparted an additional release of triaxial stressed on
SCFs, resulting in the formation of an enlarged process zone near the crack tip [96]. In another study, Zhang and colleagues [241] also reported synergistic improvements to the $G_{IC}$ values of a multi-scale toughened epoxy polymers containing 0D SiO$_2$ nanofillers and SCFs.

![Graph showing fracture toughness values](image)

**Fig. 2.20.** (a) Mode I fracture toughness of epoxy polymers containing CNFs, nano-silica or/and SCFs. Illustration of failure under the plane-strain condition for (b) epoxy polymers reinforced with SCFs only and (c) reinforced with both SCFs and CNFs[96].

### 2.3.2 Multi-scale toughening of fibre reinforced epoxy composites

Hybridising two or more fillers is proven to beneficial in synergistically enhancing the tensile, fracture toughness and other properties of bulk epoxy polymers. Achieving synergies in the interlaminar fracture toughness of fibre reinforced polymer composites is often desired at relatively low filler contents [49, 68, 230]. However, a few studies multi-scale interlaminar
toughening of fibre-polymer composites. In one of the few studies, Kostagiannakopoulou et al. [67] investigated the modes I and II toughening of carbon fibre reinforced epoxy composites using both GNPs and CNTs. Kostagiannakopoulou et al. [67] reported substantial improvements on the interlaminar fracture toughness (see Table 2.5) when combining GNPs and CNTs, however, toughening effect was less than additive. Other reports on hybridising block copolymer with core-shell rubber particles [242], or combining nano-silica and nano rubber particles [243] on the mode I interlaminar fracture toughness properties of carbon-epoxy composites are summarised in Table 2.5. This table contains the fracture toughness properties for composites containing reinforcements/fillers when used separately and in combination [49, 67, 242, 243]. Hybridising the reinforcements leads to improvements in the toughness properties when compared to the unmodified composite (i.e. $G_0$). By considering the $G_{Ic-ss}$ values of the composites containing the first filler type (i.e. $G_1$) or the second filler type (i.e.) from [67, 242, 243], the expected fracture toughness value for the multi-scale reinforced composite ($G_{i+2}$) when taking the sum of individual toughening contribution is:

$$G_{1+2} = G_0 + (G_1 - G_0) + (G_2 - G_0)$$

(4)

is greater than the measured values. The synergistic improvement over the expected additive enhancement listed in Table 2.5 from each study can be calculated using the equation [49].

$$Synergy \ (\%) = \left( \frac{G_{i+2} - G_0}{(G_1 - G_0) + (G_2 - G_0)} - 1 \right) \times 100\%$$

(5)

The multi-scale toughened composites reported in [67, 242, 243] exhibited a lower-than-additive or, at best, additive [243] enhancement in the $G_{Ic-ss}$ values. If the fracture toughness were simply additive, this would mean that there were no interactions between the two fillers. Rather, the lower-than-expected additive effect suggests that the addition of a second toughening phase may inhibit the toughening mechanisms of the other phase, or vice-versa, which is often due to the increased packing density and agglomeration at higher filler loadings [57, 96, 230].
### Table 2.5. Steady-state mode I interlaminar fracture toughness properties and synergistic improvement of multi-scale fibre reinforced epoxy composites.

<table>
<thead>
<tr>
<th>Source</th>
<th>Measured $G_{IC}$ of unmodified composite ($G_0$)</th>
<th>Measured $G_{IC}$ of composite containing toughening agent 1 ($G_1$)</th>
<th>Measured $G_{IC}$ of composite containing toughening agent 2 ($G_2$)</th>
<th>Measured $G_{IC}$ of multi-scale toughened composite ($G_{1+2}$)</th>
<th>Expected $G_{IC}$ of multi-scale toughened composite ($G_{1+2}^E$)</th>
<th>Synergistic Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Kostagiannakopoulou et al. [67] - (Carbon Fibre Epoxy Composite toughened with GNPs and CNTs modified epoxy)</td>
<td>0.550 kJ/m$^2$</td>
<td>0.700 kJ/m$^2$ (0.5 wt% GNP)</td>
<td>0.720 kJ/m$^2$ (0.5 wt% GNP)</td>
<td>0.760 kJ/m$^2$ (0.5 wt% GNP + 0.5 wt% CNT)</td>
<td>0.870 kJ/m$^2$ (0.5 wt% GNP + 0.5 wt% CNT)</td>
<td>-34.4%</td>
</tr>
<tr>
<td>2) Klingler et al. [242] - (Carbon Fibre Epoxy Composite toughened with block copolymer (BCP) and core-shell rubber (CSR) modified epoxy)</td>
<td>0.310 kJ/m$^2$</td>
<td>0.711 kJ/m$^2$ (5 wt% CSR)</td>
<td>0.577 kJ/m$^2$ (5 wt% BCP)</td>
<td>0.964 kJ/m$^2$ (5 wt% CSR + 5 wt% BCP)</td>
<td>0.978 kJ/m$^2$ (5 wt% CSR + 5 wt% BCP)</td>
<td>-2.1%</td>
</tr>
<tr>
<td>3) Zeng et al. [243] - (Carbon Fibre Epoxy Composite toughened with nano-silica (SiO$_2$) and nano-rubber (RB) modified epoxy)</td>
<td>0.520 kJ/m$^2$</td>
<td>0.640 kJ/m$^2$ (4 wt% SiO$_2$)</td>
<td>0.66 kJ/m$^2$ (4 wt% RB)</td>
<td>1.02 kJ/m$^2$ (4 wt% SiO$_2$ + 4 wt% RB)</td>
<td>1.01 kJ/m$^2$ (4 wt% SiO$_2$ + 4 wt% RB)</td>
<td>+1.2% (additive)</td>
</tr>
<tr>
<td>4) Ladani et al. [49] - (Carbon Fibre Epoxy Composite toughened with CNF modified epoxy and carbon fibre/BMI z-pins (0.288 dia and 5 mm long))</td>
<td>0.720 kJ/m$^2$</td>
<td>1.410 kJ/m$^2$ (1 wt% CNF)</td>
<td>2.650 kJ/m$^2$ (0.5 vol% z-pins)</td>
<td>3.62 kJ/m$^2$ (1 wt% CNF + 0.5 vol% z-pins)</td>
<td>3.34 kJ/m$^2$ (1 wt% CNF + 0.5 vol% z-pins)</td>
<td>+10.7%</td>
</tr>
</tbody>
</table>

### 2.4 SUMMARY AND RESEARCH GAPS

Nano-, micron- or macro-dimensional scale reinforcements, when used separately, can improve the fracture toughness properties of bulk polymers and the delamination resistance fibre reinforced epoxy composite structures [36, 61, 65, 68, 69, 244]. The fracture toughness properties
of composites are dependent on the type, morphology, volume fraction and orientation of fillers or reinforcements.

Adapting hierarchical toughening approaches by hybridising two or more reinforcements at multiple dimensional scales has shown to promote synergistic improvement on the fracture toughness properties of epoxy polymers, that far exceeds the expected additive enhancement when the reinforcements are used separately. For instance, Zhang et al.[96] has demonstrated that adding both randomly oriented 0.73 – 1.1 wt% CNFs and 14.3 wt% SCFs within a epoxy polymers can yield to synergistic enhancements (<80%) in the mode I fracture toughness. Several reports have shown that electrically aligning CNTs, CNFs or GNPs normal to the crack propagation direction resulted in a higher toughness (~30%) for the epoxy composites compared to when these reinforcing fillers were randomly oriented [50, 57, 141]. However, the electric field alignment of micron-dimensional scale CNFs and/or SCFs in an epoxy resin and its effect on the toughness of epoxy polymers is not well understood, which is addressed in Chapter 3 and Chapter 4. Studies have shown that carbon nanofillers are effective at improving the interlaminar fracture toughness, as well as the impact damage tolerance (further detailed in Chapter 5) [245-248]. However, the effects hybridizing both CNFs and SCFs within the epoxy matrix on the modes I and II interlaminar fracture toughness and impact damage tolerance of carbon fibre reinforced epoxy composites is not well understood, as these aspects are addressed in Chapter 5.

Ladani et al. [49] recently shown that combining a single concentration of CNFs (1 wt%) and inserting z-pins (0.5 vol%) within a carbon fibre reinforced composite in the a synergistic increase in steady-state mode I interlaminar fracture toughness of ~10% when compared to total toughening contribution from the CNFs and pins being used separately, as shown in Table 2.5. On top of the CNF enhancing the $G_{IC}$ value, the observed synergistic toughening effect was due the CNFs increasing toughening efficacy of the z-pins. Since Ladani et al. [49] only considered a single concentration of CNFs and z-pins, the effect of CNF and z-pin content, at different combinations, on the synergistic mode I interlaminar toughening effect in carbon-epoxy composites is not well understood. In addition, there are no reports concerning the effects of combining CNFs and z-pins on the mode II interlaminar fracture toughness crack growth resistance properties. The effect of CNF content on the z-pin traction response under mode I and mode II loading conditions are not well understood. Also, it not known whether other types of carbon-
based nanofillers such as CNTs or GNP can also promote or generate even higher synergistic
toughening effect on the delamination resistance z-pinned composites, as well as the structural
properties of composite T-joints. Indeed, z-pins can improve the structural properties of composite
T-joints [26, 36, 183, 209, 249-251]. The gaps described above are addressed in *Chapters 6, 7, 8
and 9.*
Chapter 3: Electric field alignment of short carbon fibres to increase the toughness of epoxy polymers

Abstract

This chapter presents an investigation on improving the fracture toughness properties of epoxy/short carbon fibre (SCF) composites by the alignment of SCFs using an externally applied alternating current (AC) electric field. Firstly, the effects of the SCF length, SCF content and AC electric field strength on the rotational dynamics and alignment of the SCFs suspended in liquid (i.e. uncured) epoxy resin are investigated both experimentally and analytically. Secondly, it is shown that the mode I fracture toughness of epoxy polymers increases dramatically with the weight fraction of SCFs up to a limiting value (5 wt.%). Thirdly, the toughening effect is even greater when the SCFs are aligned using an electric field normal to the direction of crack growth. It was found that the SCFs increases the fracture toughness by inducing multiple intrinsic and extrinsic toughening mechanisms. Based on the identified toughening mechanisms, an analytical model is proposed to accurately predict the enhancement of the fracture toughness due to the electric field alignment of the SCFs.

The research presented in this chapter has been published in the following:


3.1 INTRODUCTION

Thermosetting polymers, such as epoxy, are widely used in engineering structures as coatings, adhesives and the polymer-matrix phase in fibre-reinforced composites. However, unmodified epoxies are relatively brittle materials, and are susceptible fracture [57]. The addition of a second phase, such as thermoplastic [62] or rubber [79, 252] particles, is a technique commonly used to increase the fracture toughness of epoxies. An alternative technique includes the addition of carbon based nanofillers to improve the fracture toughness of the epoxies, as described in Chapter 2. Significant increase in fracture properties can be achieved with relatively low concentrations, i.e. typically under about 2 wt.%. Proven nanofillers include carbon nanotubes (CNTs) [137], carbon nanofibres (CNFs) [57, 96], and graphene nanoplatelets (GNPs) [58]. More recently, research has shown that carbon nanofillers, such as CNFs [57] and GNP5 [50, 58], can be rapidly aligned in a liquid epoxy resin using an alternating current (AC) electric field [50, 57, 58, 253] or a direct current (DC) electric field [143]. It was found that the mode I fracture toughness, $G_{IC}$, was increased significantly when the direction of crack growth was normal to the direction of alignment.

Another approach to improve the toughness of epoxies is the inclusion of short fibres at the micron-scale, such as short carbon fibres (SCFs) [96]. The appeal of using SCFs is their relatively low material and processing costs combined with their high stiffness and strength [60]. Studies have shown that SCFs extracted from waste material, such as off-cuts from dry carbon fabrics and pyrolyzed carbon fibre-polymer laminates, can be recycled and used as low-cost reinforcements, additives, interleaves and veils to improve the fracture toughness of bulk epoxy polymers and fibre-reinforced epoxy composite materials [60, 96, 120, 254, 255]. For example, Cholake et al. [60] demonstrated that blending 5 wt.% of milled and randomly oriented SCF into an epoxy yielded a 260% increase in the mode I fracture toughness. Due to the high dimensional aspect ratio of SCFs (i.e. being typically up to about 250), improvements to the properties of the resulting composite material are strongly dependent on the orientation of the SCFs [15, 132]. Indeed, magnetophoretic techniques have been reported to align SCFs within liquid thermosetting and elastomeric resins [144, 145]. However, the electric field alignment of SCFs in an epoxy resin and its effect on the toughness of epoxy/SCF composites is not well understood.
The main aims presented in this chapter are to investigate the fracture toughness properties of epoxy/SCF composites and the effect of the alignment of SCFs using an externally applied AC electric field. Firstly, the dielectrophoresis mechanism controlling the rotation, orientation and tethering of SCFs in the liquid (i.e. uncured) epoxy resin is investigated experimentally and analytically modelled. The procedure for aligning the SCFs in the epoxy resin can, therefore, be readily optimised with respect to the aspect ratio of the SCFs and the applied electric field strength. Secondly, the values of the mode I fracture toughness are determined for (cured) epoxy/SCF composites containing different weight fractions of SCF, i.e. up to 10 wt.%. The SCFs were randomly orientated or aligned via the AC electric field procedure, as adapted from [50, 57, 58, 253]. Thirdly, the toughening mechanisms responsible for the improvements in the fracture toughness due to the alignment of the SCFs are identified. Finally, a model based on these toughening mechanisms is proposed and used to predict the experimentally measured values of the fracture toughness.

3.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

3.2.1 Materials

The SCFs, with an average diameter of 7 μm, were cut into 1.8 to 3.5 mm long sections from continuous carbon fibre tows (T300 carbon fibres supplied by Colan Pty Ltd, Australia [256]) by using a paper guillotine, as shown in Fig. 3.1. The SCFs were then blended into the liquid epoxy resin at a weight fraction of 10 wt.% by hand-mixing for five minutes. The epoxy resin was a two-part blend of bisphenol-A and bisphenol-F resins (Resin 105® from West System, Australia).

![Fig. 3.1. Microscopy images of chopped SCFs (a) before (taken using optical microscopy) and (b) after the three-roll milling process (taken using scanning electron microscopy).](image-url)
The SCF-epoxy mixture was then passed four times through a three-roll mill (Dermamill 100, Australia) operated at 50 rpm, as shown in Fig. 3.2. The gap between the rotating rollers was progressively reduced with each pass of the epoxy-SCF mixture, down to a final gap size of 20 μm. This process separated the chopped SCF tows into individual fibres and dispersed them uniformly in the liquid epoxy resin. However, the shearing force generated in the three-roll milling process did fracture the SCFs and reduced their length, as may be seen from Fig. 3.1. The average length of the SCFs after milling was 0.72 mm, with a standard deviation of ±0.21 mm, as shown in the length distribution plot in Fig. 3.3. The lengths of SCF before and after milling was measured from the optical microscope images of the epoxy containing 0.10 wt% SCFs using the ImageJ processing software (ImageJ, NIH, USA). In generating a percentage frequency distribution, a minimum of 500 fibres were measured. Following the milling process, the mixture which contained SCFs (at a weight fraction of 10 wt.%) was diluted by adding more resin to obtain the other desired concentrations, i.e. 0.5, 1, 1.5, 2 and 5 wt.%. The epoxy hardener (Resin 206® from West System, Australia) used was a blend of aliphatic amines and aliphatic amine adducts based on diethylenetriamine and triethylenetetramine [257]. The hardener was added, at the concentration recommended by the supplier (i.e. 5:1 resin-to-hardener ratio), to the epoxy resin mixture to activate crosslinking and curing, which was undertaken at room temperature, i.e. 25°C for 48 h [257]. It should be noted that the given weight concentrations of the SCFs are relative to the weight of the combined epoxy resin and hardener. The mixtures were hand-stirred and degassed to remove the entrapped air bubbles within the epoxy resin and hardener.

Fig. 3.2. Dermamill 100 three roll milling machine.
Fig. 3.3. Frequency distribution plot of the lengths of the SCFs before and after the three-roll milling process.

3.2.2 Electric field alignment of short carbon fibres

Two types of experiments were performed to study the SCF alignment process. Either a single SCF or multiple SCFs were aligned in the liquid epoxy resin, without any hardener being present, using an externally applied AC electric field. Fig. 3.4 presents a schematic of the apparatus used to measure the degree of alignment of the liquid epoxy resin containing a single or multiple SCFs when subjected to an applied AC electric field.

Fig. 3.4. (a) Schematic of a single SCF within the liquid epoxy resin during electric field alignment and (b) schematic of the test method used to electrically align and measure the angle of the single SCF.

For the single SCF studies, two parametric investigations were conducted to assess the influence of the length of the SCF and the strength of the AC electric field with respect to the time
needed for rotation and alignment of the fibres in the liquid epoxy resin. The electric field was generated between two polymer-coated copper electrodes, with a 5.0 mm spacing, placed on both sides of the liquid epoxy resin/single SCF mixture using an AC signal generator (Tektronix CFG250) along with a pre-amplifier (Kronhnikrit 7602M) operated at a frequency of 10 kHz, as shown in Fig. 3.5. The single SCF was positioned approximately at an equal distance between the electrodes at an initial orientation of 88±0.5º relative to the direction of the applied electric field, which is taken to be the 0º direction. In assessing the effect of the length of the SCF, an electric field strength of 30 V/mm was applied using a single SCF, that was either 0.2, 0.6, 1.2 or 4.0 mm in length in the liquid resin. Three values of the electric field strength, i.e. 30, 50 and 75 V/mm, were also investigated in the study of the influence of the AC electric field strength using an SCF, which was 0.6 mm in length, placed in the liquid epoxy resin.

Fig. 3.5. Photograph of AC power supply used to align the fillers along the applied field direction.

For evaluating the general effects of the electric field alignment of multiple SCFs in the liquid epoxy resin, the epoxy/SCFs mixture was poured on a glass slide between the two polymer-coated copper electrodes with a separation distance of 5.0 mm. The weight fraction of SCFs in the epoxy resin was 0.1 wt.%, and they were initially randomly orientated in the mixture. The electric field was generated (as described above) between the two electrodes using an AC signal generator along with a pre-amplifier, with a strength of 30 V/mm and frequency of 10 kHz.
In both studies, time-lapse photographic images were taken using a Leica optical microscope and videos were recorded using a Dynocapture USB microscope camera to observe the rotation and alignment of the single or multiple SCFs with increasing exposure time to the electric field. The orientation of the SCF(s) relative to the electric field direction was measured from the optical microscope images using the ImageJ processing software (ImageJ, NIH, USA).

3.2.3 Composite manufacturing and mode I fracture toughness testing

The values of the mode I fracture toughness for the unmodified epoxy and the epoxy/SCF composites were measured using the double cantilever beam (DCB) test procedure described by Ladani et al. [58] and Wu et al. [50, 258]. The DCB test specimens consisted of a 2 mm thick layer of the epoxy bonding two substrates, which were cured fibre reinforced polymer laminates and were each 2.5 mm in thickness. These two composite substrates sandwiching the epoxy layer acted as the electrodes, as illustrated in Fig. 3.6. The substrate acting as the positive electrode was manufactured entirely from 12 plies of unidirectional T700 continuous carbon fibre/epoxy prepreg (VTM264, Lavender Composites, Australia). The negative electrode was made using a cured hybrid-fibre composite substrate consisting of ten plies of continuous unidirectional T700 carbon fibre/epoxy-prepreg and two surface plies of continuous E-glass fibre/epoxy prepreg (MTM57, Applied Composites Group, Australia). It should be noted that both composite arms of the DCB test specimens had the same value of flexural modulus (within experimental error). The glass fibre plies in the negative electrode acted as a dielectric barrier to prevent short-circuiting during application of the AC electric field. The composites used for the positive and negative electrodes were cured and consolidated in an autoclave at 120°C and 620 kPa for one hour. The bonding surfaces of the substrates were then sandblasted, cleaned in water, and finally degreased using acetone to remove any remaining surface impurities before being employed as the substrate materials.

The DCB specimens were manufactured by placing a mould made of mastic tape between the two composite substrates, as shown in Fig. 3.6. The mould acted as a dam to prevent the liquid epoxy and hardener mixture from overflowing when poured between the composite substrates/electrodes. The thickness of the epoxy layer was accurately controlled using 2 mm thick glass slides that were placed between the substrates and then removed after curing. For those
specimens where alignment of the SCFs was to be studied, an AC electric field with a strength of 30 V/mm and frequency of 10 kHz was applied between the composite electrodes to align the SCFs in through-the-thickness direction, i.e. at 90° to the electrodes. The AC electric field was applied during the first hour of the 48 h curing time at 25°C since after about 1 h the viscosity of the epoxy and hardener mixture was relatively high, and no further orientation of the SCFs could occur. The epoxy and hardener mixture was cured for 48 h at 25°C in accordance with resin supplier’s guidelines [257].

![Diagram](image)

**Fig. 3.6.** Manufacturing process of adhesive bonded joints.

Based on the manufacturing process discussed above, the DCB test specimens consisted of a 2 mm thick layer of an unmodified epoxy or an epoxy/SCF composite, bonding together the composite substrates, which had acted as the positive and negative electrodes when the SCFs needed to be aligned (see **Figs. 3.6 and 3.7**). One end of the DCB specimen contained a 40 mm long, 11 μm thick film of polytetrafluoroethylene (PTFE) that was located within the unmodified epoxy or epoxy/SCF composite layer and was placed approximately at an equal distance between the composite substrates. This film acted to initiate the crack under mode I (tensile opening) loading. Before fracture testing, the DCB specimens were gently wedged open at the pre-cracked end to extend the initial crack length to 50 ±2.5 mm in order to create a sharp crack tip.
Fig. 3.7. Schematic and dimensions of the double cantilever beam (DCB) test specimen. The direction of the aligned SCFs is indicated.

DCB tests were performed in accordance with ISO 25217 [259] by loading the cracked end of the specimens at a displacement rate of 1 mm/min using a 10 kN Instron universal testing machine (Instron, Australia), as shown in Fig. 3.8a. The $G_{IC}$ values of the corresponding DCB specimens was measured using modified beam theory [259]:

$$G_{IC} = \frac{3P\delta}{2b(a+|\Delta l|)} \quad (1)$$

where $P$ is the mode I applied load, $\delta$ is the crack opening displacement, $a$ is the crack propagation length, and $b$ is the sample width. A correction factor, $|\Delta l|$, is determined from the change in the DCB specimen compliance to account for the vertical displacement and rotational effects at the measured crack tip. The fracture toughness values were measured at the onset of crack propagation at the corresponding load (i.e. maximum load), crack opening and crack propagation length. The crack length was measured with the aid of a travelling optical microscope. Using these data, the ‘corrected beam theory’ approach [259] was used to calculate the mode I fracture toughness.

Five DCB samples were tested for the unmodified epoxy and each of the epoxy polymers containing the different weight fractions of SCFs up to 10 wt.%. The SCFs were either randomly orientated or aligned in the direction of the electric field, i.e. normal to the direction of crack growth along the length of the DCB specimen. In all the DCB tests the crack grew cohesively through the unmodified epoxy or the modified epoxy polymer layer in an unstable stick-slip
behavior shown in Fig. 3.8b. Up to three to four data point were attained for each DCB specimen. The manufacturing and testing process described above is adapted from the earlier reports on the AC electric field alignment of CNFs and GNPs in epoxy polymers [50, 57, 58, 253].

Fig. 3.8. (a) Photo of the experimental DCB test setup for measuring the mode I fracture toughness properties. (b) Load versus crack opening displacement curves for the epoxy polymers containing 1.0 wt%, 2.5 wt% and 5.0 wt% SCFs before and after application of an AC electric field.

3.3 RESULTS AND DISCUSSION

3.3.1 Electric field alignment of SCFs

3.3.1.1 Effect of SCF aspect ratio and AC electric field strength on SCF orientation

The influence of the length of the SCF on the alignment process was investigated using a single SCF suspended in the liquid epoxy resin and exposed to an AC electric field strength of 30 V/mm at 10 kHz for increasing times. The length of the SCF was varied between 0.2 to 4.0 mm and, as shown in Fig. 3.9a. The single SCFs at every length aligned to ±2° of the direction of the applied electric field within 300 s, from an initial angle of 88° ±0.5°. When a rod (e.g. single SCF) is suspended in a dielectric liquid (e.g. a liquid epoxy resin) and then subjected to an AC electric field, the rod becomes polarised due to its shape anisotropy, dielectric properties and electrical conductivity being different to that of the liquid resin. As a result, a greater density of opposing
charges are induced at the ends of the rod, as indicated in Fig. 3.4a. The interaction of this dipole with the electric field gradient during the dielectrophoresis process generates a torque which leads to rotation and alignment of the SCFs in the direction of the applied electric field [142, 260]. Furthermore, the total time of 300 s needed to reach almost perfect alignment with the direction of the electric field was very similar for the different lengths of SCFs, where the values of the aspect ratio were in the range of 30 to 575. Interestingly, Kim and Shkel [142] also reported a minimal influence of the length (or the aspect ratio) of short glass fibres on the total rotation time when subjected to an AC electric field strength of greater than 700 V/mm. However, the aspect ratio of the glass fibre were only in the range of 10 to 33 [142].

![Fig. 3.9. Effects of (a) the fibre length (with an AC electric field strength of 30V/mm at 10 kHz) and (b) the AC electric field strength on the rotation time for a single SCF (0.6 mm length) in the liquid epoxy resin. (The rotation time is defined as the time needed to orient the fibres from the initial angle of ~88° to ~2°, with 0° being the direction of the applied electric field.)](image)

The rotation rate of the single SCFs was more sensitive to the strength of the AC electric field than the length of the SCF, particularly when the length of the single fibre was 4 mm (i.e. an ~575 aspect ratio). The time to align a single SCF in the direction of the electric field decreased rapidly with increasing electric field strength, i.e. from 30, 50 to 75 V/mm, as shown in Fig. 3.9b. Wu et al. [50] showed that increasing the electric field strength increases the torque acting on conductive particles suspended in a dielectric liquid, which is responsible for the more rapid alignment of the SCFs. By treating a single SCF as a thin oblate spheroid and by assuming that
there is no interaction with neighbouring fibres, the time, $t_r$, required to rotate the SCF from an initial angle, $\theta_0$, under an AC electric field of strength, $E_o$, can be calculated using [50]:

$$
    t_r = \left( \pi - \frac{d_f}{l_f} \right) \frac{8\eta}{\pi \varepsilon_m \varepsilon_0 E_0^2} \ln \frac{\tan \theta_0}{\tan \theta'}
$$

This equation is based on the assumption that the electric field induced torque is balanced against the viscous torque acting on the SCF. The viscosity ($\eta$), the dielectric constant ($\varepsilon_m$) of the epoxy and the vacuum permittivity ($\varepsilon_0$) are 0.55 Pa.s [257], 6.0 [142] and 8.85 x 10^{-12} F/m [142], respectively. The terms $l_f$ and $d_f$ are the length and diameter of the SCF, respectively. $\theta'$ denotes the relative angle between the SCF orientation and the applied electric field direction. As shown in Fig. 3.9, the calculated rotation times from 88º to 2º agree with the experimentally measured times. However, the model does not accurately capture the rotational trend with the experimentally measured values for the 4 mm long (or higher aspect ratio) filler. This may suggest that additional interactions could take place such as inertial effects due to geometry and flow or rotational instability due to dielectrophoresis [142]. Unstable flow imparts additional vorticity around the fibres resulting in a mismatch between (a) the viscous drag moment acting on the fibre and (b) the torque generated on the ends on fibre due its charging of the fibres by the AC electric field [142]. However, it is important to note that the proposed model is relatively simplistic. The derivation of the analytical formulation presumes that both moments (i.e. drag and dielectrophoresis) acting on the fibre are equal [50].

3.3.1.2 In-situ alignment studies of SCFs in liquid epoxy resin

In-situ alignment studies were also conducted by measuring the dielectrophoretic response of multiple SCFs in the liquid epoxy resin when subjected to an AC electric field strength of 30 V/mm at 10 kHz. The liquid epoxy resin (without added hardener) contained a weight fraction of SCFs of 0.1 wt.%. Fig. 3.10a and Fig. 3.10b show the random orientation of the SCFs at $t = 0$ s (i.e. the time at which the electric field was first applied) and the aligned orientation of the SCFs at $t = 300$ s after the application of the electric field, respectively. Fig. 3.10b shows that chain-formation of the SCFs has occurred between the electrodes, and this was due to the opposing charges present at the ends of the SCFs during the dielectrophoresis process [142]. Fig. 3.10c presents the population density for the orientation of the SCFs before and after application of the electric field for 300s.
The application of the electric field has resulted in about 85% of the SCFs being oriented within ±30° of the direction of the electric field within 300 s from the start of it being applied.

![Image of SCF alignment](image.png)

**Fig. 3.10.** In-situ alignment of 0.1 wt% SCFs in the liquid epoxy resin using an AC electric field strength of 30 V/mm at 10kHz. (a) t = 0 s containing randomly-oriented SCFs, (b) t = 300 s containing aligned SCFs and (c) comparison of the fibre-angle distribution of the SCFs before and after the AC electric field had been applied for 300 s.

### 3.3.1.3 Effect of SCF content on fibre orientation distribution in cured epoxy

The weight fraction of the SCFs in the epoxy polymers had a strong influence on the alignment process under the externally applied AC electric field. In quantifying the degree of alignment, polished cross-sections of the cured epoxy/SCF composite samples containing different contents of SCFs up to 10 wt.% were examined using an optical microscope to measure the 2D distribution of the fibre angles. The effects of the electric field, at a strength of 30 V/mm at 10 kHz with an
application time of 1 h during curing, and weight content of the SCFs on the measured fibre angle distribution are shown in Fig. 3.11. In this figure, the angles 0° and 90° are the directions parallel and normal to the electric field direction, respectively. The results for the orientation frequency of the SCFs are grouped into one of three ranges of their orientation distribution as: (a) -30° to +30°, (b) -60° to -30° and +30° to +60° and (c) -90° to -60° and +60° to +90°.

![Fig. 3.11. Effect of SCF content on the distribution of the fibre angle of the epoxy/SCF composites (a) containing randomly orientated SCFs or (b) after the composites had been subjected to an AC electric field of 30V/mm at 10 kHz.](image)

In a perfectly randomly orientated condition, there would be an equal proportion of SCFs at all angles. However, this was not the case for the epoxy/SCF composites that were not subjected to the electric field. Instead, the highest proportions of SCFs are within the range of -90° to -60° and +60° to +90°, and this proportion increases as the SCF content is increased. These observations may be attributed to the wetting of the composite substrates by the ‘liquid epoxy + hardener + SCFs’ mixture, followed by the shear flow induced alignment of the SCFs when casting this resin mixture between the composite substrates [134]. With an increase in the SCF concentration, the greater packing and increased fibre-fibre contact density increase the probability of the fibres orientating along the flow direction or, in the case observed, along with the in-plane direction of the DCB specimen [261]. This behaviour is a well-known phenomenon and has been previously reported [134] with the increase in fibre content.
For the epoxy/SCF composites subjected to the AC electric field during their preparation, the proportion of SCFs aligned relatively close to the direction of the electric field, i.e. 30° to +30°, is highly dependent on the content of the SCFs. At the lowest content studied, i.e. 0.5 wt.%, about 55% of the SCFs were oriented within -30° to +30° of the electric field direction. However, the percentage of SCFs so closely aligned with the direction of the electric field decreased rapidly with increasing weight content due to the increased fibre-fibre contact impacting the rotating process.

3.3.1.4 Optimisation of the procedure for orientating the SCFs in the epoxy polymers

From the above experimental and theoretical studies on the single SCFs in the liquid epoxy, several key observations were made. Firstly, the length of the SCF has little influence on the time needed to rotate the SCF from ±88° to within ±2° relative to the direction of the applied AC electric field. Secondly, the AC electric field strength is inversely related to the time needed to rotate the SCFs to within ±2° relative to the direction of the electric field. Thirdly, it was observed that there was significant alignment of the SCFs after the composite had been subjected to an electric field of a strength of 30 V/mm after 300 s, see Fig. 3.9b. Therefore, this level of electric field strength and exposure period were selected for manufacturing the DCB epoxy/SCF composites, especially since (a) an AC electric field strength of 30 V/mm for 300 s was readily achievable using the present epoxy/hardener combination.

3.3.2 Fracture toughness of the epoxy/SCF composites

3.3.2.1 Effect of SCF content and alignment

The effects of the weight content and alignment of SCFs on the fracture toughness, $G_{IC}$, of the bulk epoxy polymers are shown in Fig. 3.12. It should be noted that crack growth always occurred in an unstable (i.e. stick-slip) manner and the locus of crack growth was always cohesive in the unmodified epoxy or the epoxy/SCF composites, midway between the two substrates. Irrespective of the composite type, three to four data points could be acquired from the DCB specimens. From Fig. 3.12 it may be seen that the fracture toughness increased with the SCF content up to ~5 wt.%, above which it reached a plateau with a greater than 10-fold increase in the value of $G_{IC}$, compared to the unmodified epoxy. The plateau in $G_{IC}$ value with fibre volume content in a polymer matrix has also been reported by Nikpur et al. [262]. Subjecting the SCFs to an AC electric field to attempt
to orientate the SCFs along the through-the-thickness direction of the epoxy polymers increased the toughening effect by about 30%, but only when their content in the epoxy was up to about 2 wt.%. The approximate 30% improvement was validated using an ‘unpaired t-test’ employing the values of the mean and standard deviation between the measured $G_{Ic}$ values from the corresponding SCF epoxy samples, with a sample size of fifteen. The difference between the samples that were exposed to the AC electric field and the ones not exposed to the electric field were found to be statistically significant with a 99.9% confidence level (i.e. a two tailed P-value of less than 0.001). These findings demonstrate that the electric field alignment of the SCFs in the epoxy/SCF composites is an effective technique to toughen such materials, but only at relatively low contents of SCFs. Upon increasing the SCF content to above 5.0 wt.%, then the application of the electric field did not provide any additional enhancement to the fracture toughness.

![Graph showing the effect of SCF weight content on the mode I fracture toughness of the epoxy/SCF composites containing randomly orientated SCFs ('Without E-field') or after the composites had been subjected to an AC electric field ('With E-field').](image)

**Fig. 3.12.** Effect of SCF weight content on the mode I fracture toughness of the epoxy/SCF composites containing randomly orientated SCFs ('Without E-field') or after the composites had been subjected to an AC electric field ('With E-field').

### 3.3.2.2 Comparison to literature values

The improvements to the fracture toughness values of the present epoxy/SCF composites are compared to results from previous studies in **Table 3.1**. The values of $G_{Ic}$ are similar for the present
composites to those reported by Zhou et al. [32], where similar fibre lengths and SCF contents were used. On the other hand, for a significantly shorter SCF length, Cholake et al. [60] reported a much lower $G_{Ic}$ value of 940 J/m$^2$ at 5.0 wt.% of SCFs compared to the composite studied here, where the value of $G_{Ic}$ was 1770 J/m$^2$. Although, at a content of SCFs of 10.0 wt.%, similar values are obtained in the present study and that by Cholake et al. [60]. While any differences may be attributed to the relatively low SCF length used by Cholake et al. [60], other factors such as the matrix type [263] will influence the fracture toughness. Finally, the present study mainly addresses the effect of the electric field alignment on the fracture toughness, as shown in Fig. 3.12 and in Table 3.1. However, the overall level of improvements in the values of $G_{Ic}$, compared to the unmodified epoxy polymer, are shown to be significantly greater in the present study than the values reported by Cholake et al. [60], Zhou et al. [32] and Zhang et al. [96].

Table 3.1. Comparison of $G_{Ic}$ values of the epoxy/SCF composites measured in the present study with reported values in the literature. (For values of $G_{Ic}$, the standard deviations are given in brackets.)

<table>
<thead>
<tr>
<th>Source</th>
<th>Fillers [fibre length (μm)]</th>
<th>Content (wt.%)</th>
<th>$G_{Ic}$ (J/m$^2$)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Present study</strong></td>
<td>Unmodified Epoxy</td>
<td>-</td>
<td>136 (± 20)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SCF-Without E-Field [720 ±210]*</td>
<td>1.0</td>
<td>710 (± 63)</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>SCF-Without E-Field [720 ±210]*</td>
<td>2.5</td>
<td>1240 (± 42)</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td>SCF-Without E-Field [720 ±210]*</td>
<td>5.0</td>
<td>1770 (± 144)</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>SCF-Without E-Field [720 ±210]*</td>
<td>10.0</td>
<td>1960 (± 160)</td>
<td>1340</td>
</tr>
<tr>
<td></td>
<td>SCF-With E-Field [720 ±210]</td>
<td>1.0</td>
<td>990 (± 81)</td>
<td>625</td>
</tr>
<tr>
<td></td>
<td>SCF-With E-Field [720 ±210]</td>
<td>2.5</td>
<td>1360 (± 110)</td>
<td>885</td>
</tr>
<tr>
<td><strong>Zhou et al. [32]</strong></td>
<td>Unmodified Epoxy</td>
<td>-</td>
<td>275 (± 50)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SCF [750 ±200]</td>
<td>1.0</td>
<td>770 (± 52)</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>SCF [750 ±200]</td>
<td>2.5</td>
<td>1360 (± 330)</td>
<td>390</td>
</tr>
<tr>
<td><strong>Cholake et al. [60]</strong></td>
<td>Unmodified Epoxy</td>
<td>-</td>
<td>260 (± 10)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SCF [200 ±100]</td>
<td>5.0</td>
<td>940 (± 20)</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>SCF [200 ±100]</td>
<td>10.0</td>
<td>2060 (± 50)</td>
<td>690</td>
</tr>
<tr>
<td><strong>Zhang et al. [96]</strong></td>
<td>Unmodified Epoxy</td>
<td>-</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SCF [55 ±21]</td>
<td>7.2</td>
<td>230</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>SCF [55 ±21]</td>
<td>14.3</td>
<td>370</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>SCF [55 ±21]</td>
<td>21.5</td>
<td>425</td>
<td>255</td>
</tr>
</tbody>
</table>

*The SCFs within the epoxy was not subjected to an externally applied AC or DC electric field.
3.3.2.3 Toughening mechanisms

Scanning electron microscopy (SEM) examination of the crack initiation region (i.e. at the onset of crack growth) for the epoxy/SCF composites revealed a number of intrinsic and extrinsic toughening mechanisms. These mechanisms are illustrated schematically in Fig. 3.13. This figure also shows the main difference due to electric field alignment of the SCFs, where a greater density of fibre pull-out occurs.

Fig. 3.13. Cross-sectional schematics of the toughening mechanisms operative during crack growth in the epoxy polymers that contain (a) randomly aligned SCFs and (b) SCFs that were aligned by the externally applied AC electric field. The inset of the area bound by the red dashed lines are a higher magnification schematic of the main crack tip encompassed by the solid red line.
Irrespective of whether the epoxy samples were exposed to an applied electric field, ahead of the main crack front, the intrinsic toughening mechanisms identified were epoxy void growth, interfacial debonding of SCFs from the epoxy matrix and microcracking. As shown in Fig. 3.14a, fractographic evidence of plastic shear yielding [122], void growth [78] and interfacial debonding sites surrounding the SCFs from the epoxy matrix within the process zone ahead of the crack front was present. The voids are an indication of the high-strain plastic flow of the epoxy within the process zone. The triaxial stress field within the process zone is sufficiently high to cause debonding of the SCFs from the epoxy, resulting in the plastic void growth mechanism. The progressive interfacial debonding at the epoxy/SCF interfaces, followed by the growth of the voids, promotes toughening via the dissipation of plastic strain energy [6]. The extent of the interfacial debonding and void growth sites increased with the SCF content, contributing to the increased fracture toughness. Some of the SCFs fractured within the debonding sites (see Fig. 3.14a), and this occurs when their interfacial bond strength with the epoxy exceeds the fibre rupture stress. Even though the T300 based SCFs have a relatively high tensile failure stress, the roll milling process is expected to weaken the fibres via fibre/fibre contact (i.e. abrasion). The finding that the milling process broke many of the SCFs, and thereby reduced the range of fibre lengths (shown in Fig. 3.1b) is clear evidence of fibre damage having occurred. Debonding of the SCFs, which also initiated at the fibre ends, leads to the limited formation of multiple microcracking sites (typically under about 15 μm long) within the process zone ahead of the main crack front, as shown in Fig. 3.14b. However, the density of these microcracks was observed to be relatively low compared to the number of SCFs within the same volume.
Fig. 3.14. Scanning electron micrographs of epoxy/SCF composites showing the intrinsic toughening mechanisms within the process zone ahead of the main crack. (a) Of the fracture surface showing interfacial debonding and plastic void growth (for a 1.5 wt.% SCF composite subjected to an AC electric field) and (b) of the cross-section surrounding the main crack tip showing microcracking (for a 1.0 wt.% SCF composite subjected to an electric field).

The extrinsic toughening mechanisms are illustrated in Fig. 3.15. These extrinsic toughening mechanisms take place behind the main crack front and were identified as (a) fibre pull-out from the epoxy matrix, (b) bridging of the fibres across the crack faces, (c) snubbing and (d) rupture of the SCFs. Firstly, Table 3.2 presents the measured volume fraction, $V_{\text{po-counted}}$, of SCFs that were pulled-out and were measured on the fracture surfaces of the composites from scanning electron micrographs. A total of twenty micrographs, each with a surface area of 500 µm by 500 µm, were analysed for each epoxy/SCF composite. Previous studies have employed this technique for composites containing CNFs [57], CNTs [264, 265] and glass fibres [266]. The areal density of SCFs that were pulled-out was significantly higher when the SCFs were oriented normal to the crack growth direction. This condition arose upon the application of the AC electric field and when a relatively low SCF content, i.e. up to 2 wt.%, was present. At the higher contents of 2.5, 5 and 10 wt.% of SCFs the volume fractions of SCFs that were pulled-out from the aligned SCF composites were similar in value to those of the randomly orientated SCF composites. As discussed previously, this occurred because the SCFs found it increasingly difficult to align normal to the crack growth direction at high contents due to the increased fibre-to-fibre contact impeding
the rotation and alignment process under the applied electric field, as shown in Fig. 3.11. Now, an interfacial friction sliding stress is also induced as the debonded SCFs are pulled-out, imparting significant energy dissipation from the work of friction [6, 267]. SCFs aligned near-normal to the crack growth direction have a higher probability of being intersected by the crack and undergoing pull-out. Therefore, the pull-out toughening mechanism was more dominant in the composites containing a low content of aligned SCFs, as illustrated schematically in Fig. 3.13b.

Fig. 3.15. Scanning electron micrographs showing examples of the extrinsic toughening mechanisms behind the main crack in the epoxy/SCF composites. (a) A SCF bridging the crack faces (for a 1.5 wt.% SCF composite subjected to an AC electric field), (b) SCF snubbing (for a 1.5 wt.% SCF composite subjected to an AC electric field) and (c) an SCF having been pulled-out (for a 1.0 wt.% SCF composite subjected to an electric field).

Secondly, since the SCFs were much longer than the crack opening displacement near the crack tip, it was possible for the SCFs to bridge the crack, as shown for example in Fig. 3.15a. Therefore, the SCFs generated discrete traction loads at each bridging site which lowered the stress exerted on the crack tip, thereby increasing the fracture toughness. Bridging of the crack faces by the SCFs more readily occurred when the SCFs were aligned nearly normal to the direction of crack growth. Thirdly, concurrently during crack fibre bridging, the traction energy generated during pull-out of the SCFs is further enhanced by snubbing [266, 268, 269], as shown in Fig. 3.15b. Snubbing is a toughening mechanism whereby the bridged SCFs, which have a much higher modulus than the epoxy, are pressed laterally into the surrounding epoxy matrix as they attempt to rotate and align in the direction of the crack opening. In this process, the SCFs cause local plastic
deformation of the surrounding epoxy matrix thereby increasing the local interfacial shear friction stress. This increases the value of the fracture toughness. Snubbing is most effective as a toughening mechanism when the bridged SCFs are slightly misaligned from the crack-opening direction, since when perfectly aligned the SCFs simply pull-out without snubbing. Because crack bridging is required for snubbing to occur, this mechanism accounts in part for the epoxy/SCF composites that were exposed to an electric field having higher toughness values compared to the randomly orientated SCF composites, at low contents of SCFs. Fibre pull-out will occur providing the SCFs were inclined below the critical angle, $\theta_c$, relative to the fracture plane. Above the critical angle, fibres are more likely to fracture along the crack propagation plane. At higher contents (i.e. 2.5 to 10 wt.% of SCFs), where a greater proportion of fibres were aligned along 60° to 90°, further fractographic studies revealed that the SCFs were orientated nearly parallel along the crack propagation plane with no evidence of tensile rupture. This suggests that a lower proportion of those fibres would participate in the toughening process due to fibre pull-out. Table 3.2 also presents the measured volume fractions, $V_{f\text{-int}}$, of fibres that were ruptured, and these values were measured as described above.

Table 3.2. Measured values of the volume fraction of SCFs which pulled-out, $V_{p_\text{o-counted}}$, and which ruptured, $V_{f\text{-int}}$. The measured volume fractions, $V_{p_\text{o-45}}$, of the SCFs in the composites with an orientation distribution range from -45° to +45°, relative to the through-the-thickness direction, are also given. (Standard deviations are given in brackets.)

<table>
<thead>
<tr>
<th>SCFs (wt.%)</th>
<th>$V_f$ (%)</th>
<th>$V_{p_\text{o-counted}}$ (%)</th>
<th>$V_{p_\text{o-45}}$ (%)</th>
<th>$V_{f\text{-int}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without E-Field</td>
<td>With E-Field</td>
<td>Without E-Field</td>
<td>With E-Field</td>
</tr>
<tr>
<td>1.0</td>
<td>0.58</td>
<td>0.15 ($\pm0.03$)</td>
<td>0.31 ($\pm0.05$)</td>
<td>~ 0.16</td>
</tr>
<tr>
<td>1.5</td>
<td>0.87</td>
<td>0.22 ($\pm0.03$)</td>
<td>0.39 ($\pm0.08$)</td>
<td>~ 0.17</td>
</tr>
<tr>
<td>2.0</td>
<td>1.16</td>
<td>0.26 ($\pm0.05$)</td>
<td>0.40 ($\pm0.04$)</td>
<td>~ 0.23</td>
</tr>
<tr>
<td>2.5</td>
<td>1.45</td>
<td>0.34 ($\pm0.09$)</td>
<td>0.39 ($\pm0.07$)</td>
<td>~ 0.29</td>
</tr>
<tr>
<td>5.0</td>
<td>2.93</td>
<td>0.48 ($\pm0.08$)</td>
<td>0.49 ($\pm0.08$)</td>
<td>~ 0.48</td>
</tr>
<tr>
<td>10.0</td>
<td>6.00</td>
<td>0.49 ($\pm0.05$)</td>
<td>0.48 ($\pm0.05$)</td>
<td>~ 0.49</td>
</tr>
</tbody>
</table>
3.3.2.4 Modelling the fracture toughening mechanisms

In modelling the fracture energy of the composite, the primary toughening were: (a) interfacial debonding of the SCFs, (b) plastic void growth of the epoxy matrix (enabled by the debonding mechanism), (c) pull-out of the SCFs and (d) rupture of the SCFs. These mechanisms can be analysed to compute their contributions to the fracture toughness, \( G_c \), of the epoxy polymers using:

\[
G_c = G_{CU} + \Delta G_v + \Delta G_{db} + \Delta G_{rupture} + \Delta G_{pull-out}
\]  

(3)

where \( G_{CU} \) is the toughness of the unmodified epoxy polymer and \( \Delta G_v, \Delta G_{db}, \Delta G_{rupture} \) and \( \Delta G_{pull-out} \) are the contributions to the overall toughness arising from the toughening mechanisms of plastic void growth, SCF debonding, SCF rupture, and SCF pull-out (including snubbing), respectively. The value of \( G_{CU} \) for the epoxy used in this study was measured to be 136 J/m\(^2\).

The fracture energy for debonding of a single SCF from the epoxy matrix can be calculated using [265]:

\[
\Delta G_{db} = V_{po} \frac{l_{crit}G_f}{2d_f} = (V_{po-counted}) \frac{l_{crit}G_f}{2d_f}
\]

(4)

where \( V_{po} \) is the volume fraction of SCFs pulled-out, \( l_{crit} \) is the critical pull-out length and \( d_f \) is the SCF diameter. Here we take \( V_{po} \) to be equivalent to the measured volume fraction, \( V_{po-counted} \), of SCFs that were pulled-out, as given in Table 3.2. The term \( G_f \) is the interfacial debonding energy between the SCF and epoxy matrix. Considering the type of carbon fibres (T300) and polymer matrix used within the present study, Liu et al. [270] measured the interfacial debonding energy between T300 carbon fibres and epoxy to be 1600 J/m\(^2\). Therefore, the \( \Delta G_{db} \), value of 1600 J/m\(^2\) was used in the present study.

Following interfacial debonding, plastic void growth of the epoxy further increases the fracture toughness. The energy contribution from the plastic void growth mechanism can be calculated using the equation formulated by Huang and Kinloch [70]:

\[
\Delta G_{void} = \left(1 + \frac{\mu_m}{\sqrt{3}}\right)^2 (V_{void} - V_f)\sigma_y r_y K_{vm}^2
\]

(5)

where \( K_{vm} \) is maximum stress concentration for the von Mises stresses around a debonded SCF and \( \mu_m \) is a material constant allowing for the pressure-dependence of the yield stress of the
unmodified epoxy [70]. The parameters $r_{yu}$ and $\sigma_y$ are the process zone radius at fracture and the tensile yield stress of the unmodified epoxy, respectively. The radius of the process zone is calculated using [70]:

$$r_{yu} = \frac{1}{6\pi} \frac{E_m G_{cu}}{(1-\nu^2)\sigma_y^2}$$  \quad (6)

where $E_m$ is the tensile modulus and $\nu$ is the Poisson’s ratio of the unmodified epoxy polymer. From SEM fractographic observations, the volume fraction, $V_{\text{void}}$, of voids may be determined by assuming their shape to be a truncated cone where the diameter of the void is two times the diameter of the fibre. This results in $V_{\text{void}} = 1.5 \, V_f$.

The SCFs either pull-out or fracture depending on their orientation and embedded length within the epoxy matrix. An SCF above a critical length will rupture because the pull-out stress exceeds the fibre fracture stress. Below the critical length, the SCFs will pull-out, and not rupture. The critical length, $l_{\text{crit}}$, for a single SCF which is aligned normal to the direction of crack growth can be calculated using the Kelly-Tyson formulation, i.e. $l_{\text{crit}} = \sigma_f d_f/2\tau_i$ [6]. The longest length, $l_{\text{po}}$, of an SCF that can be pulled-out is then equal to half the critical length, i.e. $l_{\text{po}} \leq l_{\text{crit}}/2$, and is calculated using:

$$l_{\text{po}} = \frac{\sigma_f d_f}{4\tau_i}$$  \quad (7)

where $\sigma_f$ is the tensile failure stress and $\tau_i$ is the interfacial shear failure stress of the SCF. Many different values of $\tau_i$, ranging from 21 MPa to 30 MPa, for an epoxy matrix/carbon fibre interface have been reported in [32] and [271], respectively. The maximum interfacial friction shear stress is defined by the tensile yield strength of the epoxy matrix, which using the Tresca yield criterion is $\tau_i = 25$ MPa. The maximum $l_{\text{crit}}$ is calculated to be 505 $\mu$m, whereby the maximum possible pull-out length is $l_{\text{po}} = l_{\text{crit}}/2 = 253$ $\mu$m. Via fractographic analysis, the mean pull-out SCF length, $l_{\text{mea}}$, was measured to be approximately 116 $\mu$m; which is approximately equivalent to $l_{\text{crit}}/4$. This is the expected statistical average pull-out length, as reported in many studies for short fibre reinforced polymer composites [6, 132, 133].

When the length of the SCF exceeds the critical length, then the SCF ruptures and the contribution from $\Delta G_{\text{rupture}}$ is given by [272]:
\[\Delta G_{\text{rupture}} = \frac{V_{f-int} \sigma_f^2 \varepsilon_{\text{max}}^2}{2} = \frac{V_{f-int} \sigma_f^2 l_{\text{crit}}}{2E_f}\]

where \(E_f\) is the Young’s modulus and \(\varepsilon_{\text{max}}\) is the tensile failure strain of an SCF, respectively, and \(V_{f-int}\) is the measured volume fraction of SCFs that ruptured along the crack propagation plane (see Table 3.2).

The contribution to the overall toughness from pull-out of a single SCF which is perfectly aligned normal to the crack plane can be determined from the models of Hull [267] and Cottrell-Kelly [6, 273]:

\[\Delta G_{\text{pull-out}} = \frac{2V_{po} \tau_{\text{pull}}^2 l_{po}^2}{d_f}\]

where \(V_{po}\) is the volume fraction of SCFs that are pulled-out from the fracture surface of the epoxy. However, most SCFs are pulled-out at an angle relative to the crack propagation plane. Fractographic examination revealed that the maximum fibre angle, \(\theta_{\text{crit}}\), was approximately 45°. So, considering snubbing effects on the pull-out energy for inclined fibres and the fibre orientation distribution for the corresponding epoxy polymers, Eq. (9) can now be re-stated as [132, 266]:

\[\Delta G_{\text{pull-out}} = \int_{\theta_f=0^\circ}^{\theta_f=\theta_{\text{crit}}} \left( \frac{2V_f \tau_{\text{pull}}^2}{d_f} \exp(\mu \theta_f) \right) \rho(\theta) d\theta_f\]

where \(\mu\), \(\theta_f\) and \(\rho(\theta)\) are respectively the snubbing friction coefficient, SCF angle and probability density of SCFs oriented in a given orientation range, respectively. This model considers the density of SCFs within the orientation range from -45° to +45° taken from the fibre orientation probability-density plot, based on a 2D orientation distribution presented in Fig. 3.16 (expanded from Fig. 3.11). The fibre orientation distribution relative to the through-the-thickness direction (i.e. 0°) were measured using optical micrographs of polished specimen cross-sections along the length (x-axis) and thickness (z-axis) plane. Image processing software (ImageJ – Areal Analyser, NIH, USA) was used to measure the fibre orientation distribution and probability density. The method of measuring the fibre orientation distribution is adapted from various studies [274, 275]. Over twenty 1000 μm by 1000 μm images were analysed for each SCF-modified epoxy that were and were not subjected to an electric field. The value of the density or fraction of the SCFs that were subjected to pull-out, as presented in Table 3.2, is confirmed by the calculated volume
fraction, $V_{po-\pm45^\circ}$, of fibres that have an orientation distribution ranging from $-45^\circ$ to $+45^\circ$. $V_{po-\pm45^\circ}$ was calculated by multiplying the corresponding volume fraction of the epoxy polymers by the density of fibres that were within the orientation distribution range from $-45^\circ$ to $+45^\circ$. The $V_{po-\pm45^\circ}$ values are within the bounds of the measured $V_{po-counted}$ values from the fractographic studies, which again suggests that any fibres above $\sim45^\circ$ would fracture along the crack propagation plane.

**Fig. 3.16.** 2D fibre orientation probability density of the SCFs in the epoxy/SCF composites (a) containing randomly orientated SCFs or (b) after the composites had been subjected to an AC electric field (‘With E-field’). (Note: the probability density for each of the corresponding angles is in increments of $\pm2.5^\circ$).

Eq. (3) may now be used to calculate the fracture toughness, $G_{fc}$, of the epoxy/SCF composites as a function of the content of the SCFs, whether they were randomly orientated or aligned. The values used in the calculations are given in Tables 3.2 and 3.3. A comparison of the experimentally measured values and predictions from the theoretical model for values of $G_{fc}$ is presented in Fig. 3.17 for the epoxy/SCF composites. For the composites subjected to the electric field, the agreement between the experimental and theoretical values is very good. For the randomly orientated SCF composites, the agreement is still good, although the theoretical predictions are somewhat low at intermediate contents of SCFs. However, considering that no fitting factors are involved in the theoretical calculations and that all the various input parameters needed for the modelling studies were directly calculated or measured experimentally, the overall
agreement between the experimentally measured values and the predicted values of $G_{IC}$ is acceptable. The observed agreement provides clear confirmation that the proposed toughening mechanisms are indeed responsible for the observed increases in toughness of the epoxy/SCF composites.

![Graph](image)

**Fig. 3.17.** Comparison of the experimental and analytically calculated values of the fracture toughness of the epoxy/SCF composites. The composites contained either randomly orientated SCFs (i.e. ‘Without E-field’) or aligned SCFs using an electric field of (i.e. ‘With E-field’).

**Table 3.3. Values used in the analytical modelling studies.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF diameter</td>
<td>$d_f$</td>
<td>μm</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>SCF average length after milling</td>
<td>$l_f$</td>
<td>μm</td>
<td>720</td>
<td>This study</td>
</tr>
<tr>
<td>Tensile strength of SCF</td>
<td>$\sigma_f$</td>
<td>MPa</td>
<td>3530</td>
<td>[256]</td>
</tr>
<tr>
<td>Young’s modulus of SCF</td>
<td>$E_f$</td>
<td>GPa</td>
<td>230</td>
<td>[256]</td>
</tr>
<tr>
<td>Density of SCF</td>
<td>$\rho_f$</td>
<td>kg/m³</td>
<td>1760</td>
<td>[256]</td>
</tr>
<tr>
<td>Density of unmodified epoxy</td>
<td>$\rho_e$</td>
<td>kg/m³</td>
<td>1011</td>
<td>[257]</td>
</tr>
<tr>
<td>Tensile yield strength of unmodified epoxy</td>
<td>$\sigma_y$</td>
<td>MPa</td>
<td>50.5</td>
<td>[257]</td>
</tr>
<tr>
<td>Young’s modulus of unmodified epoxy</td>
<td>$E_m$</td>
<td>GPa</td>
<td>3.18</td>
<td>[257]</td>
</tr>
<tr>
<td>Maximum von Mises stress concentration</td>
<td>$K_{vm}$</td>
<td>-</td>
<td>2.11</td>
<td>[265]</td>
</tr>
<tr>
<td>Epoxy/SCF interfacial fracture energy</td>
<td>$G_i$</td>
<td>J/m²</td>
<td>1600</td>
<td>[270]</td>
</tr>
<tr>
<td>Pressure dependent yield stress constant</td>
<td>$\mu_m$</td>
<td>-</td>
<td>0.2</td>
<td>[70]</td>
</tr>
<tr>
<td>Snubbing friction coefficient</td>
<td>$\mu$</td>
<td></td>
<td>1.25</td>
<td>[127]</td>
</tr>
</tbody>
</table>
Fig. 3.18 presents a stack-bar plot of the calculated contributions from each of the toughening mechanisms to the improvement in the fracture energy. The pull-out of the SCFs, which includes the snubbing mechanism, is the most dominant toughening mechanism followed by interfacial debonding. The contribution from the toughening mechanism of plastic void growth in the epoxy matrix around debonded SCFs is relatively small.

![Stack-bar plots of the contributions from the various toughening mechanisms to the overall increase in toughness from analytical calculations for the epoxy/SCF composites containing either randomly orientated SCFs (i.e. ‘WO E-field’) or aligned SCFs (i.e. ‘W E-field’).](image)

*Fig. 3.18. Stack-bar plots of the contributions from the various toughening mechanisms to the overall increase in toughness from analytical calculations for the epoxy/SCF composites containing either randomly orientated SCFs (i.e. ‘WO E-field’) or aligned SCFs (i.e. ‘W E-field’).*
3.4 CONCLUSION

Previous research has shown that the mode I fracture toughness, $G_{IC}$, of epoxy can be improved using short carbon fibres (SCFs) with a randomly oriented distribution. This chapter demonstrates that the $G_{IC}$ can be further enhanced by aligning the SCFs using an external AC electric field along the through-the-thickness direction. Experimental testing and modelling revealed that the rotation rate of the SCF was inversely proportional to the electric field strength and was only weakly dependent on the SCF. The dependence of the SCF content revealed that majority of the fibres (about 85%) were oriented within ±30° of the direction of the electric field when their content was relatively low (i.e. up to 0.1 wt.% in epoxy). However, with the increase in content, the reduction of free space between the fibres which increased the probability of contact which prevented them from rotating and aligning within the epoxy resin. These studies allowed the alignment process for the epoxy/SCF composites to be optimised.

The fracture toughness, $G_{IC}$, of the epoxy/SCF composites increased steadily with SCF content up to about 5 wt.%, above which reached a plateau with a greater than 10-fold increase in the $G_{IC}$ value compared to the unmodified epoxy. Aligning the SCFs in a through-the-thickness direction further increased their toughening effect by about 30%, but only up to about 2 wt.%. The intrinsic toughening mechanisms imparted by the SCFs were: (a) interfacial debonding of the SCFs from the epoxy matrix, (b) plastic void growth in the epoxy matrix around the debonded SCFs and (c) microcracking. The extrinsic toughening mechanisms induced by the SCFs were: (a) fibre pull-out from the epoxy matrix, (b) bridging of the fibres across the crack faces, (c) snubbing and (d) rupture of the SCFs.

A theoretical model approach based upon these toughening mechanisms was developed to calculate the toughness values of the epoxy/SCF composites. The experimental and analytically measured $G_{IC}$ values were in good agreement. Results from the analytical modelling quantitatively capture the contributions from each toughening mechanisms.

The use of an AC electric field may prove to be useful in orientating micron-diameter sized SCFs in epoxy and other thermosetting polymers for industrial moulding, extrusion and lamination applications.
Chapter 4: Multi-scale toughening of epoxy polymers via electric field alignment of carbon nanofibres and short carbon fibres

Abstract

This chapter demonstrates that multi-scale reinforcements such as carbon nanofibres (CNFs) and short carbon fibres (SCFs) can significantly improve the mode I fracture toughness of epoxy polymers through multiple toughening mechanisms. A comparative assessment on the toughening performance promoted by CNFs and SCFs is presented along with the effects of aligning the fillers normal to the crack growth using an applied alternating current (AC) electric field. For SCF concentrations of up to 1.5 wt%, with a concentration of CNFs of 1.0 wt%, the multi-scale reinforcements additively toughen the epoxy polymer, with the measured fracture toughness being up to about fourteen times the value of the unmodified epoxy polymer. For the same concentrations of SCFs and CNFs, the electric field induced alignment of the CNFs and the SCFs further increased the fracture toughness of the multi-scale toughened epoxy polymer by up to twenty times that of the unmodified epoxy polymer. An analytical model has been proposed based on the identified toughening mechanisms.

The research presented in this chapter has been published in the following:

4.1 INTRODUCTION

In reference to the previous chapters, a second toughening phase or fillers are often added to improve the fracture toughness of bulk epoxy composites [276]. Carbon based nanofillers, such as one-dimensional carbon nanotubes (CNTs) [29, 72, 265] and carbon nanofibres (CNFs) [58, 95, 110, 152, 253] and two-dimensional graphene nanoplatelets (GNPs) [50, 75, 277, 278], can increase the mode I fracture toughness \( (G_{IC}) \) of polymer nanocomposites. As reported in Chapter 3, micron-scale fillers such as short carbon fibres (SCFs) can also increase the fracture resistant properties of epoxies [6, 32, 60, 96, 132, 262, 268, 279, 280] with the toughening effect dependent on the volume fraction, length and orientation of the SCFs.

Until recently, most research studies have been concerned with using nano- or micron-scale reinforcement separately. However, there has been an interest in adapting multi-scale toughening methodologies into existing engineering composites structure. Multi-scale or hierarchically toughened structures are often based on natural materials, such as nacre and bone [47], which contain multiple reinforcement phases of different length scales. These multi-scale toughening methodologies have been used to promote additive, or greater than additive, improvements in the toughness properties of bulk polymer composites [65, 83, 96, 133, 241]. For example, Zhang et al. [96] reported that combining randomly oriented CNFs with SCFs in an epoxy gave rise to a synergistic improvement in the \( G_{IC} \) value which exceeded the expected additive toughening effect provided by the reinforcements when they were used separately. However, in this study [96], the multi-scale fibrous fillers possessed a random orientation and no attempts have so far been reported to try to maximise the toughening effect of such multi-scale reinforcements by preferential alignment.

Both nano-scale and micron-scale carbon fillers can be aligned prior to cure of the epoxy resin using an electric field [74, 260, 279], magnetic field [137, 258], and mechanical deformation [135] techniques. Previous investigations into the toughening effects and mechanisms of carbon-based reinforcements have shown that GNPs [50, 58], CNFs [57, 58, 152, 253] and SCFs [279] can be aligned using an alternating current (AC) electric field. Aligning the GNPs, CNFs or SCFs normal to the crack propagation direction resulted in a higher toughness for the epoxy composites compared to when these reinforcing fillers were randomly oriented [57, 58, 152, 253, 279]. However, these previous studies into the alignment of such reinforcements to promote additional
improvements to the fracture toughness properties have only considered a single type of filler material, and have not explored using combinations of reinforcements at multiple length scales.

As an extension to Chapter 3, the current work presents an investigate into the effect of multi-scale fibre toughening or hybridization (i.e. CNFs and SCF), with and without electric field alignment, on the mode I fracture properties and toughening mechanisms of bulk epoxy polymers. Firstly, the electrophoretic process of the rotation and alignment of CNFs and SCFs, when used separately and together in a liquid epoxy resin, is investigated. Secondly, the fracture toughness properties of the resulting epoxy polymers containing CNFs or/and SCFs are experimentally measured and used to assess the effects of their concentration, combination and orientation. Based on analytical models proposed for CNFs [58] and SCFs [279], fracture energies of the multi-scale reinforced composites are predicted by accounting for the identified toughening mechanisms. Lastly, the model predictions are compared with the experimental data and provide an assessment of the various contributions to the increases in the fracture toughness imparted by the two filler types.

4.2 MATERIALS AND EXPERIMENTAL DETAILS

4.2.1 Materials and electric field alignment

In being consistent with Chapter 3, the epoxy resin system used was Resin 105 and Hardener 206 from West System. Vapour-grown carbon nanofibers, Pyrograf®-III PR-24-HHT (supplied by Applied Sciences Inc., USA), were used as the nano-scale reinforcements. The diameter and length of the supplied CNFs were in the range of 70-300 nm and 30-200 μm, respectively. SCFs with a diameter of 7 μm were obtained by cutting continuous T300 carbon fibre tows (supplied by Colan Pty Ltd.). Further details of the epoxy system and the preparation of the SCFs are presented in Section 3.2.1 (Chapter 3).

The epoxy polymer composites were made containing different weight fractions of CNFs, SCFs, or CNFs and SCFs (i.e. multi-scale reinforced), and the compositions studied are listed in Table 4.1. For the multi-scale reinforced epoxy polymers using both the CNF and SCF reinforcements, the SCF concentration was varied between 0.5 and 2.5 wt% whilst the concentration of CNFs was kept constant at 1.0 wt%. The CNFs and/or SCFs were initially hand
mixed in the liquid epoxy resin and then further dispersed using a three-roll milling machine (Dermamill 100). The process parameters for the three-roll milling process is adapted from Chapter 3 and are detailed in Section 3.2.1. In adapting the protocol for dispersing the CNFs only within the epoxy matrix [49, 98, 281], solvent-free acrylate copolymers/surfactants (Disperbyk-191 and -192 supplied by BYK®) were added to the liquid resin at the weight ratio of 1:1:1 for D-191:D-192:CNFs prior to the milling process. This process is used when blending CNF only into the epoxy matrix in the next chapters. Due to the shearing action generated by the milling process, the average lengths of the CNF and SCF reinforcements were reduced to 19.1 \( \mu \text{m} \) (\( \pm 5.0 \mu \text{m} \)) and 720 \( \mu \text{m} \) (\( \pm 210 \mu \text{m} \)), respectively.

### Table 4.1. Composition of the epoxy polymers, with or without electric field alignment.

<table>
<thead>
<tr>
<th>Material</th>
<th>CNF Content (wt%)</th>
<th>SCF Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified epoxy polymer</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-reinforced epoxy</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>polymers</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>SCF-reinforced epoxy</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>polymers</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>Multi-scale reinforced</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>epoxy polymers</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Based on the previous chapter [279], the CNF and/or SCFs were aligned in the liquid epoxy using an externally applied alternating current (AC) with a field strength of 30 V/mm at a frequency of 10 kHz. The electric field was applied between two parallel electrodes (polymer
coated copper) using an AC signal generator (Tektronix CFG250) connected to a wideband amplifier (Krohnhit 7602M).

A study into the rotation and alignment of the CNFs and SCFs in-situ within the liquid epoxy resin, without hardener, was performed using specimens containing (a) 0.1 wt% of CNFs, (b) 0.1 wt% of SCF, and (c) 0.10 wt% of SCF + 0.10 wt.% of CNF multi-scale reinforcements. The experimental details on the alignment studies are described in Section 3.2.2 (Chapter 3).

4.2.2 Specimen manufacturing and fracture toughness testing

The mode I fracture toughness properties of the different epoxy materials listed in Table 4.1 were measured using double cantilever beam (DCB) specimens. The DCB specimen design and manufacturing process is detailed in Section 3.2.3 (Chapter 3) and in based on previous reports [57, 58, 152, 253, 279], so only brief details are provided below. As shown in Fig. 4.1a, the DCB specimens were made by using the unmodified epoxy or carbon filler reinforced epoxy interlayer as an adhesive between two pre-cured composite laminates, which were therefore used as both the substrates for the adhesively-bonded joint and as the electrodes for electric field alignment.

![Figure 4.1](image) (a) Schematic and dimensions of the double cantilever beam (DCB) specimen. The main direction of the alignment of the CNFs and SCFs after exposure to the AC electric field is indicated. (b) Load versus crack opening displacement curves for the epoxy polymers containing 1.0 wt% CNFs and/or 1.0 wt% SCFs before and after application of an AC electric field.
To manufacture the adhesively bonded joints, the unmodified epoxy or the carbon reinforced epoxy containing CNFs or/and SCFs were hand mixed with the hardener and degassed in a vacuum chamber for 5 minutes to remove entrapped air bubbles. The epoxy mixture with hardener was then poured between the gaps of two pre-cured composite substrates with a layer of ~2 mm in thickness. Thus, using the same methodology as from the previous chapter, the thickness of the epoxy layer was controlled using 2 mm thick glass slides as spacers. An AC electric field of strength of 30 V/mm and at a frequency of 10 kHz was applied to align the filler along the through-the-thickness direction as illustrated in Fig. 4.1a. The electric field was applied for one hour continuously as the epoxy underwent gelation and cure, thereby locking in place the aligned CNFs and SCFs.

The mode I fracture toughness ($G_{IC}$) of the composites specimens were measured in accordance with ISO 25217 [259], and the test methodology is further described in Section 3.2.3 (Chapter 3). Five replicate test specimens were tested for each epoxy polymer type. Crack growth was observed to always occur cohesively within the epoxy adhesive layer in an unstable ‘stick-slip’ for the unmodified epoxy and the filler reinforced epoxy polymer, as shown in Fig. 4.1b. As reported in the previous chapter, only three to four data points could be acquired per DCB sample irrespective of the composite type.

4.3 RESULTS AND DISCUSSION

4.3.1 Electric field alignment of SCF and CNF in epoxy resin

The responses of the CNFs and SCFs to the external AC electric field while suspended in the liquid epoxy resin were observed experimentally. Typical optical microscopy images of the liquid epoxy resin containing CNFs (at 0.1 wt.%) or SCFs (at 0.1 wt.%) before and during exposure to the electric field are presented in Fig. 4.2. When used separately, many of the CNFs and SCFs rotated and aligned towards to the electric field direction within a short time, i.e. typically under five minutes. This is due to a dielectrophoresis effect which causes opposing charges to be generated along the fibre length and fibre ends [279, 282, 283], as illustrated in Fig. 4.3. This, in turn, generates a torque that forces the CNFs and SCFs to rotate and align in the direction of the electric field [282, 284]. It was observed that, as the CNFs and SCFs rotated, the negatively charged end
was electrically attracted to the positive end of a nearby fibre to create a ‘chain-like’ network aligned in the electric field direction, as shown in Fig. 4.2b and Fig. 4.2d [142].

Fig. 4.2 Alignment of the CNFs or the SCFs (at 0.1 wt%) in the liquid epoxy using the AC electric field. (a) Randomly oriented CNFs before exposure to the electric field, (b) aligned CNFs at $t = 300$ s after exposure to the electric field, (c) randomly oriented SCFs before exposure to the electric field, and (d) aligned SCFs at $t = 300$ s after exposure to the electric field.
When the epoxy resin containing both CNFs and SCFs, each at 0.1 wt%, was exposed to the electric field, both fillers aligned in the field direction. This is shown by the time-lapse images in Fig. 4.4a to c, which shows the alignment angle of the CNFs and SCFs as a function of the exposure time to the electric field. Fig. 4.4d shows the measured time taken for a SCF and a CNF to rotate from ~90° to the direction of the applied electric field to an angle of ~2°. The rotation rates for the CNFs and SCFs were identical under the electric field conditions used. Intra-chaining between the two types of reinforcement, as well as the deposition of CNFs onto the SCF surfaces, occurred under exposure to the electric field (see Fig. 4.4e). Indeed, as shown in Fig. 4.4f, the CNFs deposited along the length of the SCFs, with their surface density being highest at the ends where the dipole charges are highest [282, 283] (see Fig. 4.3). Analysis of the optical micrographs revealed that a relatively very low concentration, of approximately 3.9% (±0.72%) of the CNFs in the epoxy resin containing 0.1 wt% of CNFs, were deposited onto the SCFs. The remainder of the CNFs were aligned along the direction of the electric field, as shown in Fig. 4.4e. The adhesion forces acting between the CNFs and SCFs will be relatively weak Van-Der Waals bonds, since there is no physical grafting or chemical adhesion possible. Other studies report the electrophoretic
deposition of CNFs [285], CNTs [74], and GNRs [278, 286] onto continuous carbon fibres. However, these observations from the present study appear to be the first demonstration of the in-situ deposition of CNFs onto discontinuous SCFs.

**Fig. 4.4** Electric field of alignment of a single SCF and multiple CNFs in the liquid epoxy after (a) t = 0 s, (b) t = 50 s, and (c) t = 100 s in the presence of the AC electric field. (d) Experimental measurements of the rotation time for a SCF and a CNF to rotate from ~88° to ~2° relative to applied electric field direction (i.e. 0°). (e) Intra-chaining of CNFs and SCFs upon exposure to the AC electric field. (f) In-situ deposition of CNFs on a SCF during exposure to the electric field. (Note: images and measurements were taken from an epoxy resin containing 0.1 wt% SCFs and 0.1 wt% CNFs.)

### 4.3.2 Fracture toughness of epoxy polymers

#### 4.3.2.1 Effect of electric field alignment on the fracture toughness

The effect of the type, concentration and alignment of the CNFs or SCFs, when used separately, is on the $G_{IC}$ value of the epoxy polymer containing is shown in **Fig. 4.5**. With or
without exposure to the electric field, the $G_{lc}$ values increased rapidly with the concentration of CNFs or SCFs up to about 1.5 wt%, above which the toughening rate diminished due to agglomeration and increased packing density of the fillers. Alignment of the CNFs or SCFs using the electric field resulted in a higher toughness than when the fibres were randomly orientated up to 1.5 wt% CNF and 2.0 wt.% SCF, respectively. The improvements in the $G_{lc}$ values due to electric field alignment at a given weight fraction of the CNFs or SCFs were found to be statistically significant with a 99.9% confidence level via an ‘unpaired t-test’ employing the values of the mean and standard deviation for a minimum of fifteen data points per configuration. On a weight fraction basis, the results also reveal that the CNFs were more effective in enhancing the fracture toughness than the SCFs irrespective of the application of an electric field.

![Bar chart](a) Mode I Fracture Toughness, $G_{lc}$ (J/m$^2$)

Fig. 4.5 Effect of increasing concentration of (a) CNFs and (b) SCFs, when used separately, on the fracture toughness of the polymers, without and with exposure to the electric field.

The effect of combining CNFs at a fixed weight fraction of 1 wt% with SCFs at varying concentrations on the fracture toughness of the multi-scale reinforced epoxy polymers is shown in Fig. 4.6. Without the application of an electric field, combining the CNFs and SCFs gives, at best, an additive improvement to the $G_{lc}$ value. This may be readily seen from the two dashed lines in Fig. 4.6 which show that additive toughening, from the CNFs and SCFs added separately, correlates very well with the experimental results for the multi-scale reinforced epoxy polymers with SCF concentrations less than 1.5 wt%. Electric field alignment of the CNFs and SCFs induced a substantial toughening effect up to a concentration of 1.5 wt% SCFs, with the $G_{lc}$ values being
much greater than for the multi-scale reinforced epoxy polymers that were not exposed to an electric field. With the application of an electric field, the combining and aligning of the CNFs and SCFs up to 1.5 wt% for the multi-scale reinforced composites gives at best an additive improvement on the $G_{ic}$ value when compared to the expected additive improvement from the CNFs and SCFs when added separately. With increase in the SCF weight content above 1.5 wt%, the improvement for the multi-scale reinforced epoxy is less than the expected additive enhancement. However, it is important to note that no apparent synergy that is statistically significant is shown in Fig. 4.6 when considering of the standard deviations associated with the measured fracture toughness values.

![Graph showing the effects of electric field alignment and SCF concentration on fracture toughness](image)

**Fig. 4.6** Effects of electric field alignment and SCF concentration on the fracture toughness of the multi-scale reinforced epoxy polymers containing various concentrations of SCFs and 1 wt.% CNFs. The dashed lines represent the values of the expected fracture toughness if the average contributions from the SCFs and CNFs, when employed separately, are simply additive, i.e. the fracture toughness $G_{ic} = G_0 + \Delta G_{SCF} + \Delta G_{CNF}$. 
4.3.2.2 Effect of electric field alignment on the toughening mechanisms

Fractographic examination of the DCB specimens revealed many toughening mechanisms induced by the CNFs and SCFs. Scanning electron micrographs (SEM) showing the toughening mechanisms operative in the epoxy polymers containing various combinations of reinforcements are presented in Figs. 4.7-4.9. Intrinsic toughening mechanisms were induced by the CNFs and SCFs within the process zone (see Fig. 4.7a) ahead of the main crack tip. These mechanisms were interfacial debonding and plastic void growth. As shown in Fig. 4.7c, Fig. 4.8b and Fig. 4.8e, the CNFs and SCFs debonded from the epoxy matrix under the concentrated triaxial stress field within the process zone. The mechanism of interfacial debonding dissipated some of the stored strain energy which was followed by shear banding or yielding of the epoxy matrix surrounding the fillers. Following debonding and shear yielding, voids initiated and grew due to localised plastic flow of the epoxy matrix adjacent to the CNFs (see Fig. 4.8d and Fig. 4.8e) and SCFs (see Fig. 4.8b). The density of such void growth within the process zone increased with the concentration of the reinforcement, which partly accounts for the fracture toughness increasing with the concentration of CNFs and/or SCFs. The CNFs were more effective at developing such void growth than the SCFs, per unit volume. The maximum void diameter was measured to be 7 to 9 times the diameter of the CNFs, but only 1.5 to 2.0 times the SCF diameter. Also, due to the greater number of CNFs per unit volume than the SCFs for a given weight fraction, a much greater density of voids developed in the process zone of the CNF-reinforced epoxy polymers. This resulted in a higher toughening effect (Fig. 4.5a) and, indeed, the CNF-reinforced epoxy polymers exhibited a much higher toughness than for the epoxy reinforced with SCFs (Fig. 4.5b). Limited sites of microcracking within the process zone ahead of the main crack tip were also observed. Microcracking resulted in the bifurcation and branching of the main crack tip, as shown in Fig. 4.7c and Fig. 4.7e. However, the toughening mechanisms of microcracking and crack branching occurred in the SCF-reinforced and multi-scale reinforced epoxy at a much lower density within the process zone, as shown in Fig. 4.7.
Fig. 4.7 (a) Schematic representation of the intrinsic and extrinsic toughening mechanisms in the epoxy polymers. Cross-sectional SEM images of the fracture surface of (b) the unmodified epoxy, (c) 1 wt% SCFs, (d) 1 wt% CNFs and (e) 1 wt% SCF + 1 wt% CNF multi-scale reinforcements in the epoxy polymers after exposure to the electric field. Note: the subscripts on Figs. c-e denotes where the SEM images were captured: (1) behind the advancing crack tip and (2) near the crack tip.
Fig. 4.8 SEM images of the fracture surface of the epoxy polymers. (a) 1.5 wt.% SCFs without exposure to the electric field, (b) 1.5 wt.% SCFs after exposure to the electric field, along with the inset (c) depicting snubbing, (d) 1.0 wt.% CNFs after exposure to the electric field, along with the inset (e) showing the epoxy void growth toughening mechanism and (f) 1.0 wt.% CNFs after exposure to the electric field. (Note: the direction of the y-axis on the images represents the crack propagation direction).

Irrespective of the filler type, the two intrinsic toughening mechanisms described above occurred regardless of whether the CNFs and/or SCFs were randomly oriented or aligned normal to the crack growth direction using the electric field; as there was no interaction between the CNFs and/or the SCFs whether used separately or in combination. This accounts for the absence of any synergistic toughening effect but rather the observed additive improvement in the toughness of the epoxy polymers containing both CNFs and SCFs at relatively lower filler contents. At relatively high weight fractions (i.e. > 1.5 wt% CNF or SCF), when significant fibre agglomeration occurred, it was observed that the void growth was restricted when the CNFs and/or the SCFs were closely spaced, as shown in Fig. 4.9a and Fig. 4.9b. The reduced free space between the closely-packed CNFs and SCFs fibres restricted the plastic flow and the extent of the stress triaxiality needed for void growth in the epoxy matrix, thereby limiting this toughening mechanism in the multi-scale
reinforced composites with a relatively high filler contents [70, 78, 83]. These observations correlate with the less-than-additive improvement measured for such multi-scale reinforced epoxy polymers, as shown in Fig. 4.6.

![Fig. 4.6 SEM images of the fracture region ahead of the crack front in the multi-scale reinforced epoxy polymers. (a) 2.5 wt% SCF + 1 wt% CNFs multi-scale reinforcements after exposure to the electric field along with the inset (b) demonstrating impeded epoxy void growth around neighbouring SCFs at a relatively high magnification, (c) 1 wt% SCF + 1 wt% CNF multi-scale reinforcements after exposure to the electric field depicting CNF/epoxy retained on the SCFs, (d) pulled-out SCFs from the multi-scale reinforced epoxy polymer without exposure to the electric field, (e-f) pulled-out SCFs from the multi-scale reinforced epoxy polymer after exposure to the electric field.](image)

Multiple extrinsic toughening mechanisms operated behind the main crack front of the epoxy polymers reinforced with CNFs and/or SCFs, which together with the intrinsic mechanisms described above are responsible for the improvements to the fracture toughness. The extrinsic mechanisms were fibre bridging, fibre snubbing (for the SCFs), fibre pull-out and fibre rupture, as shown in Fig. 4.7, and certain of these mechanisms were magnified by the electric field alignment. Both the CNFs and SCFs bridged the crack faces (Fig. 4.7c and Fig. 4.7d) and at each bridging site the fibre generated a discrete traction load that reduced the stress exerted on the crack tip,
thereby increasing the toughness. Fibres are more likely to bridge a crack when aligned near normal to the crack growth direction, and therefore a much higher density of CNFs and SCFs bridged the crack when aligned using the electric field, as shown in Fig. 4.8, resulting in the increased toughness for such epoxy polymers containing the aligned reinforcements.

Snubbing was another toughening mechanism identified in the SCFs reinforced composites, although it was not observed for the CNFs. Snubbing is a mechanism whereby the bridged SCFs were pressed laterally into the surrounding epoxy matrix as they were forced to rotate and align in the crack opening direction [132, 266, 268, 287]. The increased contact pressure between the SCFs and epoxy matrix increases the local interfacial shear friction stress during fibre pull-out, further increasing the toughness [287]. Snubbing can only occur when the SCFs are aligned near normal to the crack growth direction, and therefore the toughening effect was greater for the composites subjected to alignment using the electric field. Snubbing associated with CNFs was not evident, and this may be due to their low bending rigidity which caused them to flex rather than being pressed into the epoxy matrix [66]. The bridging CNFs and SCFs were pulled-out behind the crack front as the crack opening displacement increased. Pull-out occurred after the CNFs and SCFs had completely debonded from the epoxy. An interfacial shear friction traction stress is generated as the CNFs and SCFs are pulled-out, thereby contributing to the increase in the fracture toughness. The CNFs and SCFs were pulled cleanly from the epoxy matrix when used separately, as evidenced by their smooth and featureless surface (Fig. 4.9d). However, for the multi-scale reinforced epoxy polymers which were exposed to an electric field, approximately 30% of the SCFs that were pulled-out had CNFs adhering to their surfaces, as well as small fragments of epoxy polymer, as measured from SEM images of the fracture surface (Fig. 4.9c, Fig. 4.9e and Fig. 4.9f). As reported within the in-situ alignment studies, a very small proportion of CNFs (i.e. ~4% from the optical micrographs) became attached to the SCFs due to the electric field alignment process (Fig. 4.4e). Electrophoretic deposition of carbon nanomaterials, such as CNTs, CNFs and GNP, on to continuous carbon fibres has been shown to increase the interfacial shear strength with an epoxy matrix [278, 285, 288]. Therefore, the resistance against pull-out of the SCFs may have been slightly increased by the electrical field induced deposition of the CNFs on the surfaces of the SCFs. This may be responsible for the higher fracture toughness of the multi-scale reinforced composites following electric field alignment.
4.3.3 Modelling the fracture toughness of the multi-scale reinforced epoxy polymers

This section describes an analytical model to calculate the fracture toughness of the multi-scale reinforced epoxy polymers containing both CNFs and SCFs. The model predictions are compared with the experimental results presented earlier. In adapting the model previously developed for CNFs [57] and the SCFs [279] from the previous chapter, the present model proposed considers the following toughening mechanisms: (a) interfacial debonding of reinforcements ($G_{db}$) [265], (b) plastic void growth formation surrounding the debonded reinforcements within the crack process zone ($G_{void}$) [70], (c) bridging and pull-out of the reinforcements ($G_{pull-out}$) [6, 132, 133], and (d) rupture of the reinforcements ($G_{rupture}$) [272] behind the crack front. The observed additive toughening effect seen for the multi-scale reinforced epoxy polymers can be described by the following model by summing the contributions from the CNFs [57] and SCFs [279]. The fracture toughness ($G_{Ic}$) of the multi-scale reinforced composite is expressed as:

$$G_{Ic} = G_o + \Delta G_{CNF} + \Delta G_{SCF}$$

(1)

where $G_o$ is the fracture toughness of the unmodified epoxy, and $\Delta G_{CNF}$ and $\Delta G_{SCF}$ are the fracture energies due to toughening mechanisms arising from the presence of the CNFs and SCFs, respectively. Since the effect of electric field alignment of the CNF and SCF (below 1.5 wt%) reinforcements resulted, at best, in an additive improvement in the values of $G_{Ic}$, it was assumed that there are no interaction effects between the CNFs and SCFs, and that both fibres act independently in their contribution to the toughening of the epoxy multi-scale reinforced composites. In an extended form, Eqn. 1 can therefore be written as:

$$G_{Ic} = G_o + (G_{db} + G_{void} + G_{pull-out} + G_{rupture})_{CNF} + (G_{db} + G_{void} + G_{pull-out} + G_{rupture})_{SCF}$$

(2)

The fracture energy contribution imparted by the CNFs can be now extended and expressed as [57]:

$$\Delta G_{CNF} = \frac{V_{CNF} \sigma_{CNF}^2 d_{CNF}^2}{2E_{CNF}} + \left(1 + \frac{\mu_m}{\sqrt{3}}\right)^2 V_{CNF} \left(\frac{d_v^2}{3d_{CNF}^2} + \frac{d_y}{3d_{CNF}} - 1\right) \frac{E_m G_o K_{2m}^2}{6(1-v^2)\sigma_y^2} + \frac{V_{CNF} \sigma_{CNF}^2 d_{CNF}^2}{8\tau_i}$$

(3)

and for the SCFs may be expressed as from Section 3.3.2.4 (Chapter 3) [279]:

101
\[
\Delta G_{SCF} = \frac{V_{po \pm 45} l_{crit} G_{CNF}}{2d_{SNF}} + \left( 1 + \frac{\mu m}{\sqrt{3}} \right)^2 V_{SCF} \left( \frac{d_f^2}{3d_{SCF}^2} + \frac{d_v}{3d_{SCF}} - 1 \right) \frac{E_m G_o K_{mn}}{6\pi (1-\nu^2) \sigma_y} + \int_{\theta_f=\theta_{crit}}^{\theta_f=0^o} \left( \frac{V_{SCF} l_{crit} G_{CNF}}{8d_{SCF}} \exp(\mu \theta_f) \right) \rho(\theta) d\theta_f + \frac{V_{SCF} \sigma_{SCF} l_{crit}}{2E_{SCF}}
\]

(4)

The definition and values for majority of the input parameters in Eqns. 3 and 4 are given in Tables 4.2 and 4.3. The parameter \( V_f \) is the volume fraction of CNFs or SCFs, \( d \) (i.e. \( d_{CNF} \) and \( d_{SCF} \)) is the corresponding fibre diameter, \( \nu \) is the Poisson’s ratio and \( G_i \) is the interfacial debonding energy between the CNF or SCF and the epoxy matrix. From SEM fractographic observations of the crack surfaces, the volume fraction of voids, \( V_{void} \), was determined by considering the ratio between the diameter of the voids, the diameter of the filler and assuming their shape to be a truncated cone (see Eqn. 3 and Eqn. 4), as adapted from [57, 58, 279]. The diameter of the void, \( d_v \), was nearly nine and two times the diameters of the CNFs and SCFs, respectively.

**Table 4.2. Calculated volume fraction of SCFs that pulled-out, \( V_{po \pm 45} \), from the epoxy within an orientation distribution range from -45° to +45°, relative to the through-the-thickness direction.**

<table>
<thead>
<tr>
<th>SCFs (wt%)</th>
<th>( V_f ) (%)</th>
<th>( V_{po \pm 45} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without E-Field</td>
<td>With E-Field</td>
</tr>
<tr>
<td>0.5</td>
<td>0.29</td>
<td>~ 0.11</td>
</tr>
<tr>
<td>1.0</td>
<td>0.58</td>
<td>~ 0.16</td>
</tr>
<tr>
<td>1.5</td>
<td>0.87</td>
<td>~ 0.17</td>
</tr>
<tr>
<td>2.0</td>
<td>1.16</td>
<td>~ 0.23</td>
</tr>
<tr>
<td>2.5</td>
<td>1.45</td>
<td>~ 0.29</td>
</tr>
</tbody>
</table>

Considering the fracture energy due to pull-out, a fibre can only pull-out if it is below a critical length, \( l_{crit} \); above the critical length the fibre will rupture because the pull-out stress exceeds the fibre fracture stress, \( \sigma_f \). The value of \( l_{crit} \) is calculated using the Kelly-Tyson formulation (i.e. \( l_{crit} = \sigma_f d_f/2\tau_i \) [6]. The term \( \tau_i \) is the interfacial shear friction stress and from the Tresca yield criterion is 25 MPa, which is based on half of the tensile yield strength of the unmodified epoxy, \( \sigma_y \). From the upper-bound diameter of the CNFs, the maximum value of \( l_{crit} \) for the CNFs and SCFs is 18.1 \( \mu m \) and 505 \( \mu m \), respectively, where the maximum pull-out length is calculated to be \( l_{po} = l_{crit} 2 = 9.1 \mu m \) and 253 \( \mu m \), respectively. From fractographic analysis, the mean pull-out lengths of the CNFs and SCFs, \( l_{mea} \), were approximately 5.2 \( \mu m \) and 116 \( \mu m \),
respectively. Fractographic analysis of the epoxy polymers revealed that the SCFs bridged the crack and pulled-out at a critical fibre angle, $\Theta_{\text{crit}}$, less than $\sim45^\circ$. During pull-out, the SCFs inclined from the through-thickness direction were pressed laterally into the epoxy, inducing a snubbing effect. The enhanced friction stress due to snubbing [132, 133, 266] is considered into Eqn. 4 where $\theta_f$ and $\rho(\theta)$ are respectively the SCF angle and the probability density of SCFs inclined for a given range of angles [279]. The density of SCFs within the orientation range from $-45^\circ$ to $+45^\circ$ may be taken from Fig. 3.16 (Chapter 3), and equates to the volume fraction of SCFs that were subjected to pull-out, $V_{\text{po}}$, as listed in Table 4.2.

Using Eqns. 1, 3 and 4, and the input values from Tables 4.2 and 4.3, the fracture toughness values for the multi-scale reinforced composite, with randomly orientated or aligned reinforcements, were calculated and compared with the experimental values, as shown in Fig. 4.10a. The calculated toughness values are highly sensitive to the CNF diameter used in the modelling studies, due to its effect on the pull-out traction energy. Therefore, the model was solved using the values of the minimum, $d_{\text{min}}$, or maximum diameter, $d_{\text{max}}$, for the CNFs, which were 70 nm and 200 nm, respectively. As seen in Fig. 4.10a, the model predicts (a) a progressive increase in the values of the fracture toughness with increasing SCF concentration and (b) that the toughness values are higher when the CNFs and SCFs are aligned. The agreement between the calculated and measured toughness values is good up to a concentration of SCF of $\sim1.5$ wt%, above which the model over-predict the values of $G_{\text{IC}}$ due to fibre agglomeration and increased packing density reducing the additive toughening effect that was measured experimentally.

Table 4.3. Values used in the analytical modelling study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF diameter</td>
<td>$d_{\text{SCF}}$</td>
<td>$\mu$m</td>
<td>7</td>
<td>The present study</td>
</tr>
<tr>
<td>CNF average diameter</td>
<td>$d_{\text{CNF}}$</td>
<td>nm</td>
<td>70 - 200</td>
<td>[289]</td>
</tr>
<tr>
<td>SCF average length after milling</td>
<td>$l_{\text{SCF}}$</td>
<td>$\mu$m</td>
<td>720</td>
<td>The present study</td>
</tr>
<tr>
<td>CNF average length after milling</td>
<td>$l_{\text{CNF}}$</td>
<td>$\mu$m</td>
<td>18.1</td>
<td>The present study</td>
</tr>
<tr>
<td>SCF tensile strength</td>
<td>$\sigma_{\text{SCF}}$</td>
<td>MPa</td>
<td>3530</td>
<td>[256]</td>
</tr>
<tr>
<td>CNF tensile strength</td>
<td>$\sigma_{\text{CNF}}$</td>
<td>MPa</td>
<td>8700</td>
<td>[289]</td>
</tr>
<tr>
<td>Young’s modulus of SCF</td>
<td>$E_{\text{SCF}}$</td>
<td>GPa</td>
<td>230</td>
<td>[256]</td>
</tr>
<tr>
<td>Young’s modulus of CNF</td>
<td>$E_{\text{CNF}}$</td>
<td>GPa</td>
<td>320</td>
<td>[289]</td>
</tr>
</tbody>
</table>
Density of SCF \( \rho_{SCF} \) kg/m\(^3\) 1760 [256]
Density of CNF \( \rho_{CNF} \) kg/m\(^3\) 1400 [289]
Density of unmodified epoxy \( \rho_e \) kg/m\(^3\) 1011 [257]
Tensile yield strength of unmodified epoxy \( \sigma_y \) MPa 49.9 The present study
SCF/epoxy interface fracture energy \( G_{SCF-i} \) J/m\(^2\) 1600 [270]
CNF/epoxy interface fracture energy \( G_{CNF-i} \) J/m\(^2\) 3.3 [290]
Young’s modulus of unmodified epoxy \( E_m \) GPa 3.18 The present study
Pressure dependent yield stress constant of unmodified epoxy \( \mu_m \) - 0.2 [70]
Maximum von Mises stress concentration around debonded fillers from the matrix \( K_{vm} \) - 2.11 [265]
Snubbing friction coefficient between the SCFs and epoxy \( \mu \) - 1.25 [127]

Fig. 4.10 (a) Comparison of the calculated and experimental fracture toughness values for the various reinforced epoxy polymers. (b) Stack-bar plots of the calculated contributions to the overall fracture toughness from the different toughening mechanisms for the CNF (1 wt%) and SCF (1.5 wt%) reinforcements used separately in the epoxy polymers and for the multi-scale reinforced epoxy polymers containing 1wt% CNFs and 1.5 wt% SCFs. All values are for the composites after exposure to the electric field. (Values for \( d_{min} \) and \( d_{max} \) are shown for the CNFs.)

The model may also be used to compute the contributions of the different toughening mechanisms to the fracture toughness of the reinforced epoxy polymers. Considering the example of the epoxy composites containing 1.5 wt% SCFs and/or 1 wt% CNFs that were exposed to the
AC electric field, Fig. 4.10b presents a stack plot of the calculated contributions from the different toughening mechanisms. The dominant toughening mechanism promoted by the CNFs and SCFs when used separately was (a) plastic void growth of the epoxy induced by debonding of the CNFs [57] and (b) fibre pull-out [279].

4.4 CONCLUSION

The fracture properties of multi-scale reinforced epoxy polymers can be tailored by the alignment of appropriate combination carbon reinforcements using carbon nanofibres (CNFs) and short carbon fibres (SCFs). It has been shown that:

- The CNFs and SCFs, when used separately or together, may be rapidly aligned in the epoxy prior to its gelation in the direction of the applied AC electric field.
- The fracture toughness, $G_{IC}$, of the epoxy polymers increased with filler content. On a weight fraction basis, the toughening efficacy was much greater for CNFs when compared to SCFs.
- Combining the CNFs and SCFs together to create multi-scale reinforced composites has an additive toughening effect, until relatively high concentrations of the SCFs (~1.5 wt%) were used. This additive toughness effect was further enhanced by using the electric field alignment process. In comparison to the unmodified epoxy, the $G_{IC}$ value of the multi-scale reinforced epoxy polymers was increased up to about 20-fold using a combination of electrically aligned CNFs and SCFs.
- The toughening mechanisms were fibre/matrix interfacial debonding, plastic void growth adjacent to the fillers within the process zone, snubbing (for the SCFs), fibre bridging and pull-out, and fibre rupture. The plastic void growth process was more prevalent for CNF reinforced composites.
- An analytical model, based upon these toughening mechanisms, has been proposed to predict the $G_{IC}$ values of the multi-scale reinforced composites.

This work has demonstrated the high toughening efficacy that may be derived by combining fibres of multiple length and diameter scales, and aligning them using an electric field, which can translate into the enhancement of their functional properties in future work.
Chapter 5: Multi-scale delamination toughening and low-velocity impact damage resistance of fibre composites using CNFs and SCFs

Abstract

This chapter presents an experimental study into the low-velocity impact damage resistance and post-impact compression strength properties of carbon fibre composite laminates toughened by multi-scale carbon fillers, used separately or in combination within the epoxy matrix, which include carbon nanofibres (CNFs) and short carbon fibres (SCFs). Laminates were subjected to a low-velocity point impact loads at various impact energies. Non-destructive evaluation and structural testing of the impacted samples revealed that the delamination resistance and the residual compression strength were dependent on the filler type. Hybridising the CNFs with SCFs results in substantial improvements to the damage resistance (~24%) and the compression after impact (CAI) strength (~29%) of the composite laminates, where these enhancements were greater than using the CNFs or SCFs separately. The improvements to the damage area reduction and CAI strength values were due to the increases to the modes I and II interlaminar fracture toughness properties of the toughened composite laminates.

5.1 INTRODUCTION

Carbon fibre reinforced epoxy composites exhibit high in-plane mechanical properties. However, due to the lack of reinforcements along the through-thickness direction of the laminate and the weak mechanical properties of the polymer matrix, these materials are prone to matrix cracks and delaminations when subjected to out-of-plane impact load, under low- or high-velocity conditions [36, 180, 271]. For aircraft structures, examples of these damage scenarios include bird strike and foreign object impact damage during routine flight operations. Fibre damage and barely visible delamination cracks can grow which further reduces the load-bearing properties (e.g. compression strength) of a composite structure. Delamination growth is predominantly governed
by the interlaminar tearing and shear stresses (i.e. mixed mode I/II) introduced by the bending of the laminate during the localised impact event. Therefore, the delamination resistance and damage tolerance properties are essential for the survivability of an operating composite structure [1, 291-294].

Several techniques can increase the interlaminar fracture toughness, impact damage resistance and post-impact mechanical properties of fibre composites. These include modification of the laminate design [295-297], thermoplastic interleaving [31], use of short fibre veils [173, 298, 299] and the insertion of macro-scale through-thickness reinforcements (i.e. 3D stitching or z-pinning) [36, 40, 41, 291]. More recently, numerous studies have been performed to improve the impact resistance and compression after impact (CAI) strength using toughened epoxies containing either nano- or micron-dimensional scale fillers [19, 298, 300-302]. Examples of these fillers include nano silica, nanoclay, carbon nanotubes (CNTs), graphene nanoplatelets (GNPs) and short Kevlar fibres. These fillers can also be employed to improve the interlaminar fracture toughness properties of fibre reinforced composites [59, 67, 153, 219, 303-306]. For example, Kostopoulos et al.[247] reported the effect of dispersing 0.5 wt% CNTs within the epoxy matrix on the impact delamination resistance and post-impact properties of carbon fibre composites. By subjecting the composite at an incident impact energy of 20 J, it was found that the use of 0.5 wt% MWCNTs resulted in a 5% reduction in the delamination area and a 20% increase in the CAI strength [247] when compared to the baseline composite. Carbon nanofibres (CNFs) have also has attracted much interest in enhancing the delamination properties of fibre composites [66]. Yokozeki et al. [169], reported that the low-velocity impact properties were dependent on the CNF content (i.e. 5 wt% and 10 wt%) resulting in a 3% reduction in the delamination area and 7.5% increase in CAI strength. The reduction to the damage size was correlated to an increase to the interlaminar fracture toughness properties of the laminates. Toughening mechanisms that increased the impact resistance include bridging and pull-out of the nanofillers from the epoxy matrix along the delamination front [169, 247]. In reviewing the relationship between the toughness properties and the residual strength properties, Tang et al. [300] found that the CAI strength was dependent on both the modes I and II interlaminar fracture toughness properties of a fibre composite. Other parameters that affect the post-impact mechanical properties include the type of polymer matrix used, fibre preforms, manufacturing techniques employed and interlaminar shear strength properties [161, 219, 300].
Rahman et al. [245] found that the application of functional groups (i.e. oxides) to the nanofiller surface improved the low-velocity impact delamination resistance properties. The addition of 1 wt% oxidised CNFs into the epoxy matrix resulted in reduction of the composites material’s impact damage area of 30%, 70% and 58% at impact energies of 10 J, 20 J and 30 J, respectively [245]. Mannov et al. [307] measured a 55% improvement to the CAI strength of glass fibre composite containing a low content (0.3 wt%) of thermally reduced graphene oxide [41].

Carbon nano- and micron-scale fillers have been used separately to enhance the interlaminar fracture toughness, impact resistance properties and CAI strength of fibre reinforced composites [19, 298, 300-302, 308]. Multi-scale toughening involving the hybridisation of two or more toughening techniques have been reported to promote additive, or greater than additive, improvements to the fracture toughness of composites [47-49]. For instance, Zhang et al. [96] reported that combining randomly oriented CNFs with short carbon fibres (SCFs) in bulk epoxy polymers resulted in a synergistic improvement to the mode I fracture toughness. However, the effects of hybridising CNFs and SCFs towards the interlaminar fracture toughness and low-velocity impact damage resistance of carbon fibre laminates are not well understood.

Building on Chapter 4, this chapter presents an experimental investigation into the multi-scale interlaminar toughening effect of carbon fibre reinforced epoxy composites using CNFs and SCFs. Composite laminates were manufactured using a liquid compression moulding approach. Firstly, the mode I and mode II crack growth resistance properties of the laminates containing CNFs or/and SCFs are measured. Key toughening mechanisms are then identified along the fracture surface using scanning electron microscopy. The intrinsic tensile, flexural and interlaminar shear strength properties are measured. Secondly, the composite laminates containing the fillers were then subjected to low-velocity out-of-plane impact loads using the drop-weight test performed at various incident impact energies. The damage behaviour and projected delamination area of the impacted samples are characterised and compared with the respective interlaminar properties. Also, the CAI strength of the impacted composite specimens are measured.
5.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

5.2.1 Composite materials and manufacturing

Four types of carbon fibre reinforced epoxy composites were manufactured for testing which include (a) unmodified (i.e. baseline), (b) CNF-reinforced (1.0 wt% CNF), (c) SCF-reinforced (1.0 wt% SCF), and (d) multi-scale reinforced containing both 1.0 wt% CNF and 1.0 wt% SCF within the epoxy matrix. The composite laminates contained 20 plies of 200 gsm plain woven carbon fibre fabric (AC220127 supplied by Colan Ltd.). The matrix phase used was a two-part bisphenol-A based epoxy resin (Resin-105 and Hardener-206 supplied by Westsystem®). The ratio of epoxy resin-to-hardener used was 5-to-1 by weight. The weft and warp tows of the plies were oriented along the length and width of the test specimens, respectively.

In using the same reinforcing fillers from Chapter 3 and 4, vapour-grown carbon nanofibers, Pyrograf®-III PR-24-HHT (supplied by Applied Sciences Inc., USA), were used as the nano-scale reinforcements. The diameter and length of the supplied CNFs were 70-300 nm and 30-200 μm, respectively. The SCFs have a diameter of 7 μm and were obtained by cutting continuous T300 carbon fibre tows (supplied by Colan Pty Ltd.) into lengths of 2 to 3 mm using a paper guillotine. Before adding hardener, the CNFs and SCFs were initially hand mixed in the liquid epoxy resin at a weight fraction of 1.0% each. The multi-scale reinforced composite contained both 1.0 wt% CNF and 1.0 wt% SCF within the epoxy matrix. These contents selected as they promote optimal mode I fracture toughness improvement for the bulk epoxy composites reported previously in Chapter 4. The nano- and micron-scale were dispersed using a three-roll milling machine (Dermamill 100). The epoxy resin mixture containing the fillers was passed four times through the milling machine operated at 50 rpm. The gap size was progressively reduced with each pass with a final gap setting of 20 μm. In adapting the protocol for dispersing the CNFs within the epoxy matrix [49, 98, 281], solvent-free acrylate copolymers/surfactants (Disperbyk-191 and -192 supplied by BYK®) were added to the liquid resin at the weight ratio of 1:1:1 for D-191:D-192:CNFs prior to the milling process. The average lengths of the CNF and SCF reinforcements were reduced to 19.1 μm (±5.0 μm) and 720 μm (±210 μm), respectively, after the milling. The hardener was then mixed into the epoxy resin mixture before impregnation into the fibre preform.
The carbon fibre epoxy laminates were manufactured using a liquid compression moulding process (see Fig. 5.1a) via manual layup process followed by high pressure (350 kPa) curing in a hydraulic press as shown in Fig. 5.1b). During the layup process, the epoxy resin mixture was pre-impregnated into the individual carbon fibre plies stoichiometrically, to achieve a fibre volume fraction of ~50% [49]. The laminates were then cured under the high pressure for 24 hours and then 72 hours at 25°C following the epoxy supplier’s guidelines [257]. The manufacturing process described above in attaining a fibre volume fraction of ~50% and a cured thickness of ~5mm is directly adapted from [49]. The composite laminates were demoulded from the compression moulding tool with the use of a non-perforated 25 μm thick polytetrafluoroethylene (PTFE) film as shown in Fig 5.1a. Laminates were then cut into the designated test specimens using a benchtop diamond-tip table saw.

**Fig. 5.1.** (a) Schematic of the liquid compression moulding process using (b) Soton development press.

### 5.2.2 Mode I and mode II interlaminar fracture toughness characterisation

The mode I and mode II interlaminar fracture toughness of the corresponding composite specimens were measured using (a) double cantilever beam (DCB) tests in accordance with ASTM D5528-13 [309], and (b) end notch flexure (ENF) tests as per the ESIS protocol [310]. As schematically presented in Fig. 5.2, the DCB and ENF specimens consisted of a central region made from plain
woven carbon fibre laminate and outer reinforcing stiffeners/tabs. Each composite was bonded with two 12-ply unidirectional carbon fibre epoxy strips (~2.5 mm thick VTM-264 supplied by Advanced Composites) using an epoxy-based adhesive (Araldite 420 supplied by Huntsman®) to prevent localised failure at the outer sublaminate arms and, thereby, promoting crack growth along the mid-plane during testing. The width of the DCB and ENF specimens is $w = 22$ mm. The total thickness and support span of the ENF specimen is $t = 10$ mm and $2L = 250$ mm, respectively.

One end of the DCB specimens contained a 50 mm long mid-plane pre-crack using a 25 μm thick PTFE film. DCB tests were conducted by applying a monotonically increasing tensile load on the tabbed region of the DCB specimens (see Fig. 5.2a). Tests were conducted at a displacement rate of 1.0 mm/min using Instron 10 kN universal testing machine, as shown in Fig. 5.2. 

![Schematic of (a) double cantilever beam and (b) end-notch flexure samples.](image)

**Fig. 5.2.** Schematic of (a) double cantilever beam and (b) end-notch flexure samples.
5.3. The mode I fracture toughness \( G_{ic} \) values of the corresponding DCB specimens was measured using modified beam theory [309]:

\[
G_{ic} = \frac{3P_I \delta_I}{2b(a+|\Delta l|)}
\]  

where \( P_I \) is the mode I applied load, \( \delta_I \) is the crack opening displacement, \( a \) is the crack propagation length, and \( b \) is the sample width. A correction factor, \( |\Delta l| \), is determined from the change in the DCB specimen compliance to account for the vertical displacement and rotational effects at the measured crack tip.

![DCB Specimen](image)

**Fig. 5.3.** Photo of the experimental DCB test setup for measuring the mode I interlaminar fracture toughness and crack propagation length.

ENF specimens contained a 50 mm long mid-plane pre-crack from one end of the roller supports. A 25 \( \mu \)m thick PTFE film was inserted along the mid-plane of the ENF specimen to be used as a pre-crack (see **Fig. 5.2b**). The ENF samples were loaded under three-point bending, using Instron 50 kN universal testing machine, at a thickness-to-support span \((t/2L)\) ratio of approximately 1-to-25, as shown in **Fig. 5.4**. The ENF tests were conducted by applying a monotonically increasing bending displacement to the ENF specimens. The specimens were loaded at a centre-point displacement rate of 1.0 mm/min until the delamination extended from the
initial pre-crack to the centre roller loading support. The mode II interlaminar fracture toughness \( (G_{IIc}) \) of the corresponding ENF specimens was calculated using [310]:

\[
G_{IIc} = \frac{9a^2P_{II}\delta_{II}}{2b(2L^3+3a^3)}
\]  

(2)

where \( P_{II} \) is the applied bending force, \( \delta_{II} \) is the bending displacement, \( a \) is the crack propagation length. The \( b \) and \( 2L \) values are the width and the support span length of the samples, respectively. The load and displacement were taken at the onset of crack propagation. The crack propagation length was measured using a travelling optical microscope as shown in Figs. 5.3 and 5.4. Five DCB and ENF samples were tested for each specimen type.

![Fig. 5.4. Photo of the experimental ENF test setup for measuring the mode I interlaminar fracture toughness and crack propagation length.](image)

5.2.3 Tensile, flexural and interlaminar shear property characterisation

The tensile modulus and ultimate strength (i.e. peak load) of the laminates were measured using rectangular-shaped specimens (150 mm gauge length x 25.5 mm wide), as illustrated in Fig. 5.5a. The tensile test samples were loaded at a displacement rate of 1.0 mm/min using a 100 kN MTS testing machine until failure in accordance with ASTM D3039 [311]. The strain was measured using a 25 mm clip-on extensometer attached to the gauge section of the tensile sample. A minimum of five samples was tested for each material. The Young’s modulus was calculated by considering the in-plane tensile stresses within the 0.05% to 0.20% strain range.
The flexural modulus and strength of the laminates were measured using the three-point bend test method following ASTM D7264 [312]. As shown in Fig. 5.5b, the flexural specimens were loaded under bending with a support span-to-thickness ratio of 16:1. The flexural samples were subjected to a three-point bending load at a centre point displacement rate of 1 mm/min using a 50 kN Instron testing machine. The interlaminar shear strength (ILSS) of the laminates were determined using the short beam shear test in accordance with ASTM D2344 [313]. The dimensions of the samples are given in Fig. 5.5c. The short beam shear samples had a support span-to-specimen thickness ratio of 4:1 and were loaded in three-point bending load at centre point displacement rate of 0.5 mm/min until failure using 50 kN Instron testing machine, which involved the growth of a mid-plane shear crack. Five flexural and short beam shear samples were tested for each specimen type.
5.2.4 Low velocity impact and non-destructive evaluation of impact damage

Low velocity impact tests were performed by dropping a 2.9 kg hemispherical (8 mm dia) hardened steel impactor on the composite laminates, as shown in Fig. 5.6a. The test samples have a length of 150 mm, width of 100 mm and thickness of ~5 mm. Using a drop-weight tower (see Fig. 5.6b), the impactor was dropped by free-fall on to the centre of the clamped composite laminate. The incident impact energies of 10 J, 20 J, 30 J, 40 J and 50 J were controlled by changing the drop height. The impactor was equipped with a dynamic force transducer to measure the impulse load-time response upon impact with the composite laminate. The impulse load-time response was recorded at a sampling rate of 19.2 kHz. For each impact energy, three samples per material type were tested.

Fig. 5.6. (a) Schematic of composite laminate subject to low velocity drop weight impact. (b) Photo of the drop-weight tower.

Following the impact tests, the laminates were non-destructively inspected using X-ray micro-computed tomography (μ-CT, DE Phoenix v/tome/xS) characterise the damage size, shape and type (see Fig. 5.7). The μ-CT imaging was performed using an X-ray source voltage operated at 280 μA and 60 kV. During the scans, the laminates were rotated through the X-ray beam in increments of 0.2° at an average exposure time of 333 ms and a voxel size of 19 μm to provide sufficient resolution to quantify the damage. Post-processing of the μ-CT images and damage assessment was performed using a volume analysis tool (VG Studio Max software [314, 315]). The projected damage areas from the μ-CT images was measured using image correlation software (ImageJ, NIH, USA).
5.2.5 Compression after impact property characterization.

After non-destructive evaluation, the non-impacted (i.e. 0 J) and post-impacted (i.e. 10 J, 20 J, 30 J, 40 J and 50 J) compression strength of the laminates were measured in accordance with ASTM D7137 [316]. As shown in Fig. 5.8, a purpose-built anti-buckling rig was used to hold the laminates vertically. Compression tests were performed on the samples at a displacement control rate of 1.0 mm/min using a 250kN MTS testing machine (see Fig. 5.8).
5.3 RESULTS AND DISCUSSION

5.3.1 Interlaminar fracture toughness properties of multi-scale reinforced laminates

The modes I and II load-displacement and crack growth resistance (R-) curves, and the interlaminar fracture toughness values are presented in Figs. 5.9 and 5.10 for the designated laminates. The mode I R-curves for the unmodified laminate as well as the composites containing the CNFs or SCFs increased over the first 5-10 mm of crack length in reaching the steady-state fracture toughness value (see Fig. 5.9b). This R-curve behaviour was attributed to the cross-fibre bridging between delaminated plies behind the advancing crack tip [49]. The mode II fracture toughness for the laminates also increased with crack extension up to 15-25 mm (see Fig. 5.10b). The mode II R-curve effect was due to the physical interlocking and resultant shear-induced frictional resistance against sliding between the opposing crack faces in the ENF samples via a crack-tip shielding effect [177, 317-319]. The crack tip-shielding process zone length increases and then stabilises with crack extension resulting in the mode II R-curve effect observed.

![Graph](image)

**Fig. 5.9.** Mode I (a) load-displacement curves, (b) crack-growth resistance curves and (c) interlaminar fracture toughness values for the composite laminates containing unmodified, CNF-, SCF-, and CNF + SCF modified epoxy matrix.
Both 1.0 wt% CNFs and 1.0 wt% SCFs, when added separately, were effective at improving the steady-state mode I and mode II interlaminar fracture toughness properties when compared to the unmodified laminate. However, CNFs promoted a much higher steady-state interlaminar toughening effect when compared SCFs, which are consistent to observations in the mode I fracture toughness values of the bulk epoxy composites reported in Chapter 4. The mode I initiation fracture toughness at the initial crack length condition was also enhanced with the addition of the nano- and micron-scale fillers (see Fig. 5.9c). The mode II initiation fracture remains unchanged with the addition of CNFs considering the standard deviation in the fracture energy from every specimen type. However, a minor improvement in the mode initiation toughness value (~7-9%) exhibited by the SCF reinforced and multi-scale reinforced laminate, as presented in Fig. 5.10c.

As expected, hybridising both 1.0 wt% CNFs and 1.0 wt% SCFs within the laminate (i.e. multi-scale) lead to substantial improvements in the magnitude of the steady-state delamination toughness. With consideration to the individual toughening contributions from the unmodified laminate ($G_{\text{unmodified}}$), CNF-reinforced ($G_{\text{CNF}}$) and SCF-reinforced ($G_{\text{SCF}}$) laminate, combining the
CNFs and SCF give a less-than-additive improvement towards the mode I steady-state interlaminar fracture toughness values. In contrast, greater-than-additive improvements were observed for the steady-state mode II fracture energy, which can be readily seen from the dashed lines in Figs. 5.9b and 5.10b. The percentage of synergy values can be calculated using [49]:

\[
\text{Synergy (\%)} = \left( \frac{G_{\text{CNF+SCF}} - G_{\text{unmodified}}}{(G_{\text{CNF}} - G_{\text{unmodified}}) + (G_{\text{SCF}} - G_{\text{unmodified}})} - 1 \right) \times 100\%
\] (3)

where \(G_{\text{CNF+SCF}}\) is the interlaminar fracture toughness values of the multi-scale toughened laminates. The percentage synergy values calculated for the mode I and mode II fracture energies are -24% and 72%, respectively. The large synergistic enhancement observed towards the mode II interlaminar fracture toughness is much greater than the values reported in [57, 96, 230].

5.3.1.1 Interlaminar toughening mechanisms

Both the nano- and micron-scale fillers increased the delamination resistance through a myriad of toughening mechanisms that occurred ahead and behind the main crack tip. These toughening mechanisms are schematically illustrated in Fig. 5.11 for both modes I and II loading, processes which were based on examination along the fracture surface of the DCB and ENF specimens.

![Fig. 5.11. Schematic of the (a) mode I and (b) mode II toughening mechanisms along the crack front of the epoxy interlayer between the delaminated plies.](image)
Under the mode I loading condition, the crack opening between the delaminated faces were governed by (i) the bridging of the continuous fibres and (ii) tearing of the epoxy matrix (see Fig. 5.12a). The toughening processes invoked by the fillers occur within the epoxy matrix along the interfacial layer. As shown in Fig. 5.11a and Fig. 5.12, the intrinsic toughening mechanisms promoted by the CNFs and SCFs include interfacial debonding from the epoxy matrix, microcracking and plastic void growth of the epoxy within the process zone ahead of the main crack-tip; together with extrinsic processes that include the bridging and pull-out of the fillers behind the crack front. Detailed descriptions of these toughening mechanics under the mode I condition are explained in Chapters 3 and 4 [70, 98, 272, 279, 320, 321]. The dominant toughening mechanisms were (a) plastic void growth of the epoxy surrounding the debonded fillers and (b) traction energy generated by the pull-out of the fillers. As shown in Figs. 5.12b and 5.12c, the void size was visibly significant for the DCB specimens containing CNFs compared to SCFs. Similar findings were observed in Chapter 4. Due to the higher number of CNFs per unit volume than the SCFs for a given weight fraction within the epoxy matrix, a higher density of voids was developed in the process zone of the CNF-reinforced composite laminates (see Figs. 5.12b and 5.12c). Scan electron microscopy (SEM) along the fracture surface revealed that the epoxy matrix interlayer between the plies was ~30-50 μm, and it is expected that the SCFs due to their size (i.e. 7 μm diameter and 710 μm length) within the epoxy interlayer will be aligned near the direction of the continuous fibres from the warp and weft tows [32, 60]. Therefore, a low proportion of SCFs will participate in the pull-out process [32, 60]. Due to the small geometric size of the CNFs, many nanofillers will bridge the crack. This corresponds to the high mode I interlaminar toughening effect observed when using CNFs compared to SCFs.

For the multi-scale reinforced composite, all of the toughening mechanisms described above were observed. However, further fractographic examination revealed that the plastic void growth process much less prevalent when the CNFs and SCFs were closely spaced (see Fig. 5.12d). As reported in Chapter 4, the increased agglomeration and packing density between the CNFs and SCFs fillers restricted the plastic flow of the epoxy matrix. Consequently, this reduced the stress triaxiality needed for void growth to occur, which accounts for the less-than-expected additive mode I toughness enhancement measured for the multi-scale reinforced laminate [70, 78, 83, 320].
Fig. 5.12. Scanning electron microscope (SEM) images of the fracture surface for the DCB specimens containing (a) unmodified epoxy matrix, (b) 1.0 wt% CNF, (c) 1.0 wt% SCF and (d) 1.0 wt% CNF + 1.0 wt% SCF (i.e. multi-scale reinforced).

Under mode II loading, the initiation of the microcracks initiated due the shear stresses acting within the process zone ahead of the crack tip, resulting in the formation of the echelon cracks or wedging sites, as shown in Fig. 5.11b and Fig. 5.13a [317, 319, 322]. These echelon cracks grew in size at ~45° to the crack growth direction and coalesced which then allowed the delamination cracks to propagate. The extrinsic toughening mechanisms include bridging and pull-out fillers along the crack wake, as shown in Figs. 5.13b and 5.13c. The CNFs and SCFs within the process zone debonded from the epoxy matrix under the high stresses immediately ahead of
the crack tip. The CNFs, due to their small size and fibrous morphology, bridged the local echelon cracks between the continuous carbon fibres /tows (see Fig. 5.11b and Fig. 5.13b) which restricted the opening and growth of the echelon cracks thereby increasing the mode II fracture energy. The SCFs did not bridge the local echelon cracks, which correlates to the low mode II fracture toughness improvement. Instead, the debonded SCFs allowed for the additional formation of larger local echelon cracks due to their size.

Fig. 5.13. SEM images of the fracture surface for the ENF specimens containing (a) unmodified epoxy matrix, (b) 1.0 wt% CNF, (c) 1.0 wt% SCF and (d) 1.0 wt% CNF + 1.0 wt% SCF.
For the ENF specimens toughened by both CNFs and SCFs, assessment of the fracture surface revealed additional toughening processes not achieved when the fillers are used separately. As shown in Fig. 5.13d, these additional toughening mechanisms include the bridging of the CNFs along the echelon cracks generated by the SCFs which exerted an additional crack closure force. It is important to note that the formation of the echelon cracks under mode II loading is not a toughening mechanism [317, 319, 322]. Rather, the toughening mechanisms arise from the processes that restrict the opening and growth of the local echelon cracks. Therefore, invoking additional echelon crack formation with SCFs increases the density of CNFs participating in the pull-out process during mode II loading. This accounts in part for the synergistic improvement (~70%) observed for the mode II fracture toughness values of the multi-scale reinforced laminate.

5.3.2 Tensile, flexural and interlaminar shear properties

Table 5.1 presents the tensile, flexural and interlaminar shear properties of the composite laminates. The addition of CNFs, SCFs or a combination of both fillers had no significant effect on the tensile or flexural properties when considering the standard deviation. Since a low filler content (i.e. ~ 1 wt%) was used, these properties were dominated by reinforcing continuous carbon fibres. Other reports have shown that small additions of fillers within carbon fibre reinforced epoxy composites promoted no significant increase to the tensile stiffness and strength [49, 323, 324].

As shown in Table 5.1, the addition of CNFs slightly reduces the ILSS value of the composite. Since CNFs does not contain any functional groups that covalently bond with the epoxy matrix, the nanofillers act as sites (i.e. hard contact) for cracks to initiate within the epoxy matrix under the shear loading condition. Minor improvements (~6-7%) were measured to the ILSS value for the SCF-reinforced and multi-scale reinforced laminates when compared to the unmodified composite. These enhancement in the magnitude of the ILSS are proportion to marginal improvements to the mode II initiation fracture toughness presented in Fig. 5.10c.
Table 5.1. Properties of the composite laminates containing unmodified epoxy matrix, 1.0 wt% CNF, 1.0 wt% SCF and 1.0 wt% CNF + 1.0 wt% SCF epoxy matrix.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Unmodified</th>
<th>CNF</th>
<th>SCF</th>
<th>CNF + SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>45.2 (±1.4)</td>
<td>45.4 (±1.2)</td>
<td>46.1 (±1.8)</td>
<td>46.0 (±2.1)</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>449 (±3.1)</td>
<td>452 (±9.1)</td>
<td>454 (±19.2)</td>
<td>451 (±9.8)</td>
</tr>
<tr>
<td>Flexural Modulus (GPa)</td>
<td>34.4 (±2.3)</td>
<td>35.0 (±1.2)</td>
<td>34.9 (±2.5)</td>
<td>35.1 (±1.9)</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>471 (±13.4)</td>
<td>481 (±9.1)</td>
<td>474 (±11.1)</td>
<td>478 (±13.7)</td>
</tr>
<tr>
<td>Interlaminar Shear Strength (MPa)</td>
<td>41.3 (±1.5)</td>
<td>39.0 (±1.9)</td>
<td>44.9 (±1.8)</td>
<td>43.5 (±2.1)</td>
</tr>
</tbody>
</table>

5.3.3 Impact and post-impact properties of multi-scale reinforced laminates

5.3.3.1 Load-time response during impact

Fig 5.14 presents the load-time histories for the (a) unmodified, (b) CNF-reinforced, (c) SCF-reinforced, and (d) multi-scale reinforced (i.e. CNF + SCF) laminates at various impact energies. The response shows a maximum initial peak load followed oscillatory load-time response with a with a secondary peak load. The oscillatory and progressive reduction in the load with time past the peak load indicates the presence of progress damage formation of the reinforcing fibres (i.e. rupture) and delamination [325, 326]. Further details of the damage modes are present in Section 5.3.3.2. As expected, the contact duration between the impactor and specimens has increased with the incident impact energy [327]. However, the load-time behaviour of the four composite laminates presented in Fig. 5.14 remained unchanged up to the secondary peak load. The peak impact load recorded during impact for the laminates are presented in Fig. 5.15a. No significant changes were observed with the peak loads between the unmodified and CNF-reinforced specimens. However, the addition of SCFs resulted in a minor increase in the peak load, when compared to the unmodified laminate. The increase in the peak impact load plateaued with the increase in impact energy.
Fig. 5.14. Impulse load histories at different impact energy levels for the composite laminates containing (a) unmodified epoxy matrix, (b) 1.0 wt% CNF, (c) 1.0 wt% SCF and (d) 1.0 wt% CNF + 1.0 wt% SCF (i.e. multi-scale reinforced).

Fig. 5.15. (a) Plot of the peak impulse load versus impact energy and (b) analytically calculated critical load for the laminates containing unmodified epoxy matrix, 1.0 wt% CNF, 1.0 wt% SCF and 1.0 wt% CNF + 1.0 wt% SCF.
Davies and Zhang [328] proposed a model to predict the critical impact load \( P_{crit} \) to initiate delamination damage within a laminate during impact based on the initiation mode II interlaminar fracture toughness \( (G_{IIc-i}) \) [161, 328]:

\[
P_{crit} = \sqrt{\frac{8\pi^2 E t^3 G_{IIc-i}}{9(1-v^2)}}
\]  

(4)

where \( E \) is the flexural modulus and \( t \) is the thickness of the laminate. The Poisson ratio is denoted by \( \nu \), where a value of 0.32 was used [329]. The critical load for initiation of delamination was analytically calculated by using the initiation mode I fracture energy and flexural stiffness values presented in Fig. 5.10b and Table 5.1, respectively. As shown in Fig. 5.15b, the calculated threshold loads to initiate delamination during impact is lower than the peak loads measured at the lowest impact energy (i.e. 10J) for each laminate. This indicates that delaminations have occurred within each laminate for all impact energies investigated.

5.3.3.2 Impact-induced failure modes and damage area

Following impact tests, the composite specimens were inspected using X-ray computed tomography (CT). Along the impacted side of the laminates (see Fig. 5.16a), the visible front-face damage involved localised crushing/indentation and the formation of splitting cracks orientated in the fibre direction. Longitudinal and lateral splitting cracks were visible along the back-face, which was indicative of the failure of the reinforcing fibres, as shown in Fig. 16b. These damage modes were observed for all laminate types.
X-ray CT inspection along the cross-section of the impacted laminates revealed the damage modes and distribution. With an increase in the impact energy, the apparent density of the delaminations between the plies becomes more prevalent along with fibre damage for the unmodified laminate, as shown in Fig. 5.17. The large bending deflections result in large interlaminar shear stresses that cause delaminations and fibre rupture. It is important to note these delaminations propagate under a mixed-mode interlaminar stress state [161, 330-333]. The delamination crack length was much longer near the back-face when compared to the front-face region of the laminate, which is due to the higher tensile strains generated near the back-face [333]. The delamination cracks observed terminate at the ends of the longitudinal and lateral splitting cracks, which were used to measure the projected back-face damage area. Considering the specimen type, the degree of delamination was less visible in order of the SCF-reinforced, CNF-reinforced and multi-scale reinforced composite at an impact energy of 50 J, as shown for example in Fig. 5.18. However, fibre damage was observed for all laminates types.
Fig. 5.17. Cross-sectional X-ray CT scans of unmodified laminate at different impact energies. The scans were captured along the length and thickness plane at the centre of the laminate.

Fig. 5.18. Cross-sectional X-ray CT scans of the different types of composite laminate subject to impact energy of 50 J. The scans were captured along the length and thickness plane at the centre of the laminate.
The delamination cracks along the back-face terminate at the ends of the longitudinal and lateral splitting cracks. The projected delamination along the length-width plane was rhomboid shaped (i.e. ‘diamond shaped’), as shown in Fig. 5.19. This projected delamination mode was present for all four laminate types at different impact energies. The back-face damage area ($A_{dmg}$) was calculated by using:

$$A_{dmg} = \frac{1}{2} L_{c-lat} \times L_{c-long}$$

(5)

where $L_{c-lat}$ and $L_{c-long}$ are the lateral and longitudinal lengths of the splitting cracks, respectively, along the back-face.

Fig. 5.19. Projected delamination mode along the back-face of the unmodified composite laminate at 40 J.
**Fig. 5.20** shows the effect of the incident impact energy on the projected back-face damage area for the unmodified, CNF-reinforced, SCF-reinforced and multi-scale reinforced laminates. Overall, the addition of the fillers significantly reduced the damage size in the order of SCFs, CNFs and the hybrid reinforcements being the most effective. However, the addition of SCFs or CNFs provides no significant damage resistance at a low impact energy of 10 J. With the increase in the impact energy, it was found that the percentage reduction in the damage area increases up to 30 J. This is due to the substantial interlaminar toughening effect achieved at large delamination crack lengths (i.e. R-curve effect) [41], as presented in Figs. 5.9b and 5.10b. The highest improvements in the damage reduction (24%) was achieved with the multi-scale reinforced composite at 30J (see Fig. 5.20).

![Damage Area vs Impact Energy](image)

**Fig. 5.20.** Effect of impact energy and laminate type on the impact damage area. (Note: the percentage value indicates the reduction in the damage area in comparison to the unmodified laminate, at the corresponding impact energy).

Plots of the modes I and mode II steady-state strain energy release rates for the different laminates against the impact damage area of the corresponding composite laminate are shown in **Fig. 5.21.** There is a good correlation between the reduction in damage area and the increase in

---
fracture toughness, however, the trend is less clear at the low impacted energy of 10 J when the damage is relatively small. Therefore, these results indicate that increasing the fracture toughness (see Fig. 5.18) via the addition of CNFs or/and SCFs results in the increased impact damage resistance. Improvements to damage resistance can be attributed to the intrinsic and extrinsic toughening mechanisms discussed in Section 5.3.1.1.

![Diagram showing steady-state interlaminar fracture toughness](image)

**Fig. 5.21.** Plots of the mode I and mode II steady-state interlaminar fracture toughness against the impact-induced back-face damage area of the four types of laminates tested at various impact energies.
5.3.3.3 Compression-after impact strength properties

The non-impacted and post-impacted laminates were subjected to a compressive load where the specimens failed at the peak load. For the non-impacted materials, the failure mode was governed by bucking of the composite above the anti-buckling plates (see Fig. 5.8) followed by local instability and kink failure of the individual delaminates plies/sub-laminates. For the impacted laminates, the same failure bucking and kinking mode occurred where the composite failed within the impacted region [161]. The non- and post-impact residual compressive strengths of the composite laminates at various impact energies are shown in Fig. 22.

![Graph showing compression after impact strength vs. impact energy for different laminate types.](image)

**Fig. 5.22.** Effect of impact energy and laminate type on the compression-after-impact strength. (Note: the percentage value indicates the relative residual compression strength improvements in comparison to the unmodified laminate, at the corresponding impact energy).

As shown in Fig. 5.22, the non-impact compression strengths of the four types of laminates were similar when accounting for the standard deviation. This is due to the low content of fillers being used and minimal variation in the interlaminar shear strength properties [219], as presented
in Table 5.1. The addition of the nano- and micron-scale fillers resulted in higher compression-
after-impact (CAI) strengths compared to the unmodified laminate. The CAI strengths were lowest
when adding SCFs and highest with the hybrid reinforcements. Also, the percentage improvement
in the CAI strength increases with impact energies up to 30 J (see Fig. 5.22), which is due to a
maximum relative reduction in the damage area. The multi-scale reinforced composite exhibited
the highest relative enhancement in the CAI strength (29%) at 30 J (see Fig. 5.22). Improvements
in the residual compression properties were due to a reduction in the damage area as evident in
Fig. 5.23. The addition of the nano- or micron-scale fillers, when used separately or together,
enhanced the damage tolerance of the laminate, as indicated by the dashed lines (Fig. 5.23) [247].

![Figure 5.22: Plots of the impact-induced back-face damage area against the CAI strength of the four types of composite laminates.](image)

**5.4 CONCLUSION**

The results presented in this chapter contributes to the fundamental understanding of the
delamination toughening using carbon-based fillers on the interlaminar fracture toughness and the
impact damage tolerance of carbon fibre reinforced epoxy composites. The impact damage
resistance and post-impact compression strength properties of carbon-epoxy composites can be enhanced significantly with the addition and combination of nano- and micron-scale fillers. The mode I and mode II interlaminar fracture toughness can be improved by blending SCFs and CNFs, when used separately, into the epoxy matrix. The CNFs were much more effective at improving the delamination resistance when compared to using SCFs. Improvements observed towards the interlaminar fracture toughness properties were due to the intrinsic and extrinsic toughening mechanism invoked by the fillers surrounding the crack-tip; which include interfacial debonding, plastic void growth of the epoxy within the process, and pull-out of the fillers along the crack wake. However, substantial synergistic (i.e. greater-than-additive) improvements were observed towards the mode II interlaminar fracture toughness properties of the multi-scale reinforced composite containing both CNFs and SCFs.

The tensile, flexural and compression strength properties of the modified composites remained unchanged due to the low filler contents used (~1-2 wt%). Subjecting the laminates to a low-velocity impact loads resulted in delamination growth and fibre damage. The amount and size of the impact damage increased with the incident impact energy. However, the addition of CNFs and/or SCFs reduced the impact damage area, thereby improving the residual compression strength. Reduction to the damage area from the toughened composite was due to the increased modes I and II interlaminar fracture toughness properties, with the laminates containing both CNFs and SCFs being the most effective at improving the impact damage tolerance.
Chapter 6: Synergistic mode I delamination toughening of carbon fibre composites using carbon nanofibres and z-pins

Abstract

This chapter presents an investigation of the synergistic enhancements into the mode I interlaminar fracture toughness of fibre-polymer composite laminates using multi-scale carbon reinforcements. By combining carbon nanofibres (CNFs) dispersed in the matrix and z-pins in the laminate thickness at various contents, an extra toughening mechanism is created which synergistically improves the mode I delamination growth. Addition of nanofibres in the matrix increases the interfacial strength and frictional energy dissipation during z-pin pull-out, thus generating a greater-than-additive toughening effect that would not have existed should either the nanofibres or the z-pins been used separately. The results from this chapter revealed that the magnitude of the synergistic toughening effect is dependent on the volume fraction and combinations of CNFs and z-pins used; where synergy values ranged between 24 and 69% over the expected additive toughness value. A numerical model is developed to successfully predict the crack growth resistance and the synergistic toughening effect with filler content of the multi-scale composites.

The research work presented in this chapter, including a subset of results, have been published in the following:


6.1 INTRODUCTION

As reported in the previous chapter, carbon fibre reinforced epoxy composites are susceptible to delamination cracking when subjected to out-of-plane loads due to the poor interlaminar fracture toughness properties. The mode I interlaminar fracture toughness of composites can be increased with the addition of carbon nanofillers to the epoxy matrix. Carbon nanofillers include carbon nanotubes (CNTs) [334-336], graphene nanoplatelets (GNPs) [67, 220] or carbon nanofibres (CNFs) [168, 244, 253]. These nanofillers increase the initiation and steady-state fracture toughness by inducing multiple toughening mechanisms immediately ahead (e.g. void formation and coalescence, micro-cracking) and behind (e.g. micro-bridging) the main crack tip [67, 83, 152, 337]. However, challenges are present in dispersing carbon nanofillers within polymers at higher contents [220]. The mode I fracture toughness of composites can also be increased using macro-scale reinforcements aligned in the through-thickness direction, such as stitched fibres [178], 3D woven z-binder tows [5, 54, 188], braided tows [191, 338, 339], tufted yarns [184] or z-pins [36, 194, 198, 199, 340, 341]. Typically less than 10 mm in length, these macro-scale reinforcements increase the fracture toughness via different mechanisms than nanofillers; which involves the generation of a large-scale bridging traction zone behind the crack front [35, 36, 49].

Until very recently, nano-scale and macro-scale reinforcements have been used separately to increase the interlaminar fracture toughness of composites. However, natural composite structures, such as bone [234] and nacre [47, 229, 342] are multi-scale or hierarchically reinforced. Natural composites consist of highly-ordered constituents often spanning the nano- to macro-length scales that exhibit unique toughening mechanisms not achieved when the constituents are used separately [222, 223, 225]. This creates a synergistic reinforcing effect in natural composites whereby the multi-scale constituents induce a higher resistance to fracture than the sum contribution of their individual constituents [47, 128, 231]. The magnitude of the toughening effect
in natural composites is dependent on the relative concentrations and combinations of the constituent materials [227, 233, 234].

In adapting the multi-scale design motif of natural composites, a few studies [67, 69, 96, 320] have reported that adding carbon fillers within the epoxy, at multiple length scales, can promote an additive or synergistic enhancement in fracture toughness of polymer composites. Extending the multi-scale design motif to fibre reinforced composites, Ladani et al. [49] demonstrated that combining CNFs with carbon fibre/bismaleimide (BMI) z-pins yielded a synergistic, rather than additive, effect on increasing the mode I fracture toughness and fatigue resistance of carbon fibre reinforced epoxy composites. Ladani and colleagues only characterised a multi-scale toughened composite containing a single concentration (0.82 vol%) of CNFs and single content (0.5 vol%) of z-pins, and measured a low synergistic toughening improvement of ~10% over the expected additive toughness enhancement (~360%). The addition of CNFs simultaneously enhances the interlaminar fracture toughness and toughening efficacy of z-pins during the crack bridging process. Previous studies have reported that the interlaminar fracture toughness enhancement is dependent on the relative content of fillers when used separately [36, 220]. However, there were no reports concerned with effects of adding nanofillers and z-pins at various volume fractions and combinations on the mode I interlaminar fracture toughness. The effect of the relative amounts of nano- and through-thickness macro-scale reinforcements on the synergistic toughening effect in composite materials is not well understood. Also, predicting the crack growth resistance behaviour of multi-scale reinforced composite structures, containing both nanofillers and 3D reinforcements, have not been explored using numerical modelling techniques.

This chapter presents an experimental and numerical investigation on the effect of adding both CNFs and carbon fibre/BMI z-pins on the mode I interlaminar fracture toughness and the crack growth resistance behaviour of carbon fibre reinforced epoxy composites. Firstly, the interlaminar fracture toughness properties of the composite lamaintes containing CNFs and z-pins, used separately and together, are measured. The dependency of the filler volume fraction and combination on the fracture toughness properties are investigated. Secondly, the magnitude of the synergistic toughening effect is determined from the measured fracture properties of composites containing different combinations of CNFs and z-pins. Fracture toughening mechanisms imparted by the CNFs and/or z-pins are identified. Lastly, a finite element (FE) model is proposed using the
measured crack bridging traction properties of the z-pins at various CNF contents as inputs. The model is then used to quantify the individual additive and synergistic toughening enhancements with crack extension under mode I loading. The model predictions, which were in good agreement with experimental results, revealed that the synergistic effect was due to interactions between z-pins and the CNFs in the matrix and was dependent on the filler content.

6.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

6.2.1 Composite materials and manufacturing

Four types of carbon-epoxy composites were investigated: (i) unmodified (control), (ii) CNF reinforced only, (iii) z-pin reinforced only and (iv) multi-scale reinforced combining CNFs and z-pins. The composition of these materials is given in Table 6.1. All four types were manufactured with 20 plies of 200 gsm plain woven carbon fabric (AC220127 supplied by Colan Ltd.) and a two-part bisphenol-A based epoxy resin (Resin-105 and Hardener-206 supplied by Westsystem®). The weft and warp tows of the fabric plies were oriented along the length and width of the composites, respectively. The composites were made using liquid compression moulding process which initially involved wet-hand layup and was then followed by high pressure (350 kPa) consolidation in a hydraulic press for 24 hours at room temperature (~25ºC). The composites were then post-cured for 48 hours at 25ºC for the epoxy to reach its working strength in accordance with the epoxy supplier’s guidelines [257]. The final thickness of the cured composites was approximately 5 mm with a carbon fibre content of ~50 vol%. A detailed description of the manufacturing process for the unpinned laminates can be found in Section 5.2.1 (Chapter 5).

The unmodified composite (i.e. without CNFs and/or z-pins) was made using the process described above and is denoted as the control material for this study. The composite containing only CNFs were manufactured by doping carbon nanofibres (Pyrograf® - III, grade PR-24-XT-HHT supplied by Applied Sciences Inc.) into the liquid epoxy resin. The CNFs had a diameter and length of 70-200 nm and 50-200 µm, respectively. The CNFs were first hand-mixed into the epoxy resin (without hardener) and then further mixed using the three-roll milling process. Further details of the blending/mixing process of the CNF into the liquid epoxy can be found in Section 4.2.1 (Chapter 4) and Section 5.2.1 (Chapter 5). After the three-roll milling, hardener was added to the epoxy resin mixture followed by wet hand layup and liquid compression moulding to manufacture
the carbon fibre composites reinforced with CNFs only at contents of 1.0, 2.0 and 5.0 wt% (i.e. 0.82, 1.64 and 4.10 vol%).

**Table 6.1. Composition and fracture toughness properties of the composite materials. The mode I initiation and steady-state fracture toughness are denoted by $G_{Ic-i}$ and $G_{Ic-ss}$, respectively.**

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>CNF Content (vol%)</th>
<th>Z-pin Content (vol%)</th>
<th>$G_{Ic-i}$ (kJ/m$^2$)</th>
<th>$G_{Ic-i}$ Improvement (%)</th>
<th>$G_{Ic-ss}$ (kJ/m$^2$)</th>
<th>$G_{Ic-ss}$ Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>-</td>
<td>-</td>
<td>0.25 (±0.03)</td>
<td>-</td>
<td>0.73 (±0.04)</td>
<td>-</td>
</tr>
<tr>
<td>CNF-reinforced</td>
<td>0.82</td>
<td>-</td>
<td>0.54 (±0.11)</td>
<td>120 %</td>
<td>1.40 (±0.12)</td>
<td>90 %</td>
</tr>
<tr>
<td></td>
<td>1.64</td>
<td>-</td>
<td>0.84 (±0.15)</td>
<td>240 %</td>
<td>1.69 (±0.12)</td>
<td>130 %</td>
</tr>
<tr>
<td></td>
<td>4.10</td>
<td>-</td>
<td>0.85 (±0.20)</td>
<td>240 %</td>
<td>2.04 (±0.31)</td>
<td>180 %</td>
</tr>
<tr>
<td>Z-pin reinforced</td>
<td>-</td>
<td>0.5</td>
<td>0.22 (±0.12)</td>
<td>-10 %</td>
<td>2.71 (±0.13)</td>
<td>270 %</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>2.0</td>
<td>0.26 (±0.14)</td>
<td>4 %</td>
<td>8.90 (±0.30)</td>
<td>1100 %</td>
</tr>
<tr>
<td>Multi-scale Reinforced (CNF + z-pins)</td>
<td></td>
<td>Effect of z-pin content at a controlled CNF content</td>
<td>0.82</td>
<td>0.5</td>
<td>0.61 (±0.11)</td>
<td>140 %</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>2.0</td>
<td>0.73 (±0.23)</td>
<td>190 %</td>
<td>11.16 (±0.52)</td>
<td>1490 %</td>
</tr>
<tr>
<td></td>
<td>Effect of CNF content at a controlled z-pin content and diameter</td>
<td>0.82</td>
<td>0.5</td>
<td>0.61 (±0.11)</td>
<td>140 %</td>
<td>3.73 (±0.15)</td>
</tr>
<tr>
<td></td>
<td>1.64</td>
<td>0.5</td>
<td>0.91 (±0.21)</td>
<td>260 %</td>
<td>4.22 (±0.22)</td>
<td>470 %</td>
</tr>
<tr>
<td></td>
<td>4.10</td>
<td>0.5</td>
<td>0.91 (±0.26)</td>
<td>260 %</td>
<td>6.31 (±0.89)</td>
<td>760 %</td>
</tr>
</tbody>
</table>

The z-pinned only and multi-scale reinforced composites were manufactured by transversely inserting the z-pins within the control material and CNF-reinforced laminates, respectively, from the liquid compression moulding approach illustrated in Fig. 6.1a. The z-pins used were solid pultruded rods of unidirectional carbon fibre/bismaleimide (supplied by Albany Engineering Composites Pty Ltd.) with a diameter of 0.288 mm and initial length of 11 mm. Z-pins were inserted into the preform at 0.5 vol% and 2.0 vol%. The z-pins were supplied within a sacrificial foam carrier which was placed over the uncured composite material (without or with CNFs). The z-pins were transversely inserted by compressing the foam carrier using a hydraulic press, as shown in Fig. 6.1b, operating at 350 kPa and 25°C. Ultrasonic assisted insertion process for z-pins (UAZ) is typically used for pinning prepreg composites. However, for this and the subsequent chapters, the epoxy resin mixture is less viscous which allows for ease of insertion during the liquid compression moulding process. A balsa wood support was used to accommodate the excess length of the z-pins which completely penetrated the composites, as shown in Fig. 6.1c. The additional function of the balsa wood sacrificial layer was to prevent the z-pins from being
damaged (i.e. buckling) and minimise misalignment during the insertion process. The z-pin misalignment angle was measured to be 5.7°±2.5°. The measurements were taken from the computer tomography (see Section 5.2.4 for details) scans of z-pinned DCB samples, and the X-ray images were post-processed using the digital image correlation software ImageJ. After the composites were cured, the excess z-pins within the sacrificial balsa wood layer and carrier foam were sheared off.

![Schematic of z-pin insertion process along the through-thickness direction of the composite laminate.](image)

**Fig. 6.1.** (a) Schematic of z-pin insertion process along the through-thickness direction of the composite laminate. Photos showing (b) z-pin carrier foam and (c) sacrificial balsa wood layer containing the excess z-pins.

### 6.2.2 Mode I interlaminar fracture toughness testing

The mode I interlaminar fracture toughness properties of the composites were measured using the double cantilever beam (DCB) test in accordance to ASTM D5528-13 [309]. A schematic of the DCB specimen containing z-pins is presented in **Fig. 6.2** and the DCB samples for the other material types was the same design. Each DCB sample consisted of a 5 mm thick inner layer of one of the four types of composite material sandwiched between outer reinforcing tabs. The tabs, which were made of 2.5 mm thick unidirectional carbon-epoxy prepreg, were used to prevent
fracture of the DCB arms when under load during testing. One end of the DCB specimen contained a 50 mm long mid-plane pre-crack formed using 25 μm thick polytetrafluoroethylene (PTFE) film. The DCB test involved applying a monotonically increasing tensile load to the pre-cracked end of the specimen. The load was applied using a 10 kN Instron machine at a crack opening displacement rate of 1 mm/min. The $G_I$ value was calculated using [309]:

$$G_I = \frac{3P\delta}{2b(a+|\Delta l|)}$$  \hspace{1cm} (1)

where $P$ is the applied load, $\delta$ is the crack opening displacement, $a$ is the total delamination crack length, and $b$ is the sample width. A correction factor, $|\Delta l|$, which is determined from the DCB specimen compliance, corrected for vertical displacement and rotation at the crack tip. The crack propagation length was measured using a travelling optical microscope. Five DCB samples were tested for each type of composite material.

![Schematic of DCB specimen containing z-pins.](image_url)

**Fig. 6.2. Schematic of DCB specimen containing z-pins.**

### 6.2.3 Z-pin bridging traction and input material property

Z-pin pull-out tests were conducted to assess the effect of CNF content (0, 0.82, 1.64 and 4.10 vol%) on the mode I crack bridging traction law of the pins embedded within the fibre composite. Pull-out specimens were manufactured using the process described above. The specimens were 25
mm wide, 30 mm long and 5 mm thick, and contained through-thickness z-pins arranged in a 4 x 3 grid pattern (equivalent to 0.5 vol%). A 25 μm thick PTFE film was placed between the two middle plies of the specimen to replicate a delamination crack. The z-pin pull-out test involved loading the specimen in the through-thickness direction using a 10 kN Instron machine at a crack opening rate of 0.5 mm/min until complete pull-out. A crack opening displacement (COD) gauge was used to measure the traction-separation of the specimen. Six samples were tested for each material type.

![Schematic of z-pin pull-out test.](image)

The tensile modulus of the laminates was measured using rectangular-shaped specimens (150 mm gauge length x 25.5 mm wide) loaded at a displacement rate of 2.0 mm/min using a 50 kN Instron machine in accordance with ASTM D3039 [311]. The interlaminar shear strength of the laminates was determined using short beam test in accordance with ASTM D2344 [313]. The short beam shear samples had a support span-to-specimen thickness ratio of 4:1, and were loaded in three-point bending at 0.5 mm/min until failure, which involved the growth of a mid-plane shear crack. Further details of the testing methodology can be found in Section 5.2.2 (Chapter 5). The tensile, interlaminar shear and mode I z-pin traction properties were used as inputs for the numerical model discussed below.
6.3 FINITE ELEMENT MODELLING

A finite element (FE) model of the multi-scale reinforced DCB specimen was used to calculate the mode I fracture toughness and crack growth resistance properties. Abaqus (Standard, version 6.14, Dassault Systèmes) was used to generate a three-dimensional model of the DCB specimen as illustrated in Fig. 6.4. Two orthotropic sections representing the inner multi-scale reinforced composite material and the outer reinforcing tabs were meshed with 3D solid elements (C3D8). A minimum element size of 0.1 mm was implemented into the model, based on the reports from [188, 343, 344], to alleviate mesh dependence in attaining convergence of the numerical results. These two sections were modelled by inputting the linear-elastic material properties given in Table 6.2. The loading tabs were modelled using a multi-point (i.e. master node) coupling constraint whereby all degrees of freedom were coupled with the loading tab surfaces (i.e. slave surfaces). The bottom node was constrained in all three axes/translational directions whereas the upper node (or loading point) was constrained in the x- and y-directions, as shown in Fig 6.4.

![Fig. 6.4. DCB FE modelling scheme for multi-scale reinforced composites.](image)

**Table 6.2. Elastic properties of the composites material used for FE analysis. The elastic modulus, shear modulus and Poisson’s ratio are denoted by E, G and ν, respectively. The subscripts 1, 2 and 3 are the in-plane, transverse and out-of-plane directions in a coordinate system of fibres, respectively.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{11}$</td>
<td>45.0 *</td>
<td>100.0 *</td>
</tr>
<tr>
<td>$E_{22}$</td>
<td>45.0 *</td>
<td>7.50 [163]</td>
</tr>
<tr>
<td>$E_{33}$</td>
<td>7.50 [188]</td>
<td>7.50 [163]</td>
</tr>
<tr>
<td>$G_{12} = G_{13}$</td>
<td>3.90 [188]</td>
<td>3.90 [163]</td>
</tr>
<tr>
<td>$G_{23}$</td>
<td>2.82 [188]</td>
<td>2.30 [163]</td>
</tr>
<tr>
<td>$\nu_{12} = \nu_{13}$</td>
<td>0.32 [188]</td>
<td>0.32 [163]</td>
</tr>
<tr>
<td>$\nu_{23}$</td>
<td>0.33 [188]</td>
<td>0.33 [163]</td>
</tr>
</tbody>
</table>

* In-plane modulus values measured in accordance with ASTM D3039 [311].
The mid-plane of the DCB specimen, representing the pre-crack and pre-defined crack path, contained disconnected nodes, as indicated in Fig. 6.2. Cohesive zone modelling (CZM) [345] was used to calculate delamination growth along the mid-plane of the DCB specimen. The zero-thickness cohesive surface-based interaction was used between both surfaces of the mid-plane representing a predefined crack path. The nodal spacing along the length of the predefined crack path was 0.01 mm, which is smaller than the critical cohesive zone length to ensure adequate convergence of the damage modes, as further details are reported in [188]. The CZM method uses a bi-linear traction-separation law governed by the interlaminar stresses and fracture energy, $G_c$, for the initiation and evolution of cohesive damage. A maximum stress criterion was used to govern the initiation of cohesive damage [345]. The cohesive damage evolution was governed by the fracture energy, which was calculated using the Benzeggagh and Kenane criterion [346]. The significance of these parameters are discussed in Chapter 7, as it is based on mixed-mode fracture energy criteria.

For the loading conditions investigated with the present study, the fracture energy of the cohesive elements are governed by the mode I fracture energy, $G_{II}$. The $G_{II}$ value from initiation will initially increase with the crack propagation length (due to fibre bridging as explained later), and to model this effect a calibrated non-linear damage evolution law (i.e. tabulated tri-linear or exponential) was considered to be implemented into the FE model [201, 347, 348]. An empirical J-integral approach is required to derive the compliant traction law of the DCB specimen to capture the R-curve effect [349]. However, experimental testing revealed that the $G_{II}$ values for the unpinned laminate reached a steady-state value when the crack propagation length exceeded ~5-10 mm. For purposes of computational efficiency and minimising convergence errors, a bi-linear traction separation law was used and governed by the steady-state mode I interlaminar fracture toughness value of the unpinned composites as adapted from [188, 350, 351]. The cohesive properties to model crack growth in the multi-scale reinforced composites were obtained experimentally from the unpinned DCB specimens containing unmodified or CNF modified epoxy matrix. The input data required for the CZM modelling using the Benzeggagh and Kenane fracture criterion is given in Table 6.3.

The crack bridging traction law of the z-pins bridging the delamination crack was modelled using individual one-dimensional (1D) spring elements (SPRINGA) at the location of each z-pin
(see Fig. 6.2), thereby resulting in discrete toughening elements in the FE model for the DCB specimen containing z-pins. The location of each spring was based on the volume fraction of z-pins. The tabular spring law input was defined for the FE model using the experimental mode I traction law measured from the z-pin pull-out tests. Alternative approaches to modelling the z-pin traction law include using a user-defined global cohesive traction law [352], ‘smearing’ the influence of multiple z-pins across the elemental area via a user-defined element [198] or using an embedded finite element technique [351]. The use of spring elements has been previously implemented to successfully evaluate the fracture toughness of z-pinned composites (without CNFs) [201, 347, 353], and therefore was used here.

The reaction force ($P$) was calculated using the FE model by incrementally increasing the crack opening displacement ($\delta$) at the loading points of the DCB specimen. The reaction loads and the corresponding crack opening displacements were computed for increasing delamination length via degradation to the mid-plane cohesive surface bonds. The calculated numerical data ($P$, $\delta$, $a$) was then inputted into Eqn. 1 to compute the $G_I$ values for the FE model of the multi-scale composites.

### Table 6.3. Cohesive properties for the composites containing different CNF contents.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Penalty Stiffness, $K_{33}$ (MPa/mm)</th>
<th>Transverse strength, $\sigma_{33}$ (MPa)</th>
<th>Interlaminar Shear Strength, $\tau_{13} = \tau_{23}$ (MPa)</th>
<th>Mode I fracture toughness, $G_{IC}$ (kJ/m$^2$)</th>
<th>Mode II &amp; III fracture toughness, $G_{IIC} = G_{IIIC}$ (kJ/m$^2$)</th>
<th>Empirical Parameter for BK Criterion, $\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 vol% CNFs</td>
<td>$1 \times 10^7$</td>
<td>50.0 $^+$</td>
<td>42.0 $^*$</td>
<td>0.73</td>
<td>1.25 $^*$</td>
<td>1.2$^b$</td>
</tr>
<tr>
<td>0.82 vol% CNFs</td>
<td>$1 \times 10^7$</td>
<td>50.0 $^+$</td>
<td>40.0 $^*$</td>
<td>1.40</td>
<td>1.25 $^*$</td>
<td>1.2$^b$</td>
</tr>
<tr>
<td>1.64 vol% CNFs</td>
<td>$1 \times 10^7$</td>
<td>50.0 $^+$</td>
<td>36.0 $^*$</td>
<td>1.69</td>
<td>1.25 $^*$</td>
<td>1.2$^b$</td>
</tr>
<tr>
<td>4.10 vol% CNFs</td>
<td>$1 \times 10^7$</td>
<td>50.0 $^+$</td>
<td>29.5 $^*$</td>
<td>2.04</td>
<td>1.25 $^*$</td>
<td>1.2$^b$</td>
</tr>
</tbody>
</table>

$^+$ Transverse strength of the composite is assumed to be equal to the tensile strength of the epoxy matrix [279].

$^*$ Interlaminar shear strength measured using short beam shear test (ASTM D2344 [313]).

$^a$ Experimentally measured mode II fracture toughness values for control laminate attained from [354].

$^b$ The $\eta$ value is an empirical parameter where a value of 1.2 was used based on literature for carbon fibre reinforced epoxy composites [355].

### 6.4 RESULTS AND DISCUSSION

#### 6.4.1 Effect of CNFs or z-pins on the mode I fracture toughness

The effects of increasing CNF content, when used separately, on the crack growth resistance ($R$) curves and interlaminar fracture toughness properties for the composites are shown in Fig. 6.5. As
shown in Fig. 6.5a, the fracture toughness of the control laminate and the composites containing different volume fractions of CNFs increased over the initial 5-10 mm of crack growth and then reached their steady-state value. This R-curve behaviour was due to interlaminar fibre bridging behind the advancing crack tip [49]. The measured values for crack initiation, $G_{Ic-i}$, and steady-state crack growth, $G_{Ic-ss}$, increased with the CNF content, as shown in Fig. 6.5b and Table 6.1, and similar results have been reported elsewhere for other types of CNF-reinforced composites [152, 167].

![Fracture Toughness](image)

**Fig. 6.5.** Effect of CNF content on the (a) crack growth resistance curves and (b) fracture toughness values for crack initiation and steady-state crack growth. Z-pins were not used in these materials.

Fractographic examination of the DCB specimens containing CNF only revealed multiple intrinsic and extrinsic toughening mechanisms, as shown in Fig. 6.6, which were responsible for the improvement to the fracture toughness properties with increasing CNF content. The intrinsic toughening mechanisms induced by the CNFs within the process zone ahead of the main crack tip were interfacial debonding from the matrix, plastic void growth at the CNF-epoxy interfaces, and crack bifurcation and branching. The intrinsic mechanisms invoked by the CNFs were responsible to enhancements in the initiation mode I fracture toughness. The extrinsic toughening mechanisms behind the crack tip were bridging and pull-out of the CNFs. A complete description of the fracture toughening mechanisms of CNF-reinforced epoxy composites is provided in [49, 152, 167] and Section 5.3.1.1 (Chapter 5).
The effects of the z-pin content on the R-curve behaviour are presented in Fig. 6.7. The fracture toughness properties of the composite also increased with the z-pin content, as shown in Fig. 6.7 and Table 6.1. The z-pins did not increase significantly the crack initiation value, $G_{Ic-i}$, although the steady-state fracture toughness, $G_{Ic-ss}$, increased rapidly with z-pin content. Similar results have been reported elsewhere [51-53], and this increase was due to the z-pins creating a large-scale crack bridging zone (extending up to ~20 mm) behind the delamination front, as shown in Fig. 6.8. When the CNFs and z-pins were used separately, the fracture toughness testing revealed that the pins were much more effective than the CNFs at increasing $G_{Ic-ss}$. This was due
to the much longer pull-out length of the z-pins (~2.5 mm) compared to the CNFs (~3-10 μm) which resulted in a larger crack bridging traction zone created by the z-pins (~20 mm) compared to the CNFs (~4-30 μm). The much longer pull-out length and larger crack bridging traction zone allowed the z-pins to generate greater traction energy via their elastic deformation, debonding and pull-out [36, 216, 356], thereby resulting in greater improvements to the fracture toughness.

![Graph](attachment:graph.png)

**Fig. 6.7.** Effect of z-pin content on the (a) crack growth resistance curves and (b) fracture toughness values for crack initiation and steady-state crack growth. CNFs were not used in these materials.

![Diagram](attachment:3d_diagram.png)

**Fig. 6.8.** Three-dimensional X-ray computer tomography image of the mode I z-pin bridging process within the DCB specimen containing 0.5 vol% z-pins.
6.4.2 Effect of hybridising CNFs and z-pins on the mode I fracture toughness

The effect of combining CNFs and z-pins at different concentrations on the steady-state mode I interlaminar fracture toughness properties of the multi-scale reinforced composites is shown in Fig. 6.9 and Table 6.1. Results are shown for the composites with increasing volume content of CNFs at a fixed z-pin content (Fig. 6.9a) or increasing volume content of z-pins at a constant CNF content (Fig. 6.9b). Combining CNFs and z-pins resulted in a greater-than-additive synergistic improvement to the $G_{IC-ss}$ value when compared to the expected additive improvement, as shown in Fig. 6.9. Furthermore, the magnitude of the synergistic toughening effect increased with both the CNF and z-pin contents.

![Figure 6.9](image.png)

**Fig. 6.9.** Effects of increasing volume fractions of (a) CNFs and (b) z-pins on the steady-state fracture toughness, $G_{IC-ss}$, value when used separately (open data points) and in combination (closed data points). The solid lines show the fracture toughness calculated using the FE model. The dashed lines show the calculated fracture toughness due to an additive toughening effect of the CNFs and z-pins when used separately, i.e. the fracture toughness $G_{IC} = \Delta G_{unmodified} + \Delta G_{z-pin} + \Delta G_{CNF}$.

The toughening mechanisms operative in the multi-scale reinforced composites is shown in Fig. 6.10. The CNFs induced toughening within the crack process zone via debonding, plastic void growth and bifurcation as well as small-scale bridging and pull-out behind the crack tip. These toughening mechanisms were identical to that operative in the CNF-only composites (see Fig. 6.10e). The z-pins within the multi-scale reinforced composites formed a large-scale crack bridging traction zone, which again was operative in the composites containing z-pins only, as
shown in Fig. 6.10b. However, the unique toughening mechanism to the multi-scale composites was the interaction of the CNFs with the z-pins which altered the crack bridging traction properties.

Fig. 6.10. (a) Schematic representation of the intrinsic and extrinsic toughening mechanisms in the multi-scale reinforced composite. SEM images of the fracture surface of the multi-scale composite (1.64 vol% CNF and 0.5 vol% z-pins) depicting (a) bridging of the z-pins behind the crack tip, (b-c) z-pin/composite interface, and (d-e) CNF pull-out and plastic void growth along the delamination front of the DCB specimens.

The effect of CNFs on the bridging traction properties and toughening mechanism of the z-pins in the multi-scale reinforced composites was determined using the z-pin pull-out test, and the results are presented in Fig. 6.11. As shown in Fig. 6.11a, the z-pins exhibited a three-stage bridging traction load response with increasing crack opening: (i) elastic deformation up to a peak load, (ii) interfacial debonding causing an abrupt load drop and (iii) pull-out causing a gradual load drop. The three-stage bridging behaviour was not affected by the presence of CNFs. However, the
maximum traction load generated per z-pin was increased by the CNFs. Furthermore, the interfacial shear stress ($\tau_{fr}$) to initiate pull-out of the z-pins increased with the CNF content.

The shear stress was calculated using:

$$\tau_{fr} = \frac{P_{fr}}{\pi dl_{po}}$$  \hspace{1cm} (2)$$

where $P_{fr}$ is the traction load at the onset of z-pin pull-out, $d$ is the z-pin diameter, and $l_{po}$ is the z-pin pull-out length (which is equal to $l/2 = 2.5$ mm). The interfacial shear friction stress generated by pull-out of a z-pin increased with the CNF content up to $\sim 2$ vol%, above which there was no further improvement (see Fig. 6.11b). The interfacial shear friction stress value was taken at an opening displacement of $\sim 0.35$ mm. The total traction energy, defined by the area under the

**Fig. 6.11.** Effect of increasing CNF content on the (a) z-pin bridging traction curve and (b) interfacial shear friction stress [□] and total traction energy [●] for a single z-pin at different volume fractions of CNFs. (c) Schematics and photos comparing the pull-out surface of the z-pin/composite interfaces without and with CNFs. (d) SEM images of z-pin pull-out cavities: (d1) no CNFs, (d2) 0.82 vol% CNF, (d3) 1.64 vol% CNF and (d4) 4.10 vol% CNF.
bridging traction curve, also increased with the CNF content up to ~2 vol% (Fig. 6.11b). The increases to the peak traction load, interfacial shear friction stress and traction energy are attributed to the CNFs increasing the z-pin/epoxy interface strength as illustrated in Fig. 6.11c. It is well known that carbon nanofillers (including CNFs) increase the failure stress of polymers [96, 357], and the results in Fig. 6.11 reveal that the nanofibres were effective at strengthening the interface between the z-pins and surrounding composite material. The increases to the crack bridging traction properties were also due to CNFs inducing a friction effect opposing z-pin pull-out from the multi-scale reinforced composites. This is revealed by the increasing roughness of the holes created during the z-pin pull-out process. CNFs adhered between the z-pin/epoxy interface (see Figs. 6.10c, 6.10d and Fig. 6.11d) which increased the roughness and thereby the frictional sliding resistance during pull-out. The combination of increased interfacial shear strength and z-pin roughness promoted a synergistic toughening effect which was responsible for the greater-than-additive improvement to the fracture toughness of the multi-scale reinforced composites.

6.4.3 Comparison of experimental and numerically calculated fracture toughness values

Using the fracture toughness properties of the control laminate and the z-pin bridging traction law at the corresponding CNF content, the numerical predictions of the load versus crack opening displacement curves, mode I crack growth resistance curves, and the $G_{Ic,ss}$ values are shown in Fig. 6.12, Fig. 6.13 and Fig. 6.9, respectively. The agreement between the calculated and measured load versus crack opening displacement curves and steady-state fracture toughness values is good for all but one of the multi-scale reinforced composites. The FE model over-predicts of the fracture toughness values of the unpinned composites between the onset of crack initiation (i.e. 0 mm) and the crack propagation length of 5 mm. This difference was due to the use of the mode I steady-state fracture toughness value rather than the initiation value within the cohesive damage evolution law, thereby resulting in the flat R-curve calculated for the unpinned composites. As previously mentioned, modelling the fibre bridging effect within the unpinned composites would require a pre-calibrated non-linear cohesive damage evolution law measured using the J-integral method [358]. This method is based on calculating the J-integral along the delamination crack path and local crack opening displacement within the fibre bridging zone to determine a specimen compliant traction law based on the fracture toughness for crack initiation and crack
propagation. Blacklock et al. [351] reported that the J-integral method has minimal influence on the fracture loads of z-pinned laminates since the toughening effect is dominated by the pins. Therefore, to reduce on computation time and setup, the bi-linear traction law was used within this study, based on the mode I steady-state fracture toughness value. Hence, for this reason, the numerical model over-predicts fracture toughness values from crack propagation lengths ranging from 0 to 5 mm. However, the crack growth toughness of z-pinned and multi-scale reinforced composites is calculated with good accuracy.

The composite that was not correctly analysed using the FE model was the multi-scale reinforced composite containing 4.1 vol% CNF + 0.5 vol% z-pins. This was because this composite exhibited interlaminar crack bifurcation resulting in the concurrent growth of delaminations between multiple plies rather than a single mid-plane crack. The crack bifurcation was a result of the nanofiller agglomeration at high contents of CNFs (~4.1 vol%), thereby promoting further crack bifurcation (see Fig. 6.5c) ahead of the main crack tip. This crack growth behaviour cannot be analysed using the FE model, which only considers a single delamination propagating along the mid-plane of the DCB specimen.

![Fig. 6.12. Comparison of experimentally measured and numerically calculated load versus crack opening displacement curves the unpinned, CNF reinforced, z-pinned and multi-scale reinforced composites concerning the effect of (a) volume content of z-pins at a constant CNF content of 0.82 vol% and (b) effect CNF content at a constant z-pins content of 0.5 vol%. The crack opening displacement is the cross-head displacement at the loading points.](image-url)
Fig. 6.13. Measured and calculated crack growth resistance curves for the multi-scale reinforced composites containing different volume fractions of CNFs and z-pins. (a) Effect of increasing CNF content at a constant z-pin content (0.5 vol%). (b) Effect of increasing z-pin content at a constant CNF content (0.82 vol%). For comparison, the curves for the control laminate and composites containing only CNFs or z-pins are shown. The experimentally measured and FE prediction of fracture toughness values are shown by the data points and curves, respectively.

While the FE model implemented is simplistic in formulation, the model accurately captures the load, crack opening displacement at the loading points, and crack resistance behaviour of the z-pinned and multi-scale reinforced composites. Indeed, this demonstrates that the FE model can, in most cases, accurately calculate the synergistic improvement in mode I interlaminar fracture toughness from the composites containing a combination of CNFs and z-pins.

The FE model was then used to calculate the relative contributions of the CNFs and z-pins to the toughening of the multi-scale reinforced composites. Considering the composite material containing 0.82 vol% CNF + 2.0 vol% z-pins as an example, Fig. 6.11a presents a stack plot of the calculated individual contributions to the numerically predicted fracture energy from the unmodified composite ($\Delta G_{\text{unmodified}}$), CNFs ($\Delta G_{\text{CNF}}$), z-pins ($\Delta G_{\text{z-pins}}$), and the synergistic enhancement ($\Delta G_{\text{synergy}}$) on the crack growth resistance. The $\Delta G_{\text{synergy}}$ is calculated using:

$$\Delta G_{\text{synergy}} = \Delta G_{\text{CNF+z-pins}} - (\Delta G_{\text{CNF}} + \Delta G_{\text{z-pins}})$$

(a) 
(b)
where $\Delta G_{\text{CNF+z-pins}}$ is the additional fracture energy contribution from the composite toughened by both CNFs and z-pins over the unmodified composite. The percentage synergy with crack extension for all other multi-scale reinforced materials can be calculated by using [49].

$$\text{Synergy} \, (\%) = \frac{\Delta G_{\text{synergy}}}{\Delta G_{\text{CNF}}+\Delta G_{\text{z-pins}}} \times 100\% \quad (4)$$

**Fig. 6.11.** (a) Stacked R-curve plot showing the FE predicted contributions from the unmodified material ($\Delta G_{\text{unmodified}}$), CNFs ($\Delta G_{\text{CNF}}$), z-pins ($\Delta G_{\text{z-pins}}$) and the synergistic effect ($\Delta G_{\text{synergy}}$) to the fracture toughness of the multi-scale reinforced composite containing 0.82 vol% CNF + 2.0 vol% z-pins. (b) The level of improvement in the calculated synergy value as a function of the delamination crack length of the multi-scale reinforced composites from the FE model.

As shown in **Fig. 6.11b**, FE modelling revealed that the synergistic toughening effect was negligible for short cracks ($\leq 10$ mm) when the toughening was additive for the CNFs and z-pins. However, the synergistic effect became more dominant with increasing crack length due to the onset of debonding and pull-out of z-pins bridging the delamination, with the CNFs increasing the crack bridging traction properties. The percentage synergy increased with crack length and stabilised when the crack length exceeded $\sim 20$ mm, and this was due to the z-pin bridging traction zone reaching a steady-state condition caused by an equal number of pins joining the bridging zone at the advancing crack tip and pins exiting the bridging zone at the crack wake due to complete
pull-out. Table 6.4 presents a comparison of the experimentally measured and numerically predicted steady-state $\Delta G_{\text{synergy}}$ values and the percentage synergy exhibited by the multi-scale reinforced composites. The experimental synergy value was calculated using Eqns. 3 and 4, with consideration to standard deviation in the toughening contribution from each reinforcement (see Table 6.1). The numerical predictions are in good agreement with the experimental values with the exception for the composite containing 4.1 vol% CNF + 0.5 vol% z-pins; which exhibited a 69% synergistic enhancement from experiments. As previously discussed, the underprediction of the synergy and fracture toughness value was due to the composite exhibiting delaminations between multiple plies rather than a single mid-plane crack; a limitation that the numerical model could not capture. However, well extending over the findings from Ladani et al. [49] for a single concentration of nanofiller and z-pins, the synergistic toughening effect from the multi-scale composite increased significantly with the CNF and z-pin contents, respectively.

### Table 6.4. Comparison of the experimentally measured and numerically calculated synergistic enhancements in the steady-state $\Delta G_{\text{synergy}}$ value for the multi-scale reinforced composites.

<table>
<thead>
<tr>
<th>Multi-scale Composite</th>
<th>Experimentally Measured $\Delta G_{\text{synergy}}$ (kJ/m$^2$)</th>
<th>Percentage Synergy (%)</th>
<th>Numerically Calculated $\Delta G_{\text{synergy}}$ (kJ/m$^2$)</th>
<th>Percentage Synergy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.82 vol% CNFs + 0.5 vol% z-pins</td>
<td>0.346 (±0.21)</td>
<td>13.0 (±8.3)</td>
<td>0.273</td>
<td>12.1</td>
</tr>
<tr>
<td>1.64 vol% CNFs + 0.5 vol% z-pins</td>
<td>0.557 (±0.29)</td>
<td>19.2 (±9.9)</td>
<td>0.554</td>
<td>20.1</td>
</tr>
<tr>
<td>4.10 vol% CNFs + 0.5 vol% z-pins</td>
<td>2.290 (±0.95)</td>
<td>69.8 (±28)</td>
<td>0.842</td>
<td>27.5</td>
</tr>
<tr>
<td>0.82 vol% CNFs + 2.0 vol% z-pins</td>
<td>2.150 (±0.60)</td>
<td>24.5 (±6.9)</td>
<td>2.380</td>
<td>28.9</td>
</tr>
</tbody>
</table>

### 6.5 CONCLUSION

The mode I interlaminar fracture toughness properties of composite materials can be magnified by combining two toughening techniques which have always been used separately: carbon nanofillers and z-pins. When used with z-pins, the carbon nanofibres increase the delamination resistance via multiple intrinsic and extrinsic toughening mechanisms including interfacial debonding, plastic void growth, short-length crack bridging, and pull-out. The z-pins increase the delamination resistance via the formation of a large-scale crack bridging zone. The peak traction load, interfacial shear stress and traction energy of the z-pins is increased by the CNFs, thereby inducing a synergistic toughening effect in the multi-scale reinforced composites. The magnitude of the
synergistic toughening effect increases with CNF and z-pin contents, where synergy values ranged between 24-69% over the expected additive toughening contribution. The interlaminar fracture toughness of the multi-scale reinforced composites containing different volume fractions of CNFs and z-pins was accurately predicted using FE modelling, to an extent. The FE model revealed that the synergistic toughening effect was dependent on the delamination length. The increase in the mode I interlaminar fracture toughness from the CNFs and z-pins is additive at short crack lengths. However, when the crack is sufficiently long to cause z-pin pull-out, then the synergistic toughening effect becomes increasingly dominant until the steady-state crack growth condition was reached.

In describing a new class of delamination resistant multi-scale reinforced composites, this work demonstrates the high toughening efficacy achieved by combining CNFs and z-pins at optimum contents. It is feasible that this multi-scale toughening design motif in attaining synergy could be achieved for the mode II fracture toughness properties of fibre composites as these properties are important for composites, particularly joints, undergoing out-of-plane or in-plane shear loading. These aspects were explored in the next chapter.
Chapter 7: Synergistic mode II delamination toughening of carbon fibre composites using carbon nanofibres and z-pins

Abstract

Extending on Chapter 6, this work presents an investigation into the synergistic improvements to the mode II interlaminar fracture toughness of composites using multi-scale carbon reinforcements spanning the nano to millimetre length scales. Varying volume fractions of carbon nanofibres (CNFs) and millimetre-long carbon fibre z-pins were used to increase the mode II delamination resistance of multi-scale reinforced composites. The results reveal that adding CNFs into the epoxy matrix and transversely inserting z-pins creates a synergistic, rather than additive, improvement to the mode II fracture toughness. The magnitude of the synergistic toughening effect depends on the volume contents of both the nanofibres and z-pins, with the measured synergistic improvement to the mode II toughness being up to 26%. A finite element (FE) numerical model has been developed to accurately predict the mode II fracture properties and the synergistic toughening effect exhibited by the multi-scale reinforced epoxy composites.

The research work presented in this chapter has been published in the following:


7.1 INTRODUCTION

As reported in the previous chapters, many approaches have been developed to increase the resistance of composites to delamination cracking, including the addition of high toughness particles (e.g. elastomeric or thermoplastic fillers) [62, 126] or carbon nanoparticles [65, 69, 152, 159] to the polymer matrix, insertion of interleaves or veils between the plies [34, 165, 172-175]; and macro-scale through-the-thickness fibre reinforcement (e.g. stitching, pinning, orthogonal weaving) to promote crack bridging [10, 11, 36, 52, 54, 177, 179, 181, 198, 340, 341, 359, 360]. These approaches, to a large extent, are effective at increasing the delamination toughness of composites under mode I, mode II and mixed-mode I/II interlaminar loading.

However, the efficacy of many of the toughening approaches is often less for mode II than mode I interlaminar loading. For example, Beckermann and Pickering [176] found that electrospun nanofibre veils interleaved within a carbon-epoxy laminate were more effective at increasing the mode I than the mode II delamination resistance (up to 156% and 69%, respectively). Similarly, z-pins have been found to improve the mode I fracture toughness of carbon-epoxy laminates more than the mode II toughness [52, 203, 341]. High resistance to mode II (i.e. shear mode) delamination cracking is important to the impact resistance of composite materials [41, 191, 271, 361]. Delamination damage created by localised hard body impact loading of composite plates is often caused by high interlaminar shear stresses, as reported in Chapter 5. Mode II delamination cracks are also formed in thick-section composites subjected to extreme in-plane bending or shear stress loads.

Ladani et al. [49] recently reported on a novel bioinspired multi-scale toughened composite material that combined nano-scale and macro-scale reinforcements to promote unusually high mode I delamination resistance. Combining low fractions of carbon nanofibres (0.82 vol%) and carbon-based z-pins (0.5 vol%) induced a synergistic toughening effect (~ 10%) that increased the mode I fracture toughness to a level greater than the expected increase from the individual contributions of the nanofibres and z-pins. Extending on the preliminary work of Ladani and colleagues in Chapter 6 (Ravindran et al. [362]), it was found that the synergistic enhancement in the mode I interlaminar fracture toughness of multi-scale reinforced fibre composites were proportionally dependent on the CNF and z-pin volume content, when used in combination. However, it is not clear what effects this multi-scale reinforcement approach has on the mode II
fracture toughness properties of composites toughened by z-pins and carbon nanofillers. In addition, there have been no reports on predicting the mode II crack growth resistance behaviour of multi-scale reinforced composites, containing both carbon-based nanofillers and 3D reinforcements.

Extending on Chapter 6, this work reports on the potential synergistic effect of adding both carbon nanofibres (CNFs) and carbon fibre z-pins in toughening composites against mode II delamination cracking. The volume fractions of CNFs and z-pins are varied to investigate their effect on the magnitude of the synergistic mode II toughening. The effect of the nanofiller content on the shear traction response of the z-pins is also investigated. The toughening mechanisms responsible under the mode II loading condition are identified using fractography and X-ray computed tomography. A finite element (FE) model is proposed to predict the mode II crack growth resistance and the individual toughening contribution of the multi-scale reinforced composites. Using the measured shear traction properties of the z-pins at various CNF content as inputs, the model is then used to identify the individual additive and synergistic toughening contribution with crack extension and combinations of the toughening fillers. The model successfully predicts the mode II crack growth resistance response of the multi-scale reinforced composites at various contents and combinations of CNFs and z-pins.

7.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

7.2.1 Composite manufacturing

Four types of composite material were manufactured: (a) baseline laminate (i.e. without CNFs or z-pins), (b) laminate toughened by CNFs only, (c) laminate toughened by z-pins only, and (d) laminate toughened by both CNFs and z-pins. The volume contents of CNFs and/or z-pins used in the laminates are given in Table 7.1. The laminates were ~5 mm thick with a carbon fibre volume content of ~50 vol% (excluding CNFs or z-pins). The different laminates (see Table 7.1) were manufactured using the same manufacturing process described in Chapter 6, Section 6.2.1. The test samples were section for measuring the mode II end notch flexure (ENF) fracture toughness and shear mode traction response of the z-pins.
Table 7.1. Composition and mode II fracture toughness, $G_{IIc}$, values of the composite materials.

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>Z-pin Content (vol%)</th>
<th>CNF Content (vol%)</th>
<th>$G_{IIc}$ (kJ/m$^2$)</th>
<th>Improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>-</td>
<td>-</td>
<td>2.04 ($\pm$0.14)</td>
<td>-</td>
</tr>
<tr>
<td>CNF-reinforced</td>
<td>-</td>
<td>0.82</td>
<td>2.88 ($\pm$0.24)</td>
<td>41.0 %</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>1.64</td>
<td>3.11 ($\pm$0.19)</td>
<td>53.0 %</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>4.10</td>
<td>3.39 ($\pm$0.14)</td>
<td>66.0 %</td>
</tr>
<tr>
<td>Z-pin reinforced</td>
<td>0.5</td>
<td>-</td>
<td>3.16 ($\pm$0.18)</td>
<td>55.4 %</td>
</tr>
<tr>
<td>Multi-scale reinforced (CNF + z-pin)</td>
<td>0.5</td>
<td>0.82</td>
<td>4.26 ($\pm$0.18)</td>
<td>109 %</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.64</td>
<td>4.81 ($\pm$0.20)</td>
<td>136 %</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.10</td>
<td>5.06 ($\pm$0.22)</td>
<td>148 %</td>
</tr>
</tbody>
</table>

7.2.2 Mode II fracture toughness testing

The mode II interlaminar fracture toughness, $G_{IIc}$, of the four types of laminate given in Table 7.1 was measured using the end notch flexure (ENF) test [310]. The ENF test specimen is shown schematically in Fig. 7.1 and consisted of a composite laminate bonded between reinforcing tabs. The tabs were needed to strengthen the ENF specimen and thereby prevent the sub-laminate arms from breaking and ensure crack propagation along the mid-plane during testing. The use of reinforcing tabs to engender mode II delamination along the mid-plane of 3D reinforced epoxy composites has been reported in [51, 52, 191]. The tabs were made of high stiffness, high strength unidirectional carbon-epoxy prepreg (~2.5 mm thick VTM 264 supplied by Advanced Composites), which was bonded to the test laminate material using an epoxy-based adhesive (Araldite 420 supplied by Huntsman®).
Fig. 7.1. Schematic of end notch flexure (ENF) sample. This illustration shows the laminate material containing z-pins.

The ENF samples were loaded using a 50 kN Instron machine in three-point bending with a thickness-to-support span (t/2L) ratio of 1-to-25. One end of the ENF specimen contained a 50 mm long mid-plane crack made using 25 μm thick polytetrafluoroethylene (PTFE) film. In ENF samples which contained z-pins, the pins were inserted along the coupon except the region containing the pre-crack, as shown in Fig. 7.1. ENF tests were conducted by applying a monotonically increasing bending displacement (1.0 mm/min) until a delamination grew from the pre-crack along the mid-plane of the specimen. By controlling the displacement, the delamination was forced to grow in short increments along the mid-plane until it reached the middle loading point. During testing, the crack propagation length, Δa, was measured using a travelling optical microscope located to the side of the ENF specimen. The mode II interlaminar fracture toughness, $G_{II}$, was calculated using [310]:

$$G_{II} = \frac{9a^2P_c\delta}{2b(2L^3+3a^3)}$$  

(1)

where $P_c$ is the applied bending force, $\delta$ is bending displacement and $a$ is total delamination length. The parameters $b$ and $2L$ are the sample width and the support span length, and these were equal to 22 mm and 250 mm, respectively. Five samples of each type of laminate were tested under identical ENF conditions to determine the average value and standard deviation of the mode II interlaminar fracture toughness.
7.2.3 Material property testing

The shear traction properties of the z–pins was measured using the test shown schematically in Fig. 7.2, which is adapted from the method reported by Cui et al. [341]. The test sample consisted of two laminates (each 2.5 mm thick) separated by thin PTFE film to avoid bonding of the two laminates. The laminates were made using the same process described above, without CNFs (i.e. baseline material) or with CNFs at volume fractions of 0.82, 1.64 or 4.10 % (i.e. CNF-reinforced materials). The test samples were reinforced in the through-thickness direction with the z-pins arranged in a 6 by 6 configuration which is equivalent to a volume content of 0.5%. The shear mode z-pin bridging traction response was measured by loading the lap-shear samples as illustrated in Fig. 7.2 using a 10 kN Instron testing machine at a rate of 0.5 mm/min under uniaxial tension.

![Fig. 7.2. Schematic of z-pin shear test.](image)

The tensile loading exerted a transverse shear stress on the z-pins connecting the two laminates, and thereby mimics the interlaminar shear loading experienced by the pins during ENF
testing. Using a travelling optical microscope equipped with a digital camera, digital image correlation (DIC) was used to measure local shear traction-separation response of the sample during testing. DIC software (ImageJ, NIH, USA) was then used to calculate the local shear displacements of the individual z-pins with increasing mode II loading. Up to six specimens were tested for each of the four laminate types. The measured shear mode z-pin traction, as well as the Young’s modulus and interlaminar shear strength of the laminates measured from Chapter 6, curves were used as inputs for the discrete elements implemented within the FE model.

7.3 NUMERICAL MODELLING OF MODE II DELAMINATION CRACK GROWTH

The ENF test specimens of the laminates listed in Table 7.1 were modelled computationally using finite element (FE) analysis to predict their mode II interlaminar fracture toughness and crack growth resistance properties. A 3D finite element model was developed using Abaqus/Standard (version 6.14, Dassault Systèmes) for simulation of the load, cross-head bending displacement and crack propagation of the ENF specimens. The FE model provides a very useful tool to capture the effects of specimen geometry and loading configuration that are known to affect the mode II fracture toughness [318, 363]. Fig. 7.3 presents the key features of the FE model, which included the ENF specimen and the steel rollers to the three-point bend fixture. The sections representing the laminate material, strengthening tabs, and rollers were all meshed using 3D solid elements (C3D8). The elastic properties of these sections used to solve the model are given in Table 7.2. A minimum mesh size of 0.1 mm was used to achieve convergence in the numerical results. The top loading point was modelled using a multi-point (i.e. master node) coupling constraint whereby all degrees of freedom of the top roller were tied to those of the upper surface (i.e. slave surface). The two lower rollers were constrained in all three axis/translational directions.
Fig. 7.3. ENF FE modelling scheme indicating the corresponding element type.

Table 7.2. Elastic properties of composite materials used for FE analysis. The elastic modulus, shear modulus and Poisson’s ratio are denoted by $E$, $G$ and $\nu$, respectively. The subscripts 1, 2 and 3 are the in-plane, transverse and out-of-plane directions in a coordinate system of fibres, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Values [reference]</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{11}$</td>
<td>45.0 * [188]</td>
<td>GPa</td>
</tr>
<tr>
<td>$E_{22}$</td>
<td>45.0 * [188]</td>
<td>GPa</td>
</tr>
<tr>
<td>$E_{33}$</td>
<td>7.50 [188]</td>
<td>GPa</td>
</tr>
<tr>
<td>$G_{12} = G_{13}$</td>
<td>3.90 [188]</td>
<td>GPa</td>
</tr>
<tr>
<td>$G_{23}$</td>
<td>2.82 [188]</td>
<td>GPa</td>
</tr>
<tr>
<td>$\nu_{12} = \nu_{13}$</td>
<td>0.32 [188]</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_{23}$</td>
<td>0.33 [188]</td>
<td>-</td>
</tr>
</tbody>
</table>

* Data taken from Chapter 6.
FE modelling of the mode II crack process in the ENF samples must consider the fracture energy to initiate the main crack (i.e. mode II initiation fracture toughness) as well as the strain energy induced by geometrical interlocking and frictional sliding between the delamination surfaces behind the crack front [177, 317-319]. The mid-plane of the ENF model along which the delamination crack propagated contained disconnected nodes, as shown in Fig. 7.3. The nodes and surfaces from the upper and lower laminate near the mid-plane were spaced at 0.01 mm. The cohesive zone modelling (CZM) technique [345] and the contact interaction properties were implemented to numerically model the delamination growth. Zero-thickness cohesive surfaces via a surface-based interaction were embedded along both surfaces, and the nodes were located along the mid-plane of the ENF model. The cohesive properties presented in Table 7.3 were inputted within the Abaqus’ built-in contact interaction property (i.e. cohesive behaviour) module. The geometrical interlocking and frictional sliding between the opposing crack faces during delamination growth was analysed in the FE model based on the measured waviness of the mid-plane plies of the ENF test specimens (see Fig. 7.3b). The waviness was measured from cross-sectional images of the delamination cracks in the ENF test samples taken using X-ray computed tomography and scanning electron microscopy. These images were post-processed using 3D software (CATIA V5, Dassault Systèmes) to generate the 3D geometry of the FE model.

Table 7.3. Cohesive material input properties for the FE model of the ENF specimens.

<table>
<thead>
<tr>
<th>Epoxy Configuration</th>
<th>Mode II Penalty Stiffness, $K_{11} = K_{22}$ (MPa/mm)</th>
<th>Mode I Penalty Stiffness, $K_{33}$ (MPa)</th>
<th>Transverse strength, $\sigma_{33}$ (MPa)</th>
<th>Interlaminar Shear Strength, $\tau_{13} = \tau_{23}$ (MPa)</th>
<th>Mode I fracture energy, $G_{I-coh}$ (kJ/m²)</th>
<th>Mode II fracture energy, $G_{II-coh}$ (kJ/m²)</th>
<th>BK Law Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>$5 \times 10^4$</td>
<td>$1 \times 10^7$</td>
<td>50.0 +</td>
<td>42.0</td>
<td>0.25*</td>
<td>1.25</td>
<td>1.80</td>
</tr>
<tr>
<td>0.82 vol% CNFs</td>
<td>$5 \times 10^4$</td>
<td>$1 \times 10^7$</td>
<td>50.0 +</td>
<td>40.0</td>
<td>0.25*</td>
<td>2.05</td>
<td>1.80</td>
</tr>
<tr>
<td>1.64 vol% CNFs</td>
<td>$5 \times 10^4$</td>
<td>$1 \times 10^7$</td>
<td>50.0 +</td>
<td>36.0</td>
<td>0.25*</td>
<td>2.35</td>
<td>1.80</td>
</tr>
<tr>
<td>4.10 vol% CNFs</td>
<td>$5 \times 10^4$</td>
<td>$1 \times 10^7$</td>
<td>50.0 +</td>
<td>29.5</td>
<td>0.25*</td>
<td>2.60</td>
<td>1.80</td>
</tr>
</tbody>
</table>

† The transverse strength of the composite is assumed to be equal to the tensile strength of the epoxy matrix [279].
* Measured in [49].

The CZM method implemented within ABAQUS uses a bi-linear traction-separation law (see Fig. 7.4a), which is defined by the interlaminar stress needed to initiate damage and the fracture toughness, $G_c$, for delamination growth. The maximum nominal stress criterion was used
to predict crack initiation in the ENF specimen [345]. The Benzeggagh and Kenane criterion was used to compute crack growth under mixed-mode loading [346]:

\[ G_c = G_{Ic} + (G_{IIc} - G_{Ic}) \left( \frac{G_{II} + G_{III}}{G_{I} + G_{II} + G_{III}} \right)^\eta \]  

(2)

where \( G_I, G_{II} \) and \( G_{III} \) are the mode I, mode II and mode III strain energy release rates, respectively. The \( \eta \) value is an empirical parameter where a value of 1.8 for carbon fibre composites was used [190, 365]. The \( G_{II} \) values of the laminates were measured experimentally at increasing crack propagation length (i.e. R-curve effect), as described later. The use of a non-linear traction law in the FE model can account for the fracture energy from both crack initiation and frictional sliding between the crack surfaces. The R-curve effect in the ENF specimens can be accounted for by using a non-linear damage evolution law within the FE model, which may be either tri-linear or exponential [348]. Previous studies have shown that an empirical J-integral approach is required to determine the traction law and thereby analyse the R-curve effect [348, 349]. For purposes of computational efficiency and ease of achieving convergence, a bi-linear traction separation law was used for the cohesive surfaces [350].

\[ \Delta G_{II-coh} = G_{II-\text{ini}} \]

\[ \Delta G_{II-\text{coh}} = G_{II-\text{ini}} + \Delta G_{II-\text{CNF}} \]

\[ \Delta G_{II-\text{CNF}} \]

**Fig. 7.4.** Bi-linear shear traction law for the cohesive surfaces of the composite containing (a) unmodified epoxy and (b) CNF-reinforced epoxy containing the superposed toughening contribution from the CNFs (\( \Delta G_{II-\text{CNF}} \)). (c) Crack growth resistance curve (i.e. R-curve) depicting the contribution from \( \Delta G_{II-\text{CNF}} \).
The materials property data required for the CZM and contact modelling are given in Table 7.3 and Table 7.4. Friction coefficient values of 0.6 and 0.8 were used for the surfaces at the pre-crack region and along the pre-defined crack path, respectively [366-368]. CNFs do not change significantly the friction coefficient between two epoxy nanocomposites undergoing sliding abrasion, as reported in [366, 367], and therefore the friction coefficient values were kept constant for the laminates containing nanofibres.

Table 7.4. Transverse contact properties of the interlaminar region of the composite and the loading points.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Friction Coefficient, $\mu$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel roller support–composite material</td>
<td>0.06</td>
<td>*</td>
</tr>
<tr>
<td>Epoxy-epoxy interface within the pre-crack</td>
<td>0.6</td>
<td>[366, 367]</td>
</tr>
<tr>
<td>Abraded epoxy-epoxy interface within the pre-defined crack path</td>
<td>0.8</td>
<td>[366-368]</td>
</tr>
</tbody>
</table>

* Calibrated value to capture the sliding response of the contact points between the steel roller supports and the composite material.

The bi-linear traction law (Fig. 7.4a and Fig. 7.4b) was used for the FE analysis of the composite laminates. This law can account for the contributions of CNFs, as shown in Fig. 7.4b, by including the additional fracture energy induced by the CNFs (designated as $\Delta G_{II-CN F}$ in Fig. 7.4b). The $\Delta G_{II-CN F}$ value was determined from the experimental values for the CNF-reinforced laminate and the baseline material (as indicated in Fig. 7.4c).

The z-pin bridging traction response was incorporate into the FE model by using discrete one-dimensional (1D) spring elements (SPRINGA) at each z-pin location in the ENF test specimens, as shown in Fig. 7.3. Spring elements have been used previously to simulate the mode I [201, 347, 362, 369] and mode II [196] fracture toughness of z-pinned composites. These spring elements are connected between the nodes of both mid-plane surfaces of the ENF sample (see Fig. 7.3). The locations and spatial density of the springs were determined in accordance with the z-pin content. The user-defined tabular (i.e. force-displacement) spring law input was defined for the FE model using the mode II bridging traction response of a single z-pin, at various contents of CNFs, measured experimentally from the z-pin shear tests described earlier.
The mode II interlaminar crack growth process and the $G_{IIc}$ values for the different laminates were computed using the FE model by incrementally increasing the bending displacement at the loading point of the ENF specimen. The reaction force and deflection at the loading point were computed with increasing delamination crack length via degradation or deletion of the mid-plane cohesive surface interactions. The calculated force ($P_c$), displacement ($\delta$) and crack length ($a$) data were then input into Eqn. 1 to calculate the mode II strain energy release rate ($G_{II}$) values of the FE model of the ENF specimens.

7.4 RESULTS AND DISCUSSION

7.4.1 Effect of CNFs or z-pins on the mode II fracture toughness

The crack growth resistance results of increasing the CNF content or z-pin content under interlaminar mode II loading are shown in Figs. 7.5 and 7.6. These figures are for the laminates containing either CNFs only or z-pins only as results for the composites containing both reinforcements are discussed later within this chapter.

![Graph showing crack growth resistance curves and interlaminar fracture toughness values](image)

**Fig. 7.5.** Experimentally measured mode II (a) crack growth resistance curves and (b) interlaminar fracture toughness values for crack initiation and steady-state growth in the laminates reinforced with CNFs only.
**Fig. 7.6.** Experimentally measured mode II (a) R-curves for the composites reinforced with z-pins only, and (b) shows the mode II strain energy release rate values for crack initiation and steady-state crack growth.

**Fig. 7.5a** shows that the fracture toughness of the baseline laminate and the CNF-reinforced composites increased with crack extension up to 15–25 mm and then plateaued to a steady-state mode II interlaminar fracture toughness value ($G_{IIc}$). The R-curve effect was primarily due to the physical interlocking and resultant shear-induced frictional resistance against sliding between the opposing crack faces in the ENF samples, evident from the presence of echelon (i.e. shear or wedging) cracks. This process creates a crack-tip shielding effect and thereby increases the mode II fracture toughness [177, 317-319]. With the increase in the crack propagation length, the crack tip-shield process zone length increases and then stabilises thereby creating the R-curve effect shown in **Fig. 7.5a**. The measured $G_{IIc}$ values increased with CNF content (**Fig. 7.5b** and **Table 7.1**). Fractographic examination of the CNF-reinforced laminates revealed that the mode II delamination grew via the coalescence of shear-induced echelon cracks, as shown in **Fig. 7.7a**. These echelon cracks initiated within the process zone immediately ahead of the main crack, and then coalesced near the crack tip resulting in delamination growth (**Fig. 7.7a**). The echelon cracks also underwent bifurcation and branching. In addition, the opening of the echelon cracks, further behind the main crack tip, enlarged to an extent with crack propagation due to sliding friction between the opposing crack faces of the ENF samples (see **Fig. 7.7b**). CNFs bridged and were then pulled out of the opposing surfaces of the echelon cracks (**Fig. 7.7c**).
Fig. 7.7. (a) Scanning electron micrograph (SEM) images of the cross-section (b) near and (b) behind the main crack tip of the composite containing 1.64 vol% CNF showing shear-induced echelon cracks and crack bifurcation. (c) CNFs bridging and pull-out from the echelon cracks.

The bridging and pull-out process of the CNFs generated traction forces which opposed the progressive opening of the echelon cracks, thereby increasing the mode II fracture toughness of the CNF-reinforced laminates with crack extension. This toughening process has also been observed in composites reinforced with carbon nanofibres [153, 167] or carbon nanotubes [153, 167]. Increasing the volume content of CNFs resulted in a corresponding increase to the bridging forces within the echelon cracks, thereby increasing in the mode II steady-state fracture toughness. Because the CNFs are only effective at generating traction forces once the echelon cracks have developed, the nanofillers had no significant influence on the initiation fracture toughness (as shown in Fig. 7.5b).

The mode II steady-state fracture toughness value of the laminates also increased with the z-pin content (Fig. 7.6 and Table 7.1). The fracture toughness improvement with increase in z-pin content have also been reported in other studies [51, 52]. The micromechanics of the mode II toughening process are described elsewhere [51, 52, 370]. The toughness was increased by the z-
pins generating a large-scale bridging zone, extending up to 40 mm, behind the main crack tip (Fig. 7.8). The z-pins bridging the mode II delamination crack experienced elastic shear deformation followed by interfacial debonding, longitudinal splitting, snubbing, partial pull-out and eventually shear rupture with increasing crack sliding displacement.

![Fig. 7.8.](image)

**Fig. 7.8.** (a) X-ray computed tomography image of the z-pins bridging behind the mode II delamination crack in the laminate with 2.0 vol% z-pins. (b) SEM image of a z-pin undergoing splitting, debonding and snubbing along the crack.

When CNFs and z-pins were used separately, the ENF tests revealed that the pins were much more effective than CNFs at increasing the mode II fracture toughness value, as shown in Table 7.1. This was attributed to the multiple toughening mechanisms induced by the z-pins which occurred over a longer scale in comparison to CNFs. The crack bridging process of the z-pins occurred along the thickness of the composite (~5 mm) whereas the CNFs locally bridge along the epoxy matrix interlayer between the crack faces (~30-50 μm) behind the main crack tip. In addition, the localised pull-out length of the z-pins (~300-600 μm) was much longer compared to CNFs (~3-13 μm), hence allowing the z-pins to generate greater traction energy due to the longitudinal splitting, snubbing and partial pull-out [10, 51, 52].
7.4.2 Effect of hybridising CNFs and z-pins on the mode II fracture toughness

The mode II interlaminar fracture properties of the multi-scale reinforced laminates toughened by a combination of CNFs and z-pins are shown in Fig. 7.9 and Table 7.1 for varying volume fractions of z-pins at a constant CNF content of 0.82 vol% (Fig. 7.9a) or varying volume content of CNFs at a fixed z-pin content of 0.5 vol% (Fig. 7.9b). The mode II steady-state fracture toughness, $G_{IIc-ss}$, increased for these two conditions. Importantly, combining both CNFs and z-pins within the same composite material resulted in a greater-than-additive (i.e. synergistic) improvement to the $G_{IIc-ss}$ values. The dashed curves in Fig. 7.9 show the expected mode II toughness if the contributions by CNFs and z-pins are simply additive. The results show that the measured fracture toughness values of multi-scale reinforced composites exceed the expected additive toughness values, revealing that combining CNFs and z-pins induced a synergistic toughening effect under mode II loading. Furthermore, the magnitude of this synergistic toughening increased with the volume fractions of CNFs and z-pins. This is consistent with the synergistic effect reported in the previous chapter for mode I interlaminar loading of the multi-scale reinforced composites [49].

![Figure 7.9](image)

**Fig. 7.9.** Effects of increasing volume fractions of (a) z-pins and (b) CNFs on the steady-state fracture toughness, $G_{IIc-ss}$, value when used separately (■ data points) and in combination (● data points). The dashed lines show the calculated fracture toughness from the expected additive toughening effect of the z-pins and CNFs when used separately, i.e. the fracture toughness $G_{IIc} = G_{unmodified} + \Delta G_{z-pin} + \Delta G_{CNF}$. 
A schematic representation of the mode II toughening mechanisms operative in the multi-scale reinforced composites is shown in Fig. 7.10, based on experimental observations. Many of the toughening mechanisms observed in the multi-scale reinforced composites are the same as those operative in the laminates containing either CNFs or z-pins. That is, the CNFs induced mode II toughening by bridging and then pulling out of the echelon cracks. The z-pins increased the toughness by forming a large-scale bridging zone by undergoing debonding, partial pull-out, snubbing, splitting and eventually shear rupture. The synergistic toughening effect was induced by the interaction between CNFs and z-pins, as shown in Fig. 7.11. Although no CNFs were grafted along the surface of the z-pins, the presence of CNFs in the laminate alters the pull-out behaviour of z-pins.

Fig. 7.10. Schematic of mode II delamination toughening processes in the multi-scale reinforced laminate containing CNFs and z-pins.
Fig. 7.11. Comparison of the toughening mechanisms and fracture surfaces for the z-pinned composite containing (a) unmodified epoxy and (b) CNF-modified epoxy (i.e. multi-scale reinforced).

To characterise the interaction between CNFs and z-pins under shear deformation, z-pin shear traction tests (shown in Fig. 7.2) were carried out for different contents of CNFs. The shear force versus displacement and the total energy dissipated per z-pin during the shear tests are shown in Fig. 7.12. Regardless of the CNF content, the z-pins bridging traction exhibited four-stages with increasing shear displacement: (i) elastic shear deformation of the z-pins (as represented by the initial linear-elastic response), (ii) debonding and partial pull-out of the z-pins, (iii) longitudinal splitting and snubbing of the z-pins, and (iv) shear rupture of the z-pins. The results presented in Fig. 7.12 shows that the bridging forces generated in all four stages increased with CNF content. As a result, the CNFs increased the total mode II crack bridging traction energy generated by the z-pins, which is defined by the total area under the bridging force-shear displacement curve (Fig. 7.9b).
Fig. 7.12. Mode II (a) bridging traction load-displacement response and (b) total traction energy per z-pin at different CNF contents. The subscripts in (a) denote the response of the z-pins undergoing (i) shear-elastic deformation, (ii) longitudinal splitting and interfacial debonding, (iii) snubbing, (iv) progressive rupture.

The mode II traction energy of the z-pins increased with the CNF content up to ~2 vol%, above which no further improvement was observed, and this trend agrees with the synergistic increase to the mode II fracture toughness measured for the multi-scale reinforced composite (Fig. 7.12b). The same trend was measured for the z-pins under mode I loading, as reported in the previous chapter. The CNFs increased the bridging traction energy of the z-pins by increasing the shear failure stress of the pin/laminate interface. It is known that CNFs increase the failure stress of epoxy polymers [49, 96], and therefore this effect increased the maximum traction load (see Fig. 7.12a) needed to cause interfacial failure between z-pins and surrounding laminate material. Following debonding and partial pull-out of the z-pins, the addition of CNFs further enhances the snubbing process. As a result, the traction energy increased with the CNF content by imparting an enhanced friction and snubbing process between the z-pin/epoxy interface. This was indicative of the increased roughness of the cavities (i.e. z-pin/laminate interface) created during the z-pin bridging process, as presented in Fig. 7.13. The CNFs were also pulled out from the z-pin/laminate interface (Fig. 7.13c), which contributed to the increased roughness. This increased the frictional sliding resistance experienced by the z-pins bridging the mode II delamination crack. In summary therefore, combining CNFs with z-pins induced the synergistic toughening effect in the multi-scale reinforced composites through increasing the shear failure stress and the roughness of the pin/laminate interface.
Fig. 7.13. Scanning electron micrographs of z-pin partial pull-out cavities from mode II shear pin pull-out samples containing (a) unmodified, (b & c) 1.0 wt% CNF, (d) 2.0 wt% CNF and (e) 5.0 wt% CNF in epoxy.

7.4.3 Comparison of experimental and numerically calculated fracture toughness values

Numerical predictions of the three-point bend load-displacement response and mode II crack growth resistance curves for the different composites are presented in Fig. 7.14 and Fig. 7.15, respectively. These curves were calculated using the FE model, which was solved using the mode II fracture toughness properties (Table 7.3), interlaminar friction properties (Table 7.4), and the mode II z-pin traction law (Fig. 7.12). The predictions of the FE model for all four types of composite material, including the multi-scale reinforced laminate, are in excellent agreement with the experimental results. The bending load-displacement responses measured for the ENF samples were captured with good accuracy by the FE model. As a result, the numerical model gave a very accurate simulation of the mode II R-curves and fracture toughness values of the different materials.
Fig. 7.14. Comparison of experimental and FE (a) load-displacement curves and (b) mode II R-curves for the control, CNF reinforced, z-pin reinforced and multi-scale reinforced composites considering the effect of volume content of z-pins at 0.82 vol% CNFs in epoxy.

Fig. 7.15. Comparison of experimental and FE (a) load-displacement and (b) mode II R-curves for the control, CNF reinforced, z-pin reinforced and multi-scale reinforced composites considering the effect of CNF content at a fixed z-pin volume content of 0.5 vol%.
Using the validated FE model, the relative contributions were computed of the CNFs and z-pins to the mode II fracture toughness properties of the multi-scale reinforced composites. For example, Fig. 7.16a presents a stacked R-curve plot showing the fracture toughness of the baseline composite ($\Delta G_{\text{control}}$) and the additional toughness contributions from the composites containing CNFs only ($\Delta G_{\text{CNF}}$), z-pins only ($\Delta G_{\text{z-pins}}$), and the synergistic enhancement from combining CNFs and z-pins ($\Delta G_{\text{synergy}}$). This example is for the composite containing 0.82 vol% CNFs and 2.0 vol% z-pins, and similar trends were observed in the FE results for other multi-scale reinforced materials. As previously described, the $\Delta G_{\text{synergy}}$ value stems from the magnified crack bridging traction effect of the z-pins induced by the CNFs. The $\Delta G_{\text{synergy}}$ value was calculated using:

$$\Delta G_{\text{synergy}} = \Delta G_{(\text{CNF}+z\text{-pins})} - (\Delta G_{\text{CNF}} + \Delta G_{z\text{-pins}})$$

(3)

where $\Delta G_{(\text{CNF}+z\text{-pins})}$ is the difference between the $G_{\text{IIc-ss}}$ value of the multi-scale composite and the baseline laminate. Similarly, $\Delta G_{\text{CNF}}$ and $\Delta G_{z\text{-pins}}$ denote the difference between the baseline laminate and laminates toughened by either CNFs or z-pins only.

![Fig. 7.16](image)

*Fig. 7.16* (a) Stacked R-curve plot of the contribution to the overall increase in the mode II fracture toughness from each reinforcement type; including the synergistic contribution denoted by $\Delta G_{\text{synergy}}$. Note: data presented was calculated using the FE model for the multi-scale reinforced laminate containing 0.82 vol% CNFs and 2.0 vol% z-pins. (b) Comparison of the experimentally measured and numerically calculated synergistic enhancements in the steady-state mode II $\Delta G_{\text{synergy}}$ value from the multi-scale reinforced composites.
As shown in Fig. 7.16a, the FE modelling revealed that the magnitude of the synergistic toughening effect ($\Delta G_{\text{synergy}}$) created by combining CNFs and z-pins was dependent on the mode II delamination crack length. The $\Delta G_{\text{synergy}}$ value was very low for relatively short crack (below ~5-10 mm), and this is because none or few of the z-pins were bridging the delamination crack. However, the $\Delta G_{\text{synergy}}$ value increased with the delamination length due to an increasing number of z-pins, whose traction energy was enhanced by the CNFs, joining the bridging zone behind the crack front. The $\Delta G_{\text{synergy}}$ value plateaued when the delamination length exceeded ~30 mm, and this was because the bridging zone created by the z-pins was fully established along the crack. That is, as new z-pins joined the bridging zone near the crack front an equal number of z-pins at the rear of the bridging zone failed, resulting in the steady-state toughness condition induced by the combination of CNFs and z-pins. When considering crack propagation length required to reach the steady-state fracture toughness value (i.e. ~30 mm), the number of z-pins operative along the fully bridged zone behind the crack tip are approximately 8x6 and 16x12 pins at a volume fraction of 0.5% and 2.0%, respectively. The synergy ratio in $G_{\text{IIc-ss}}$ values of the multi-scale reinforced composites can be calculated using [49]:

$$\text{Synergy Ratio (\%)} = \frac{\Delta G_{\text{synergy}}}{\Delta G_{(\text{CNF})} + \Delta G_{(z\text{-pins})}} \times 100\% \quad (4)$$

A comparison is presented in Fig. 7.16b of the synergy ratio values of the multi-scale reinforced composite measured from the experiments and the predicted values by the FE model. The experimental synergy value was determined using Eqn. 4 with consideration to the difference in the fracture toughness values between the toughened composite (i.e. CNF, z-pinned or multi-scale reinforced) and the control laminate (see Table 7.1). The FE predictions are in good agreement with the experimentally measured values. The multi-scale reinforced composite containing 0.82 vol% CNF and 0.5 vol% z-pins exhibited a modest synergistic toughening effect of ~13%. The synergistic toughening induced in the other multi-scale reinforced composites was similar in magnitude and within the range of approximately 20-26%. It appears that above a threshold CNF or z-pin content there is no further enhancement of the synergistic toughening effect, and this is because the total bridging traction energy of the pins remains constant (as shown in Fig. 7.12b) under mode II loading.
Table 7.5 presents a comparison of the mode I (Chapter 6) and mode II percentage synergy values of the corresponding multi-scale reinforced composite. The synergistic improvement is greater under mode I for the composite containing 4.10 vol% CNFs and 0.5 vol% z-pins. However, at lower CNF contents (0.82 vol%), the modes I and II percentage synergies values are identical.

Table 7.5. Comparison of the experimentally measured synergistic enhancements in the steady-state mode I and mode II $\Delta G_{\text{synergy}}$ value for the multi-scale reinforced composites.

<table>
<thead>
<tr>
<th>Multi-scale Composite</th>
<th>Mode I Percentage Synergy (%)</th>
<th>Mode II Percentage Synergy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.82 vol% CNFs + 0.5 vol% z-pins</td>
<td>13.0</td>
<td>12.6</td>
</tr>
<tr>
<td>1.64 vol% CNFs + 0.5 vol% z-pins</td>
<td>19.2</td>
<td>26.5</td>
</tr>
<tr>
<td>4.10 vol% CNFs + 0.5 vol% z-pins</td>
<td>69.8</td>
<td>22.3</td>
</tr>
<tr>
<td>0.82 vol% CNFs + 2.0 vol% z-pins</td>
<td>24.5</td>
<td>23.9</td>
</tr>
</tbody>
</table>

* Percentage mode I synergy values were taken from Chapter 6.

7.5 CONCLUSION

This chapter demonstrated that combining CNFs and z-pins within the same material induces a synergistic improvement to the mode II toughness that is greater than when these reinforcements are used separately. The magnitude of the synergistic toughening is controlled by the volume contents of both CNFs and z-pins, where the highest synergistic improvement of 26% was measured for the multi-scale composite containing 1.64 vol% CNFs and 0.5 vol% z-pins. The synergistic toughening effect is induced by the CNFs present along the z-pin/laminate interface increasing the mode II crack bridging traction properties of the pins. The mode II crack growth resistance response and fracture toughness properties of the multi-scale reinforced laminates were successfully predicted using a finite element (FE) model that considers the geometrical frictional contact of the crack surfaces, toughening due to the CNFs, and the enhanced shear bridging traction properties of the z-pins. Using the FE model, it was found that the magnitude of synergistic toughening effect increases with the delamination length due to a greater number of z-pins becoming operative within the crack bridging zone until the steady-state crack growth condition is reached.

Together with recent findings on a synergistic toughening effect under mode I [49] in Chapter 6, the new results on mode II interlaminar toughening suggest that synergistic toughening may also occur in the multi-scale reinforced composites with other types of carbon nanofillers, such as carbon nanotubes and graphene nanoplatelets, which is investigated in Chapter 8.
Chapter 8: Multi-scale delamination toughening of z-pinned composites using 1D and 2D carbon nanofillers

Abstract

This chapter presents a multi-scale toughening approach by combining various types of carbon nanofillers with z-pins to improve delamination resistance of fibre composites, and is an extension of the research presented in Chapters 6 and 7. The nanofillers studies here include one-dimensional (1D) carbon nanofillers (e.g. carbon nanotubes, carbon nanofibres) and two-dimensional (2D) nanofillers (i.e. graphene nanoplatelets). Results of the interlaminar fracture toughness revealed that 1D nanofillers induce synergistic (greater-than-additive) improvements to both the modes I and II delamination resistance of z-pinned laminates, whereas the 2D nanofiller show virtually no effect. Observations of the z-pin pull-out surfaces and the fracture surfaces reveal the main mechanisms by which the 1D nanofillers impart a synergistic effect, but not the 2D nanofillers.

The research work presented in this chapter have been published in the following:


8.1 INTRODUCTION

A myriad of approaches has been reported to improve the interlaminar fracture toughness properties of fibre reinforced epoxy composites, as reported in the previous chapters. Examples of these techniques include the addition of fillers within the polymer matrix [59, 67, 153, 219, 303-306], introduction of toughened interleaves between the plies [176], and insertion of through-the-thickness reinforcements [36, 52, 199, 203, 341]. Until very recently, these techniques have been used separately to enhance the delamination resistant properties of fibre composites.

Multi-scale toughening approaches by hybridising two or more filler types have been adapted to promote greater-than-additive improvements to the fracture toughness properties of bulk polymers [83, 96, 240, 241]. However, as reported in Chapter 2 (Section 2.3.2), synergistic enhancements to the interlaminar toughness properties of composites by combining two or more filler types is not well achieved, as reported in [57, 96, 230]. Also, as reported in Chapter 5, adding both CNFs and SCFs within the epoxy matrix of a composite resulted in the lower-than-expected additive enhancement in the mode I interlaminar fracture toughness properties due to inhibition of toughening mechanisms from neighbouring secondary fillers, including agglomeration.

In contrast, Ladani et al. [49] recently showed that adding only 1 wt% (0.82 vol%) CNFs to the epoxy matrix of a laminate containing 0.5 vol% carbon z-pins can increase the steady-state mode I interlaminar fracture toughness by an extra of ~11% above the expected total increases when the two reinforcements were used separately. Chapters 6 and 7 demonstrated that the synergistic improvements to the mode I and mode II interlaminar fracture toughness of z-pinned laminates are dependent on the volume contents of both the CNFs and z-pins. From experimental and numerical analysis, the greater-than-additive enhancement increases with the volume content and crack extension leading to synergistic increases to both the modes I and II delamination resistance of up to nearly 70% and 30%, respectively. The synergistic toughening effect was found to be caused by the interaction between the two reinforcements where the CNFs promote a dual-scale toughening effect by (i) enhancing the interlaminar properties between the plies and (ii) enhancing the bridging traction forces of the z-pins. However, it is not well understood whether other types of carbon-based nanofillers, such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs), can also promote synergistic toughening in z-pinned laminates.
Expanding on the research work presented in *Chapters 6* and *7*, the present study examines the multi-scale toughening effects of CNTs, CNFs, and GNPs with z-pins in improving the mode I and mode II interlaminar fracture toughness of composite laminates. Firstly, the efficacy of CNTs and GNPs on the synergistic toughening effects in z-pinned laminates are compared to CNFs previously investigated. Due to their aspect ratio and morphology, CNTs and CNFs are considered one-dimensional (1D) nanofillers whereas GNPs is a two-dimensional (2D) nanofiller. Lastly, the effect of the z-pin diameter on the synergistic toughening effect induced by the different types nanofillers are determined.

### 8.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

#### 8.2.1 Composite materials and manufacturing

Four types of carbon-epoxy laminate were investigated: (i) unmodified laminates (i.e. without carbon nanofillers and z-pins), (ii) laminates containing a single type of nanofiller (CNTs, CNFs or GNPs), (iii) laminates containing z-pins only, and (iv) laminates reinforced with a combination of a carbon nanofiller and z-pins (i.e. multi-scale reinforced). All the laminates were made with 20 plies of 200 gsm plain woven T300 carbon fabric (AC220127 supplied by Colan Ltd.). The polymer matrix was made using a two-part bisphenol-A based epoxy resin (Resin-105 and Hardener-206 supplied by West System®) [257]. The laminates were consolidated and cured using liquid compression moulding and further details of the manufacturing process are provided in Section 6.2.1 (*Chapter 6*).

Two types of 1D carbon nanofillers (CNTs, CNFs) and one type of 2D nanofiller (graphene) were used, as shown in **Fig. 8.1**. The CNTs were multi-walled carbon nanotubes with an average length of ~4 μm and diameter of ~10 nm according to the supplier (Type 791431, Sigma-Aldrich®) (**Fig. 8.1a**). The as-supplied CNFs have a diameter of 70-200 nm (Pyrograf® - III, grade PR-24-XT-HHT, Applied Sciences Inc.) (**Fig. 8.1b**) and are between 50-200 μm long, although the length is reduced to ~20 μm after three roll milling [320]. These are the same CNFs as using *Chapters 4–7*. The GNPs were multi-layered graphene nanoplatelets (XGNP®, XG Sciences) with an average diameter of ~25 μm (~19 μm after three roll milling [371]) and thickness of ~15 nm (**Fig. 8.1c**).
The nanofillers were used separately in the epoxy matrix to the laminate. The nanofillers were dispersed in the liquid epoxy resin at a concentration of 1 wt% by hand mixing and then three roll milling, with further details provided in Section 6.2.1 (Chapter 6). A low nanofiller content (1 wt%) was selected to keep the resin viscosity low and minimize agglomeration, which can occur at higher contents [98, 141, 372]. In adapting the protocols for dispersing CNFs within the epoxy matrix [23-25,32,33], solvent-free acrylate copolymers/surfactants (Disperbyk-191 and -192 supplied by BYK®) were added to the liquid resin at the weight ratio of 1:1:1 for D-191:D-192:CNFs. After dispersion by milling, amine hardener was added to the liquid epoxy containing...
nanofillers, and a stoichiometrically controlled amount of epoxy resin mixture was then applied to the carbon fabrics using the wet hand lay-up prior to the liquid compression moulding process to create the composite preforms. It is important to note that the content of nanofillers within the laminates is based on the weight fraction relative to the epoxy matrix since it is expected that the nanofillers would not infiltrate completely within due to the filtration effect [152].

Prior to liquid compression moulding process, z-pins made of unidirectional carbon fibre/bismaleimide rods (supplied by Albany Engineering Composites Pty Ltd.) were inserted through the entire thickness of the composite preform using a hydraulic press, as described in Section 6.2.1. The z-pins had a diameter of ~288 μm or ~510 μm, as shown in Fig. 8.2, and in this chapter are classified as thin and thick z-pins. The z-pins were inserted at the volume content of 2% where the thin pins were evenly spaced in a grid pattern at ~1.8 mm intervals, and the thick pins were evenly spaced at ~3.2 mm. Due to the relatively low contents of nanofillers (1 wt% in epoxy) and z-pins (2 vol%) used, there was no statistically significant variation in the thickness between the different types of laminate.

![Fig. 8.2. SEM image of the thin and thick diameter z-pins.](image)

### 8.2.2 Interlaminar fracture toughness testing and fractography assessment

Double cantilever beam (DCB) and end notch flexure (ENF) tests were performed on the laminates to measure their modes I and II interlaminar fracture toughness properties. The DCB
and ENF tests were performed in accordance with ASTM D5528-13 [309] and the ESIS protocol [310], respectively. Further description of the specimen design and testing method can be found in Section 6.2.2 (Chapter 6) for the DCB tests and Section 7.2.2 (Chapter 7) for the ENF tests.

The fracture surface of DCB and ENF samples were examined using scanning electron microscopy (SEM) FEI Nova NanoSEM operated at 10-15 kV and a 5 mm working distance. The SEM samples were surface-coated with a thin layer of gold prior to examination. In measuring the pull-out length of the nanofillers from the DCB specimens, multiple high-resolution images were captured. For the DCB specimens containing the CNTs five high-resolution images were captured with an area of 15 µm by 15 µm. Five 40 µm by 40 µm and nine 60 µm by 60 µm high-resolution SEM images were captured for the samples containing CNF and GNPs, respectively. From the SEM images, the approximate pull-out length of about 65 CNTs, 80 CNFs and 50 GNPs were measured using digital image correlation software (ImageJ, NIH, USA). This SEM technique used to measure the approximate filler length was adapted from [371, 373].

8.3 RESULTS AND DISCUSSION

8.3.1 Delamination toughening using nanofillers

The mode I and mode II crack growth resistance curves as well as the initiation and the steady-state interlaminar fracture toughness values measured for the different types of laminates are presented in Fig. 8.3, Table 8.1 and Table 8.2. The mode I fracture toughness of the unmodified laminate, and the composites containing carbon nanofillers increased over the first 5-10 mm of crack extension due to fibre bridging between the delaminated plies. The mode I toughness then plateaued to a steady-state value, which was indicative of a fully-developed fibre bridging zone behind the main crack tip [150]. Under the mode II loading condition, the fracture toughness of the laminates also increased with crack length up to 15-25 mm, and this was due to the physical interlocking and the resultant shear-induced frictional sliding resistance between the opposing crack faces as reported in Chapters 5 and 7. With crack extension, the mode II toughness of the laminates reached a steady-state condition.
Fig. 8.3. Experimentally measured (a) mode I and (b) mode II crack growth resistance curves for the laminates containing unmodified epoxy, CNT, CNF and GNP modified epoxy.

Table 8.1. Mode I and mode II initiation fracture toughness values of the laminates.

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>$G_{Ic}$ (kJ/m$^2$)</th>
<th>Improvement</th>
<th>$G_{IIc}$ (kJ/m$^2$)</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>0.25 ($\pm$0.03)</td>
<td>-</td>
<td>1.22 ($\pm$0.13)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Nano-reinforced</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNTs</td>
<td>0.43 ($\pm$0.04)</td>
<td>72%</td>
<td>1.26 ($\pm$0.16)</td>
<td>3.3%</td>
</tr>
<tr>
<td>CNFs</td>
<td>0.54 ($\pm$0.11)</td>
<td>116%</td>
<td>1.25 ($\pm$0.11)</td>
<td>2.5%</td>
</tr>
<tr>
<td>GNPs</td>
<td>0.34 ($\pm$0.08)</td>
<td>36%</td>
<td>1.10 ($\pm$0.20)</td>
<td>-9.8%</td>
</tr>
<tr>
<td><strong>3D reinforced</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thin (288 $\mu$m) z-pins</td>
<td>0.26 ($\pm$0.14)</td>
<td>4.0%</td>
<td>1.23 ($\pm$0.13)</td>
<td>0.8%</td>
</tr>
<tr>
<td>thick (510 $\mu$m) z-pins</td>
<td>0.25 ($\pm$0.10)</td>
<td>0.0%</td>
<td>1.24 ($\pm$0.18)</td>
<td>1.6%</td>
</tr>
<tr>
<td><strong>Multi-scale Reinforced: Effect of nanofiller type at a controlled z-pin diameter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thick z-pins + CNTs</td>
<td>0.42 ($\pm$0.05)</td>
<td>68%</td>
<td>1.26 ($\pm$0.22)</td>
<td>3.3%</td>
</tr>
<tr>
<td>thick z-pins + CNFs</td>
<td>0.55 ($\pm$0.13)</td>
<td>120%</td>
<td>1.23 ($\pm$0.17)</td>
<td>0.8%</td>
</tr>
<tr>
<td>thick z-pins + GNP</td>
<td>0.35 ($\pm$0.06)</td>
<td>40%</td>
<td>1.18 ($\pm$0.21)</td>
<td>-3.3%</td>
</tr>
<tr>
<td><strong>Multi-scale Reinforced: Effect of z-pin diameter at a controlled nanofiller type</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thin z-pins + CNFs</td>
<td>0.73 ($\pm$0.23)</td>
<td>190%</td>
<td>1.27 ($\pm$0.23)</td>
<td>4.1%</td>
</tr>
<tr>
<td>thick z-pins + CNFs</td>
<td>0.55 ($\pm$0.13)</td>
<td>120%</td>
<td>1.23 ($\pm$0.17)</td>
<td>0.8%</td>
</tr>
</tbody>
</table>
Table 8.2. Mode I and mode II steady-state fracture toughness values of the laminates.

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>$G_{IC-ss}$ (kJ/m$^2$)</th>
<th>Improvement</th>
<th>$G_{IIc-ss}$ (kJ/m$^2$)</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>0.73 ($\pm$0.04)</td>
<td>-</td>
<td>2.04 ($\pm$0.14)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Nano-reinforced</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNTs</td>
<td>0.92 ($\pm$0.07)</td>
<td>26%</td>
<td>3.91 ($\pm$0.25)</td>
<td>92%</td>
</tr>
<tr>
<td>CNFs</td>
<td>1.40 ($\pm$0.12)</td>
<td>91%</td>
<td>2.88 ($\pm$0.24)</td>
<td>42%</td>
</tr>
<tr>
<td>GNPs</td>
<td>1.23 ($\pm$0.12)</td>
<td>68%</td>
<td>2.35 ($\pm$0.13)</td>
<td>15%</td>
</tr>
<tr>
<td><strong>3D reinforced</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thin (288 μm) z-pins</td>
<td>8.90 ($\pm$0.30)</td>
<td>1120%</td>
<td>7.10 ($\pm$0.48)</td>
<td>248%</td>
</tr>
<tr>
<td>thick (510 μm) z-pins</td>
<td>5.08 ($\pm$0.25)</td>
<td>595%</td>
<td>9.57 ($\pm$0.34)</td>
<td>370%</td>
</tr>
<tr>
<td><strong>Multi-scale Reinforced: Effect of nanofiller type at a controlled z-pin diameter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thick z-pins + CNTs</td>
<td>6.98 ($\pm$0.25)</td>
<td>856%</td>
<td>12.2 ($\pm$0.42)</td>
<td>498%</td>
</tr>
<tr>
<td>thick z-pins + CNFs</td>
<td>6.70 ($\pm$0.20)</td>
<td>817%</td>
<td>11.4 ($\pm$0.51)</td>
<td>459%</td>
</tr>
<tr>
<td>thick z-pins + GNPs</td>
<td>5.71 ($\pm$0.36)</td>
<td>682%</td>
<td>9.80 ($\pm$0.39)</td>
<td>380%</td>
</tr>
<tr>
<td><strong>Multi-scale Reinforced: Effect of z-pin diameter at a controlled nanofiller type</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thin z-pins + CNFs</td>
<td>11.6 ($\pm$0.52)</td>
<td>1490%</td>
<td>9.35 ($\pm$0.55)</td>
<td>360%</td>
</tr>
<tr>
<td>thick z-pins + CNFs</td>
<td>6.70 ($\pm$0.20)</td>
<td>818%</td>
<td>11.4 ($\pm$0.51)</td>
<td>458%</td>
</tr>
</tbody>
</table>

The carbon nanofillers were effective at improving the mode I initiation fracture toughness ($G_{c-ss}$), with CNFs being the most effective. No significant enhancements was measured to the mode II initiation fracture toughness ($G_{IIc-ss}$) values with addition of the nanofillers. In contrast, all the nanofillers were effective at increasing the steady-state modes I and II strain energy release rate ($G_{IC-ss}$ and $G_{IIc-ss}$) values of the laminates, although the magnitude of the toughening was dependent on the nanofiller type. CNFs and CNTs were the most effective at improving the steady-state mode I and mode II fracture toughness, respectively. The nanofillers increased the delamination resistance via multiple toughening mechanisms that occurred ahead of (intrinsic) and behind (extrinsic) the main crack tip. These mechanisms are shown in Fig. 8.4 and Fig. 8.7 for modes I and II loading, respectively, including schematic representations of the toughening processes which are based on experimental observation. Detailed description of these toughening mechanisms can be found in Chapters 5, 6 and 7.
Fig. 8.4. (a) Schematic of the mode I toughening mechanisms along the crack front of the epoxy interlayer, located between the plies. SEM images of the fracture surface of DCB samples containing (b) CNTs, (c) CNFs or (d) GPNPs.

Under the mode I loading condition (see Fig. 8.4), the intrinsic toughening mechanisms were interfacial debonding between the nanoparticles and epoxy matrix as well as plastic void growth next to the debonded nanoparticles. These intrinsic mechanisms contributed to the enhancements attained to the $G_{ic}$ values. Fractographic investigation revealed that the plastic void growth processes were more apparent for the specimens containing CNFs preceded by CNTs and then GNPs. Ladani et al. [98] also reported that the number and relative size of the voids formed near the fillers via the plastic void growth mechanism was much greater with the addition of CNFs compared to GNPs within a bulk epoxy matrix. Therefore, the capacity of the CNFs to generate the most microvoids within the crack tip process zone resulted in the greater improvement to the
$G_{Ic,i}$ value of the laminate. As shown in Fig 8.4, the extrinsic mode I toughening mechanisms were crack bridging, pull-out and/or fracture of the nanoparticles. The dominant toughening mechanism was the traction energy generated by pull-out of the nanofillers bridging the mode I crack. The traction energy due to the pull-out was proportional to nanofiller length. The percentage improvement to the mode I toughness of the laminate containing CNFs (91%), GNPs (68%) or CNTs (26%) correlates approximately with their length after milling: CNFs (~20 μm), GNPs (~19 μm), CNTs (~4 μm). Fractographic analysis revealed that the length of the nanofillers nearly scaled with their approximate pull-out length along the fracture surface of the DCB samples. Using digital image correlation, the average length of the CNFs, GNPs and CNTs were measured to be 7.2±2.9 μm, 7.7±1.8 μm and 0.5±0.3 μm, respectively.

Fig. 8.5. (a) Schematic of the mode II toughening mechanisms along the crack front of the epoxy interlayer, located between the plies. SEM images of fracture surfaces of ENF samples containing (b) CNTs, (c) CNFs or (d) GNPs.
For every composite specimen investigated under mode II loading, the initiation of the microcracks was due the shear stresses acting within the process zone ahead of the crack tip (Fig. 8.5a). The echelon cracks grew in size at approximately 45° to the crack growth direction and coalesced which then allowed the delamination cracks to propagate. The maximum width of these echelon cracks was ~10-30 μm. The extrinsic toughening mechanisms via crack tip shielding included wedging, bridging and pull-out of the nanofillers between the delamination faces (Fig. 8.5a), and the micromechanics are detailed in Chapter 5 and 7. Many of the nanofillers within the process zone debonded from the polymer matrix under the high stresses immediately ahead of the crack tip, thereby leading to the development of additional echelon cracks. The formation of echelon cracks under mode II loading is not a toughening mechanism, which corresponds to no enhancement to the $G_{IIc}$ values. Rather, the additional toughening processes partly stem from the processes that restrict the opening of the echelon cracks behind the main crack tip [362, 372]. The CNTs and CNFs, due to their small size and 1D morphology, bridged the echelon cracks (see Fig. 8.5b and 8.5c) and thereby exerted a crack closure force which would increase the mode II fracture toughness of the laminates. The laminate containing CNTs exhibited a higher mode II toughness (92% improvement) than the CNFs (42%) due to the higher density of smaller echelon microcracks (see Fig. 8.5b), where a great proportion of CNTs were bridging the crack. As shown in Fig. 8.5d, the GNPs did not fully bridge or restrict the opening of the echelon cracks due to their 2D morphology and larger size when compared to the CNT and CNFs (see Fig. 8.1). Rather, the debonded GNPs allowed for the additional formation of the echelon cracks which promoted crack propagation. This accounts in part for the moderate improvement to the mode II toughness (15% increase) of the laminate containing GNPs compared to the composites containing 1D carbon nanofillers. These findings are consistent with previous reports into the comparative interlaminar toughening performance between 1D and 2D carbon nanofillers [67, 159].

8.3.2 Delamination toughening using z-pins

The effect of z-pinning on the modes I and II interlaminar fracture toughness of the laminate are shown in Table 8.1, Table 8.2 and Fig. 8.6. The delamination resistant properties of z-pinned composites have been studied extensively, and the current finding from this chapter are consistent with the following studies [11-22].
Fig. 8.6. Effect of z-pin diameter (at 2.0 vol%) on the (a) mode I and (b) mode II crack growth resistance curves for the laminate containing the unmodified epoxy only.

The z-pins increased the mode I toughness of the laminate by forming a large-scale bridging zone up to ~20 mm long along the delamination crack (Fig. 8.7). The bridging z-pins increased the delamination resistance via extensional elastic deformation, interfacial debonding and pull-out [24]. When comparing the effect of pin diameter, the thin z-pins were more effective at improving the steady-state mode I interlaminar fracture toughness than the thick pins at a fixed volume fraction ($V_f$). Based on the expression [279, 287]:

$$\Delta G_{\text{pull-out}} = \frac{2V_f \tau_i l_{po}^2}{d_f}$$

this was because the fracture toughening contribution due to pull-out ($\Delta G_{\text{pull-out}}$) of an orthogonal pin is inversely proportional to the size of diameter ($d_f$) for a given interfacial shear friction stress between the z-pin/epoxy interface ($\tau_i$) and the pull-out length of the pins ($l_{po}$).

Fig. 8.7. Schematic and cross-sectional X-ray computed tomography (CT) image of the mode I interlaminar toughening of the z-pinned laminate via large-scale crack bridging.
The mode II fracture toughness of the laminate containing the thin and thick pins increased rapidly up to ~60 mm (i.e. rising R-curve) and ~40 mm of crack extension, respectively. Under the mode II loading conditions, the bridging process of the z-pins (see Fig. 8.8) consists of (i) elastic shear deformation of the pins, (ii) interfacial debonding, (iii) partial pull-out and snubbing of the pins against the epoxy composite interface, and (iv) longitudinal splitting and shear rupture of the pins [24]. The thick pins were effective at increasing the mode II fracture toughness at crack propagation lengths greater than 40 mm. X-ray computed tomography (CT) images revealed that the thin z-pins begin to rupture at approximately a crack propagation length of 40-45 mm (see Fig. 8.8). At this crack length, the thick pins continue to bridge the crack, forming a large bridging zone which results in the rising R-curve observed. Similar effects due to the z-pins diameter were also reported by Pegorin et al. [51].

Fig. 8.8. Schematic and cross-sectional X-ray CT images of the mode II interlaminar toughening of the z-pinned laminate via large-scale crack bridging.

### 8.3.3 Delamination toughening using both nanofillers and z-pins

The modes I and II interlaminar fracture toughness values of the multi-scale reinforced laminates which contain both carbon nanofillers (CNTs, CNFs or GNP) and z-pins are given in Table 8.1 and Table 8.2. Fig. 8.9 and Fig. 8.10 presents the crack growth resistance curves for the multi-scale reinforced laminates showing the effects of the nanofiller type and z-pin diameter.
Fig. 8.9. Mode I crack growth resistance curves for the laminates containing (a) z-pins + CNTs, (b) z-pins + CNFs and (c) z-pins + GNPs. Mode II R-curves for the laminates containing (d) z-pins + CNTs, (e) z-pins + CNFs and (f) z-pins + GNPs. Z-pins used had a diameter of 510 µm (thick).
Fig. 8.10. Effect of z-pin diameter on the (a) mode I and (b) mode II crack growth resistance curves of the laminates containing CNFs.

Considering the effect of the CNTs, CNF and GNPs on the modes I and II crack resistance behaviour, the additional of nanofillers promoted no significant variation in the crack in propagation length at which the z-pin bridging zone was formed, as discussed in Section 8.3.2. However, the carbon-based nanofillers increased the gradient of the R-curve (i.e. crack growth toughness) up to the steady-state fracture toughness value of the multi-scale reinforced laminate when compared the z-pinned laminate containing the unmodified epoxy matrix (see Figs 8.9 and 8.10). This was attributed to the additional toughening contribution from the CNTs, GNPs or CNFs. Improvements were more significant for steady-state values of mode I and mode II crack fracture toughness, when compared to the initiation toughness values (see Tables 8.1 and 8.2). As shown in Fig. 8.11 and Fig. 8.12, the steady-state fracture toughness values measured for the multi-scale reinforced composite are compared with the expected additive toughness values when the two materials do not infer any synergistic effect. In some of the laminates, the steady-state fracture toughness (i.e. $\Delta G_{\text{nanofiller+z-pins}}$) exceeded the value expected from an additive (no synergy) toughening effect from the individual contributions of the carbon nanofillers ($\Delta G_{\text{nanofiller}}$) and z-pins ($\Delta G_{\text{z-pins}}$) (see Figs. 8.11 and 8.12). The greater-than-additive toughening contribution ($\Delta G_{\text{synergy}}$) can be quantified using the expression [372]:
\[ \Delta G_{\text{synergy}} = \Delta G_{(\text{nanofillers}+\text{z-pins})} - (\Delta G_{\text{nanofillers}} + \Delta G_{\text{z-pins}}) \] (2)

The percentage of synergy can be calculated using [372]:

\[ \text{Synergy} \, (\%) = \frac{\Delta G_{\text{synergy}}}{\Delta G_{(\text{nanofillers})} + \Delta G_{(\text{z-pins})}} \times 100\% \] (3)

Fig. 8.11. Effect of nanofiller type on the steady-state (a) mode I and (b) mode II interlaminar fracture toughness values of the laminates containing no z-pins or thick z-pins.

Fig. 8.12. Effect of z-pin diameter on the steady-state (a) mode I and (b) mode II interlaminar fracture toughness values of the laminates containing unmodified or CNF modified epoxy.
As shown in Fig. 8.13, the magnitude of the synergistic toughening effect was dependent on the type of nanofiller and the diameter of the z-pins. The 1D nanofillers generated a synergistic toughening effect when used in combination with the z-pins, whereas the 2D nanofillers did not. The CNTs were more effective than the CNFs at synergistically increasing the mode I toughness, whereas the CNFs were slightly more effective for mode II toughness. The previous chapters into the effect of combining CNFs with z-pins showed that the synergistic toughening is induced by the nanofiller increasing the traction loads generated by the z-pins bridging mode I or II delamination cracks [49, 372]. The CNFs increase both the failure stress of the matrix-pin interface and the frictional resistance of the z-pins to pull-out (for mode I) and partial pull-out/snubbing (for mode II). These mechanisms magnify the crack bridging loads generated by the z-pins which in turn causes toughening improvement that far exceed the expected additive toughening contribution. The CNTs induced the same synergistic toughening mechanism as the CNFs, as reported in Chapters 6 and 7. This was evident by the increased surface roughness of the holes within the laminate created by z-pin pull-out, as shown in Fig. 8.14. The roughness of the holes caused by z-pin pull-out was increased significantly by both the CNTs and CNFs, which was indicative of a greater frictional sliding resistance of the z-pins during the crack bridging process (see Figs. 8.14b and 8.14c). However, the 2D GNPs showed no measurable synergistic effect with z-pins under mode I and II. Fractographic examination revealed that there were no GNPs present along the z-pin/composite interface, as shown in Fig. 8.14d. This was due to the two-dimensional shape and size of the GNPs (i.e. ~25 μm diameter), which restricted the GNP dispersion along the thin interfacial region between the z-pins and laminate material. The width of the interfacial region where no fibres were present was typically less than ~1-2 μm, with some slightly wider regions where resin-rich regions exist. To increase the bridging traction properties of the z-pins the nanofillers must be capable of fitting into this narrow interfacial region. The images presented in Fig. 8.1 show that the CNTs and CNFs are much smaller than the GNPs. The 1D shape of the CNTs and CNFs enables them to reside more easily at the z-pin/laminate interface, thereby making the 1D nanofillers active in the z-pin bridging process.
Fig. 8.13. Percentage synergistic improvements to the modes I and II steady-state interlaminar fracture toughness of the multi-scale reinforced laminates: effects of (a) nanofiller type and (b) z-pin diameter.

Fig. 8.14. Schematic and SEM images comparing the mode I pull-out surface along the z-pin/composite interface containing (a) unmodified epoxy, (b) CNTs, (c) CNFs and (d) GNP in the epoxy matrix.

It was also found that the synergistic toughening effect was dependent on the z-pin diameter, with the thinner pins being more effective. The percentage increase to the steady-state mode I delamination resistance due to the synergistic toughening effect of the CNFs was 25% and 19% for the thin and thick z-pins, respectively. Similarly, the synergistic effect on the steady-state mode II toughness for the CNF laminates containing thin or thick z-pins was 24% and 12%,
respectively. The thin z-pins were more effective because of their greater surface area per unit areal density, which increases the traction loads generated by crack bridging.

Based on the results presented here, the shape and size of the nanofillers are critical to inducing a synergistic toughening effect, with 1D nanofillers (CNTs, CNFs) being more effective than 2D nanoplatelets (GNPs) and thin z-pins being more effective than thick pins.

8.4 CONCLUSION

Chapter 8 demonstrates that combining 1D nanofillers such as CNTs and CNFs with z-pins can create a synergistic improvement in the interlaminar fracture toughness of composite laminates. The total toughening effect exceeds the expected sum of their separate increases. With the 1D nanofillers residing along the z-pin/laminate interfacial region, they generate a synergistic effect by increasing the bridging traction loads of the z-pins during delamination crack growth. The 1D nanofillers increase both the interfacial bond failure stress and the frictional resistance against z-pin pull-out and sliding. The diameter of the z-pins also influenced the magnitude of the synergistic toughening effect with 1D nanofillers. The toughening effect was stronger using thin z-pins because their total surface area per unit area of delamination crack was higher than thick z-pins. Consequently, the increase in the total bridging traction energy induced by the 1D nanofillers is magnified using thin z-pins.

2D nanoplatelets such as the GNPs investigated in this study do not induce a significant greater-than-additive toughening effect in z-pinned laminates. This was due to the restricted ability of the GNPs to infiltrate the narrow spaces between the z-pins and the surrounding composite materials. Findings from this chapter provide new insights into the hierarchical toughening effects in composites containing nano-materials and z-pins or other types of 3D reinforcement. Such multi-scale toughening methodology may also prove effective at enhancing damage tolerance of composite joints (e.g. T-joints), which is investigated in Chapter 9.
Chapter 9: Multi-scale strengthening of composite T-joints using carbon nanofillers and z-pins

Abstract

This chapter presents an experimental study into the hierarchical strengthening of carbon fibre reinforced epoxy composite T-joints using both carbon nanoparticles and z-pins. Carbon nanofillers used were carbon nanotubes (CNTs), carbon nanofibres (CNFs) or graphene nanoplatelets (GNPs). Experimental testing revealed that the initiation failure load, ultimate pull-out load and the absorbed energy capacity of the T-joints were dependent on carbon nanofiller type and the z-pins. The CNFs were the most effective at increasing the failure initiation load (~68%) in both the unpinned or z-pinned T-joints. However, hybridising the CNTs or CNFs with z-pins results in large improvements to the ultimate failure load (~54-74%) and absorbed energy capacity (~400-450%) of the joints, although only a marginally small enhancement was found with GNPs. Key strengthening and toughening mechanisms were identified. The increase to the structural properties of the T-joints were correlated to increases to the modes I and II interlaminar fracture toughness properties of the carbon nano-reinforced and z-pinned laminates.

Findings from the present chapter are being prepared for submission in:


9.1 INTRODUCTION

One of the key challenges in manufacturing stiffened structures using fibre reinforced epoxy composites is the need for joining during initial modular construction [16]. For instance,
fibre reinforced composite T-joints are widely used in maritime, civil infrastructures, aircraft structures, automotive components and other applications to stiffen and transversely connect structural components [2, 27, 163, 374-378]. **Fig. 9.1** presents a basic design of a T-joint which consists of a delta fillet region and a radius bend region where the stiffener is curved into a flange that is bonded on to the skin laminate [378]. The delta fillet region is usually filled with a polymer matrix or composite material. The skin, flange and stiffener laminates are usually joined by co-curing or adhesive bonding.

![Fig. 9.1: Schematic illustrating the basic elements to a T-joint structure with the individual subcomponents.](image)

A long-standing problem of composite T-joints is that the joining interfaces are much weaker than the mechanical properties of the skin and stiffener laminates, and therefore debonding of the interfaces (i.e. bond-line) is a common failure mode [27, 374]. Localized resin-rich regions within the fillet region and the contoured shape of the laminate at the radius bend acts as geometric stress raisers for cracks to initiate. Due to the poor interlaminar fracture toughness and brittle properties of the epoxy matrix, the bond-lines within the composite T-joints are prone to delamination when subjected to low pull-out loads along the stiffener. Hence there is a desire to enhance the structural properties of T-joints, which includes the ultimate load and extension-to-failure, as defined in **Fig. 9.2**.
Fig. 9.2. Definition of parameters for T-joint structural performance. Note: the applied load-vertical displacement curves for the composite T-joints containing unmodified epoxy matrix reported within this chapter is presented as an example.

Several methods have been reported to increase the load-bearing properties of composite T-joints when subjected to pull-off loads along the length of the stiffener (see Fig. 9.1). The most common method is the use of mechanical fasteners (e.g. rivets and bolts), however this can increase the weight and degrade the in-plane structural properties of the laminate [378, 379]. Other reported techniques include the use of fillers within the fillet region [380], interleaving the bond-lines with toughened thermoplastic interleaves or adhesives [381], intermingling the plies from the flange within the skin laminate [375] and tailoring the ply stacking sequence [2, 375, 376, 382-384] of the stiffener laminate near the fillet region to minimize the stress concentration. The use of macroscale through-the-thickness reinforcement such as three-dimensional (3D) stitching [180, 182, 385] and tufting [386] within the preform are also effective in enhancing the structural properties and damage tolerance of composite T-joints.

The insertion of carbon fibre/BMI z-pins along the thickness direction of the laminates have shown to enhance the load-bearing properties of composite T-joints [26, 36, 183, 209, 249-251]. Koh and colleagues [207] reported improvements of up to 76%, 600% and 230% in the ultimate load, absorbed energy capacity and elongation-to-failure of the carbon fibre composite T-
joint, respectively, when using 4 vol% z-pins. Improvements to the ultimate load and absorbed energy capacity are proportional on the volume fraction [207, 208] and embedded length of the z-pins [26]. However, the insertion of z-pins promotes little or no enhancement on the load-at-first failure of a composite T-joint [26, 207]. In reference to Fig. 9.2, the initiation failure load is governed by the onset of cracks near the delta fillet region, and it is a critical design metric for the structural properties of composite joints [378]. Z-pins do not toughen the resin-rich region fillet region. Rather, they extrinsically strengthen T-joints via the large-scale bridging of the z-pins along the crack wake. Experimental and numerical findings from [26, 43, 45] indicate that improvements to the structural properties are dominated by the snubbing and pull-out of the z-pins that suppresses delamination along the bond-lines [26, 207]. Therefore, the damage initiation strength of T-joints are dependent on the local ply-orientation, radius of the fillet and the local mechanical properties of the epoxy matrix within the fillet region [2, 207, 375, 378, 381, 387].

Several studies have shown that the addition of carbon nanoparticles are effective at increasing the shear failure properties of composite lap joints [388-391]. However, there are no reports concerning the effects of carbon nanofillers on the load-bearing properties of composite T-joints. Since carbon-based nanofillers can improve the intrinsic properties (i.e. tensile strength and fracture toughness) of the polymer matrix [98], the influence that CNTs, CNFs or GNP have on the damage initiation behaviour of composite T-joints is not well understood. As mentioned in the previous chapters, the addition of carbon-based nanofillers (i.e. GNPs, CNTs and CNFs) improves the delamination resistance of composite laminates [59, 67, 151, 303, 306, 320, 329, 372] and the toughening efficacy of z-pins [49, 329, 372, 392]. Therefore, the addition of carbon nanofillers to toughen the matrix may prove to be beneficial in improving the load-bearing properties of composite T-joints, which has yet to be determined.

Extending on Chapters 6, 7 and 8, this chapter presents an investigation into the multi-scale toughening effects of adding carbon-based nanofillers and z-pins on the structural properties of carbon fibre reinforced epoxy composite T-joints. The T-joints were subjected to pull-off loads along the stiffener laminate. Firstly, the effect of nanofiller type (i.e. CNTs, CNFs and GNPs) on the elastic stiffness, load-at-first failure and ultimate strength properties of the joints containing no z-pins and z-pins at 2.0 vol% were experimentally measured. The delamination behaviour along the bond-line of the T-joints during loading was recorded and toughening mechanisms were
identified. Secondly, the efficacy of the carbon nanofillers on the strengthening effect of the z-pinned composite T-joints are characterized. Lastly, the structural properties of the T-joints are compared with the modes I and II interlaminar fracture toughness properties presented in Chapter 8.

9.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

9.2.1 Composite T-joint manufacturing and testing

The composite T-joints were made using 200gsm T300 carbon fibre fabric (AC220127 supplied by Colan Ltd.) and low temperature cure epoxy via wet-hand layup process and vacuum assisted curing. The polymer matrix was a two-part bisphenol-A based epoxy resin (Resin-105 and Hardener-206 supplied by West System®) [257], which is same epoxy used in the previous chapters. Four types of carbon-epoxy composite T-joints specimens were investigated which include (i) unmodified T-joint (i.e. without carbon nanofillers and z-pins), (ii) T-joints containing a single type of nanofiller (CNTs, CNFs or GNPs), (iii) T-joints containing z-pins only, and (iv) multi-scale reinforced T-joint containing both carbon nanofillers and z-pins. Carbon nanofillers that were added separately into the epoxy matrix include CNTs, CNFs or GNPs. The CNTs were multi-walled carbon nanotubes having an average length of ~4 μm and a diameter of ~10 nm (Type 791431, Sigma-Aldrich®). The CNFs were 50-200 μm long and had a diameter of 70-200 nm (Pyrograf® - III, grade PR-24-XT-HHT, Applied Sciences Inc.). The GNPs (XGNP®, XG Sciences) were multi-layered graphene nanoplatelets with an average size and thickness of ~25 μm and ~15 nm, respectively. The nanofillers used in the previous chapter are the same.

The nanofillers were blended into the liquid epoxy resin at a content of 1 wt% by hand mixing followed by three roll-milling [98, 279, 372]. Full details of the three-roll milling process can be found in Section 8.2.1 (Chapter 8). After dispersion by milling, amine hardener was then added to the liquid epoxy containing nanofillers, and the mixture was then pre-impregnated into the individual carbon fibre plies stoichiometrically.

Preforms containing 10 plies of the 200 gsm carbon fibre fabrics pre-impregnated with the liquid epoxy resin mixture were then prepared via wet hand lay-up. These preforms were used as the stiffener/flange and skin laminates, with each laminate section containing ten plies. The weft and warp tows of the carbon fibre plies were oriented along the length and width of the T-joints,
respectively. As illustrated in Fig. 9.1 and Fig. 9.3, the joint stiffener/flange section was made by co-bonding the two preforms conformed into a L-shaped laminate with the guidance of steel caul plate. The flange section from the L-shaped composite was then co-bonded with the skin laminate (see Fig. 9.3a). Prior to curing, the fillet region of the T-joint was filled with the corresponding resin mixture. Adhesion between the stiffener/flange section and the skin laminate was achieved by co-curing the joint.

In manufacturing the z-pinned and multi-scale reinforced T-joints, carbon fibre/bismaleimide z-pins within a carrier foam were inserted in a near-orthogonal direction into the thickness of skin-flange region of the joint) using a hydraulic press which applied a compressive pressure of 350 kPa prior to curing [329, 372]. The z-pins inserted had a diameter of ~510 μm and a volume fraction of 2%, with the z-pins being evenly spaced at ~3.2 mm intervals.

Fig. 9.3. (a) Schematic and (b) photo of the manufacturing process of composite T-joints
Lastly, the T-joint preform was wrapped with a breather cloth and release films (polytetrafluoroethylene (PTFE)) inside a vacuum bag that is sealed onto a base plate (see Fig. 9.3b). The T-joints were cured under vacuum for 24 hours at 25°C in accordance to supplier specifications [257]. T-joint specimens were cut into the dimensions shown in Fig. 9.4 using a diamond tip benchtop saw. The skin, flange and stiffener laminates has a thickness of ~2.5 mm. The thickness of the joint laminate was ~5 mm. Due to the relatively low contents of nanofillers (1 wt% in epoxy) and z-pins (2 vol%) used, there was no significant variation in the thickness between the different types of T-joints. The fibre volume content of carbon fibres within the skin, stiffener and flange was ~50%, and this was controlled via the stoichiometric ratio of carbon fabric and epoxy resin used in the fabrication process.

Fig. 9.4. (a) Isometric and (b) front view of T-joint specimens containing z-pins.
9.2.2 Composite T-joint pull-off testing

Pull-off tests were conducted on the T-joint specimens where a uniaxial tensile load was applied to the joint stiffener, as shown in Fig. 9.5. The skin/flange section of the T-joints were clamped at the ends. Pull-off tests were performed at a stiffener displacement rate of 1.0 mm/min (see Fig. 9.5) using a 50 kN Instron universal testing machine. Continuous images were captured at 24 fps (720p) using a Nikon D3500 DSLR camera to monitor the crack growth behavior along the bond-line and failure modes of the T-joints during testing. The load and crosshead displacement data were also recorded continuously during testing. Tests were conducted until either (a) the delamination front between the skin and flange has reached the clamped ends or (b) the failure of the laminate has occurred, at which point testing was stopped. A minimum of three samples were tested for each T-joint specimen type.

![Photo of T-joint pull-off test setup.](image)

Data was then post-processed to determine the joint’s elastic stiffness, load-at-first failure, ultimate load and the absorbed energy capacity up to maximum load, as defined in Fig. 9.2. The load-at first failure was taken at the onset of crack formation which corresponded to the initial drop within the load-displacement curve. The absorbed energy capacity ($U_{abs}$) was calculated by taking the integral of the load-displacement curve up to the ultimate load. This $U_{abs}$ is an indirect measure
of the strain energy-to-failure or the apparent fracture toughness of T-joint when subjected to pull-off loads up to failure. Considering the classical design criteria for T-joints used in structural applications, maximum/ultimate design load and extension-to-failure past damage initiation is often based on the ultimate load carrying capacity (i.e. peak load) of the joint. It is important to note that the measured mechanical properties are considered ‘apparent’ values, since they are dependent on the specimen geometry and the compliance of the test setup, which are kept consistent throughout this study.

9.3 RESULTS AND DISCUSSION

9.3.1 Load-bearing properties of T-joints containing carbon nanofillers

Load-displacement curves measured for the T-joints with or without carbon nanoparticles are shown in Fig. 9.6. Photographs of the T-joints taken at increasing displacements and at final failure are presented in Figs. 9.7 and 9.8, respectively. The curves for the different T-joints have a similar profile, with an initial linear elastic response followed by a small load drop which is the indicator of first failure. The nanoparticles had no significant effect on the initial stiffness of the T-joint, as shown in Table 9.1. Other studies have reported that small additions of carbon nanoparticles to carbon-epoxy laminates does not significantly increase the Young’s modulus [49, 323, 324], and this would account for the stiffness of the T-joints being unchanged. First failure always occurred within the delta fillet region and was caused by the initiation of a short debond crack between the stiffener laminate and resin-rich fillet region where the stress concentration is highest. This is a common region for first failure in composite T-joints subjected to stiffener pull-off loading [375, 376, 379, 382-384, 393]. With increasing displacement, the curves continued to rise with no significant damage growth until the ultimate failure load. The unmodified T-joint and the joints containing CNTs and GNPs failed near catastrophically by rapid, large-scale crack growth along the skin/flange connection and along the mid-plane of the stiffener. This cracking caused sudden and large drops in the load-bearing capacity of these joints (Figs. 9.8a, 9.8b and 9.8d). In contrast, the T-joint containing CNFs experienced a smaller series of load drops beyond the ultimate load, and this stable, progressive failure was due to the suppression of large-scale crack growth along the skin/flange connection and along the mid-plane to the stiffener. Instead, damage to the CNF-modified joint was confined to the delta fillet region where multiple microcracks developed in the radius bend region of the flange laminate but did not extend out of this region (see Fig. 9.7).
failure of the CNF-modified joint occurred at the skin laminate and then by failure at the clamped end of the skin (Fig. 9.8c). This clearly reveals that when the epoxy matrix contains CNFs then it has the toughness to resist large-scale cracking along the connections of the T-joint, and instead failure occurred in the laminate material.

Fig. 9.6. (a) Applied load-vertical displacement curves for the unpinned T-joints containing unmodified, CNT, CNF and GNP modified epoxy matrix. (b) Effect of nanofiller type on the load-at-first failure and ultimate load of the unpinned T-joints.
**Fig. 9.7.** Photographs of crack propagation and fracture modes of the unpinned composites T-joints, containing unmodified, CNT, CNF and GNP modified epoxy matrix, at multiple cross-head displacements.
Fig. 9.8. Final failure mode of the unpinned composite T-joints containing (a) unmodified, (b) CNT modified, (c) CNF modified and (d) GNP modified epoxy matrix.

Table 9.1. Properties of the unpinned and z-pinned T-joints containing unmodified, CNT modified, CNF modified, and GNP modified epoxy matrix. The percentage values within the brackets show the measured improvements over the unmodified joint containing no z-pins.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Elastic stiffness (N/mm)</th>
<th>Load-at-first failure (N)</th>
<th>Ultimate load (N)</th>
<th>Absorbed energy capacity until ultimate failure (N.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unpinned</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unmodified</td>
<td>390 ± 44</td>
<td>589 ± 81</td>
<td>1590 ± 70</td>
<td>4.37 ± 0.16</td>
</tr>
<tr>
<td>CNT</td>
<td>404 ± 27 (3.5 %)</td>
<td>845 ± 54 (43%)</td>
<td>1890 ±110 (19%)</td>
<td>7.80 ± 0.99 (79%)</td>
</tr>
<tr>
<td>CNF</td>
<td>393 ± 41 (0.8 %)</td>
<td>987 ± 92 (68%)</td>
<td>2310 ± 21 (46%)</td>
<td>13.0 ± 1.1 (200%)</td>
</tr>
<tr>
<td>GNP</td>
<td>385 ± 29 (-1.2 %)</td>
<td>763 ± 71 (30%)</td>
<td>1640 ± 51 (3.3%)</td>
<td>4.64 ± 25 (6.4%)</td>
</tr>
<tr>
<td><strong>Z-pinned (2 vol% and 5 mm long and 0.10 mm dia)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>z-pin</td>
<td>400 ± 39 (2.5 %)</td>
<td>575± 93 (-2.4%)</td>
<td>2040 ±130 (29%)</td>
<td>12.7± 1.6 (190%)</td>
</tr>
<tr>
<td>z-pin + CNT</td>
<td>399 ± 40 (2.4 %)</td>
<td>857 ± 110 (46%)</td>
<td>2450 ±110 (54%)</td>
<td>22.1 ± 1.5 (405%)</td>
</tr>
<tr>
<td>z-pin + CNF</td>
<td>397 ± 35 (1.8 %)</td>
<td>1001± 140 (70%)</td>
<td>2740 ±140 (73%)</td>
<td>24.0 ± 1.7 (450%)</td>
</tr>
<tr>
<td>z-pin + GNP</td>
<td>395 ± 16 (1.4 %)</td>
<td>773 ± 150 (31%)</td>
<td>2160 ±86 (36%)</td>
<td>13.2 ± 2.4 (204%)</td>
</tr>
</tbody>
</table>
The structural properties of the T-joints containing the nanofillers are given in Table 9.1 and plotted in Fig. 9.6. It is evident that the magnitude of any property improvement depends on the type of carbon nanoparticle. The less effective was the GNPs, which improved the failure initiation load (~30%) but did not increase significantly the other properties. Within the bounds of experimental scatter (defined by the standard deviation values given in Table 9.1), the GNPs did not increase the ultimate load or absorbed energy capacity. The CNTs were effective at increasing the failure initiation load (43%), ultimate load (19%) and absorbed energy capacity (79%) of the T-joint. The most effective nanoparticle was the CNFs, which increased greatly the failure initiation load (68%), ultimate load (46%) and absorbed energy capacity (197%). These improvements are similar or greater than that achieved using other T-joint strengthening methods. For example, Burns et al. [384] showed experimentally and numerically that optimization of the ply orientations within the stiffener laminate to minimize interlaminar stresses increased the failure initiation load (up to by 84%), ultimate failure load (up to 39%) and energy absorption capacity (up to 144%) of a carbon-epoxy T-joint under stiffener pull-out loading. As another example, Koh et al. [207] found that z-pins did not increase the failure initiation load of carbon-epoxy T-joints, although they increased the ultimate load (up to 76%). The improvements to the joint properties gained using CNFs were similar to other strengthening techniques such as ply optimization or z-pinning, as discussed in Section 9.3.2, but is simpler to apply during manufacturing.

9.3.1.1 Strengthening mechanisms from the carbon nanofillers

The strengthening processes for the T-joints can be explained via the toughening mechanisms imparted by the nanofillers. From Chapters 5 to 8, the interlaminar fracture toughness properties of the laminate materials used in the T-joints were measured for mode I and mode II crack propagation. The key toughening mechanism due to the nanofillers were identified. However, local crack propagation mode within the T-joint can vary along the bond-line and is dependent on the loading condition (i.e. bending or tension) [2, 375, 376, 384]. Many numerical studies revealed that carbon fibre composite T-joints subjected to a pull-off load to the stiffener exhibit crack initiation within the fillet region under a combination of through-thickness tensile stress and in-plane shear interlaminar stress [45, 376, 384]. Crack growth along the bond-line of the stiffener mid-plane typically occurs under a mode I interlaminar stress state, whereas crack
propagation along the skin/flange connection occurs under a mixture of modes I and II interlaminar stress conditions [45]. Examination fracture surface of the unmodified T-joint and other joints revealed the crack propagation behaviour that occurred. The fracture surface along the stiffener joining interface showed evidence of mode I type crack growth due to the tensile tearing of the epoxy interfacial layer, as shown in Fig. 9.9. In contrast, the fracture surfaces along the skin/flange connection showed both tensile tearing (mode I) and shear echelon cracks (mode II) along the epoxy interfacial layer.

![Fig. 9.9. Schematic and scanning electron microscope (SEM) images of crack propagation along the fracture surfaces of the T-joint. SEM images were taken from the crack faces of the unmodified T-joint.](image)

Fractographic examination along the delamination surface of the carbon nano-reinforced T-joints revealed multiple toughening/strengthening mechanisms imparted by the CNTs, CNFs and GNPs. Fig. 9.10 presents scanning electron microscope (SEM) images along the fracture surface of the skin laminate near the delta fillet region. The intrinsic toughening mechanisms identified along the epoxy interfacial layer include interfacial debonding between the nanofiller and epoxy matrix, and plastic void growth of the epoxy surrounding the debonded nanoparticles. These intrinsic processes occur within the crack tip process zone and through crack-tip plasticity mechanisms, as further detailed in Section 8.3.1 (Chapter 8). Plastic void growth processes were more apparent in the joints containing CNFs and then CNTs when compared to the GNP-reinforced T-joints. As mentioned in Chapters 6 and 8, the void growth mechanisms is responsible
for increasing the initiation mode I interlaminar fracture toughness. Ladani et al. [98] reported that the number and relative size of voids formed near the nanoparticles was much greater with CNFs compared to GNP s. Therefore, the capacity to generate more plastic void growth process using CNFs is responsible for these nanoparticles being the most effective at increasing the failure initiation load as well as the ultimate failure load of the T-joint. These aspects are further explained in Section 9.3.4.

**Fig. 9.10.** SEM images of the fracture surface along the delaminated surface along the skin region near the fillet region of the unpinned T-joints containing (a) unmodified, (b) CNT, (c) CNF and (d) GNP modified epoxy matrix. Key toughening mechanisms are indicated.
The extrinsic toughening mechanisms were crack bridging and pull-out of the nanofillers, as presented in Fig. 9.10 and Fig. 9.11. The nanofillers generate discrete traction loads between the crack faces along the epoxy interfacial layer, thereby increasing the pull-off load to propagate the crack. As shown in Fig. 9.10c and 9.11a, the CNFs and CNTs, respectively, also bridged the echelon cracks due to their small size and fibrous morphology which also resisted the crack growth. The GNPs did pull-out from epoxy interfacial layer however, they did not bridge the echelon cracks due to their planar morphology, which can explain the small increase for the mode II interlaminar fracture toughness reported in Chapter 8 and the structural properties of the T-joint.

**Fig. 9.11.** SEM images of the fracture surface along the skin region 10 mm away from the fillet region of the unpinned T-joints containing (a) CNT and (b) GNP modified epoxy matrix. (Note: SEM images for the CNF reinforced joint could not be taken the crack did not complete propagate between the skin/flange laminate.)

### 9.3.2 Load-bearing properties of T-joints containing z-pins

Fig. 9.12a presents the load-displacement curves measured for the unpinned and z-pinned composite T-joints containing the unmodified epoxy. The structural properties of the unpinned and z-pinned T-joints containing no nanofillers are given in Table 9.1 and plotted in Fig. 9.12b. The load-displacement response of the z-pinned T-joints exhibited a similar profile as the unpinned T-joints with an initial linear elastic response followed by a small load drop. The z-pins had no significant effect on the initial stiffness of the T-joint, as shown in Table 9.1. Similar findings
were also reported by Koh et al.[26], where z-pins does not significantly enhance the elastic stiffness as they are dominates by the reinforcing fibres. At the first failure condition, damage initiation occurred within the z-pinned T-joint where short debond cracks were formed between the stiffener laminates and radius bend region near the delta fillet region. The introduction of z-pins within the joints containing the unmodified epoxy did not delay the crack initiation near the fillet region, therefore, the load-at-first failure remains unchanged when compared to the unmodified joint, as shown in Fig. 9.12. Allegri et al.[394], Park et al.[395] and Greenhalgh et al.[396] also observed no improvements on the load-at-first failure with changes in the pin diameter or inserting the z-pin within the resin-rich region. This is due the z-pins providing no reduction in the geometric stress concentration near the edges of the delta fillet region.

![Graph](image)

**Fig. 9.12** (a) Load-vertical displacement curves the measured failure load values for the unpinned and z-pinned composite T-joints containing unmodified modified epoxy matrix. (b) Effect of z-pins on the load-at-first failure and ultimate load of the T-joints.

Past first failure, the curves for the z-pinned composite T-joints continue to rise with no significant delamination until the ultimate load (see Fig. 9.12a). The z-pins improved the ultimate failure load and absorbed energy capacity of the joint containing the unmodified by 29% and 190%, respectively, which higher than the values measured for unmodified, CNT-reinforced, and GNP-reinforced joint. After the ultimate load with cross-head extension, the z-pinned joints containing the unmodified epoxy exhibited incremental load drops where progressive crack growth occurred along the mid-plane of the skin/flange laminate and the bond-line of the stiffeners.
laminates. This is was due to the suppression of crack growth along the bond-line due to the large scale toughening by the z-pins between the delaminated faces [26, 207], which is further discussed later. The final failure mode of the z-pinned T-joint containing the unmodified epoxy was by the rupture of the flange laminate as shown in Fig. 9.13. The final failure mode of flange rupture has been reported for T-joints containing long z-pins [26]. It is important to note that z-pins can act as geometric defects by imparting fibre crimp, local fibre misalignment and resin rich regions, which can degrade the local mechanical properties under various loading modes (i.e. tension, compression and flexural) [35, 36, 213]. This was where failure of the skin and flange laminates were present for the z-pinned T-joints.

![Fig. 9.13. Final failure mode of (a) unpinned and z-pinned T-joints containing unmodified epoxy matrix.](image)

9.3.2.1 Strengthening mechanisms from the z-pins

Computer tomography (CT) scans of the z-pinned T-joints revealed multiple strengthening mechanisms. The z-pins strengthen the T-joint through extrinsic toughening processes near the delta fillet region, which includes elastic deformation, interfacial debonding, snubbing and pull-out of the z-pins along the cracked skin/flange laminates [26, 45, 207], as presented in Fig. 9.14. This bridging process between the skin and flange laminates generates large traction loads that suppresses crack growth along the bond-lines, which increases the ultimate load and absorbed energy capacity. The gradual load-drop exhibited by the z-pinned T-joints containing the unmodified epoxy beyond the ultimate load (see Fig. 9.12a) was due to the large-scale bridging of the z-pins along the joining interface at long delamination lengths.
9.3.3 Load-bearing properties of T-joints containing both nanofillers and z-pins

Fig. 9.15a presents the load-displacement curves measured containing both carbon nanofillers and z-pins (i.e. multi-scale reinforced). The structural properties of the multi-scale reinforced T-joints are presented in Table 9.1 and Fig. 9.15b. The load-displacement response of the multi-scale reinforced T-joints exhibited initial linear elastic behaviour followed by a small load drop. As reported for the T-joints containing either the nanofillers or z-pins, hybridizing two reinforcements had no significant effect on the initial stiffness of the T-joint (see Table 9.1). This, again, was due to nanofillers or z-pin providing not stiffness enhancement in the laminates as further described in Sections 9.3.1 and 9.3.2. At the first failure condition (as described in Sections 9.3.1 and 9.3.2), the magnitude of the initiation failure load z-pinned T-joints containing CNTs, CNFs or GNP s were similar to the corresponding carbon nano-reinforced unpinned joints (see Fig. 9.15b), when considering the standard deviations. After first failure, the curves for multi-scale reinforced T-joints continue to rise with no significant delamination until the ultimate load (see Fig. 9.15a).
Fig. 9.15. (a) Load-vertical displacement curves the measured failure load values for the composite T-joints containing unmodified epoxy, CNT + z-pins, CNF + z-pins and GNP + z-pins. (b) Effect of carbon nanofiller type on the load-at-first failure of the unpinned and z-pinned T-joints.

The ultimate failure load and the absorbed energy capacity values of the unpinned and z-pinned T-joints are given in Fig. 9.16 and Table 9.1. The magnitude of these properties are dependent on the nanofiller types and/or the addition of the z-pins. When comparing the individual strengthening effect, the unpinned T-joint containing the CNFs exhibited a much greater improvement on the ultimate failure load (i.e. 46%) and absorbed energy capacity (i.e. 200%) when compared to other nanofillers used, and even the z-pins when used separately. However, as shown in Table 9.1, substantial improvements were observed the ultimate failure load and load at first failure for the multi-scale reinforced T-joint containing (a) CNTs and z-pins or (b) CNFs and z-pins. The CNFs, when used within the z-pinned T-joints, were the most effective nanoparticle at increasing the failure initiation load (~70%), ultimate failure load (~73%) and absorbed energy capacity (~450%). The GNPs were the least effective, which improved the failure initiation load (~31%) but did not significantly increase the ultimate load and the absorbed energy capacity.

When taking the individual strengthening contributions (see Table 9.1) from the nanofillers or z-pins, the improvement exhibited by the multi-scale reinforced T-joints on the ultimate failure load is simply additive. However, the absorbed energy capacity measured for the z-pinned T-joints containing CNTs and CNFs were much greater than the expected additive value
from the corresponding nanofillers ($\Delta U_{nano}$) and the z-pins ($\Delta U_{z-pins}$) used (see Fig. 12b). The percentage synergistic enhancements were calculated by using:

$$Synergy\% = \left( \frac{\Delta U_{(nano+z-pins)}}{\Delta U_{(nano)} + \Delta U_{(z-pins)}} - 1 \right) \times 100\%$$ (1)

where $\Delta U_{nano+z-pins}$ is the contribution of the absorbed energy capacity value from the multi-scale reinforced T-joint. The synergistic improvement for the CNT- and CNF-reinforced z-pinned T-joints are ~50% and ~15%, respectively. These greater than expected additive enhancement correlates to percentage synergy values in the mode I interlaminar fracture toughness properties reported for the CNT (~38%) and CNF (~19%) toughened z-pinned composite laminates in Section 8.3.3 (Chapter 8). No synergistic enhancements were measured for the T-joint containing GNPs.

**Fig. 9.16.** Effect of nanofiller type on the (a) ultimate load, and (b) the absorbed energy capacity of the unpinned and z-pinned T-joints.

Past the ultimate load with cross-head extension, the CNT- and CNF-reinforced z-pinned T-joints also underwent stable load drops beyond the ultimate load, however, delamination cracks along the bond-line were suppressed and damage was confined within the delta fillet region where multiple microcracks were formed within the radius bend region, as shown in Figs. 9.17a and 9.17b. The CNT- and CNF-reinforced z-pinned joints exhibited a final failure mode by rupture of the skin laminate near the fillet region followed by skin failure near the clamps. Similarly to the z-pinned T-joint containing the unmodified epoxy, the GNP-reinforced z-pinned joints exhibited
incremental load drops, where progressive crack growth occurred along the mid-plane of the skin/flange laminate and the final failure mode was governed by the rupture of the flange laminate (see Fig. 9.17c).

Fig. 9.17. Final failure mode of the multi-scale scale reinforced T-joints containing (a) CNT-modified, (b) CNF-modified and (c) GNP-modified epoxy.
9.3.3.1 Strengthening mechanisms from the nanofillers and z-pins

It is expected that, improvements in the structural properties of the multi-scale reinforced can be explained the toughening mechanisms imparted by the nanofillers and z-pins, as described in detail within Sections 9.3.1.1 and 9.3.2.1, respectively. The enhancements in the load-at-first failure, ultimate load and absorbed energy capacity were governed by the intrinsic toughening mechanisms (i.e. void growth and interfacial debonding) invoked by the nanofillers and the extrinsic toughening mechanism (i.e. bridging and pull-out) from both the nanofillers and z-pins along the bond-lines. For the multi-scale reinforced T-joint containing (a) CNTs and z-pins and (b) CNFs and z-pins, it is expected that 1D nanofiller would also enhance the z-pin toughening efficacy by enhancing the traction energy due to z-pin pull-out. However, the z-pin did not completely pull-out between skin/flange laminate for these T-joints as damage was confined within the fillet region, with minimal delamination along the bond-lines. This suggests that maximum toughening is achieved, where the high stresses required to propagate the crack along the bond-lines pre-emptively results in the failure of the composite T-joint. These aspects are further discussed in the next section of this chapter with consideration interlaminar fracture toughness properties reported in Chapter 8

9.3.4 Comparison of interlaminar fracture toughness and structural properties of the T-joints

The first failure occurs by the initiation of crack growth within the delta fillet region under a combination of mode I and mode II interlaminar stresses [2, 378, 383, 384]. The initiation and steady-state interlaminar fracture toughness values reported in Chapter 8 for the laminates materials used in the T-joints are presented in Fig 9.18a and Fig. 9.19a. Considering that the onset of crack propagation depends on the initiation fracture toughness, the addition of the carbon nanofillers did not provide any significant improvements to the mode II initiation critical strain energy release rate. Therefore, the improvements to the load-at-first failure values of the T-joints were due to the nanofillers increasing the mode I initiation energy (see Fig. 9.18a) through intrinsic toughening mechanisms previously discussed. Fig. 9.18b presents a plot showing that the failure initiation load for the T-joint is directly proportional with the mode I initiation interlaminar fracture toughness values measured for the corresponding laminates.
Fig. 9.18. (a) Mode I and mode II initiation interlaminar fracture toughness of multi-scale reinforced composites. (b) Plot of mode I initiation interlaminar fracture toughness against the load-at-failure.
**Fig. 9.19.** (a) Mode I and mode II steady-state interlaminar fracture toughness of multi-scale reinforced composites. Plots of the mode I and mode II steady-state interlaminar fracture toughness versus the (b) ultimate load and (c) absorbed energy capacity up to the ultimate load of the composite T-joints.
Figs. 9.19b and 9.19c present plots showing the effect of the steady-state interlaminar fracture toughness values on the ultimate failure load and the absorbed energy capacity of the T-joints. For the unpinned joint, there is some correlation between the structural properties of the joint and the mode I and II steady-state interlaminar fracture toughness. It is important to note that the crack propagation along the bond-line occurs under a combination of both modes I and II [45]. Therefore, these structural properties are not exclusively dependent on the either the mode I or mode II fracture toughness value. When using the interlaminar fracture toughness values for the z-pinned T-joint, the correlation with the structural properties is good yet skewed when considering that the steady-state interlaminar fracture toughness of the z-pinned laminates are much greater than the nano-reinforced laminates (see Fig. 9.19b and 9.19c). The fracture toughness values for the z-pinned laminates reported are for large crack-propagation lengths (i.e. 25–30 mm), which is not representative of the delamination length or failure modes observed for the z-pinned T-joints.

These findings indicate that increasing the steady-state fracture toughness via the addition of nanofillers or/and z-pins results in increased resistance to crack growth along the skin/flange interface and the mid-plane to the stiffener. Improvement to structural properties can be attributed to intrinsic and extrinsic toughening mechanisms (i.e. bridging and pull-out of the nanofillers) that occur along the bond-line, and the large-scale bridging of the z-pins along the skin/flange connection which can also be enhanced with the addition of fibrous nanofillers.

9.4 CONCLUSION

The structural properties of the composite T-joints subjected to pull-off loads along the stiffener can be significantly enhanced by the addition carbon nanofillers and the insertion of carbon fibre z-pins. The nanofillers and z-pins promoted no improvements on the elastic stiffness of the joints due low weight fraction of the nanofillers and the stiffness being dominated by the reinforcing fibres. The CNTs, CNFs and GNP were effective at increasing the load-at-first failure of the unpinned and z-pinned T-joints by supressing early onset of cracks in the delta fillet region. The CNFs were the most effective at improving the initiation failure load. The nanofillers increased the mode I crack initiation energy and, as a result, the load-at-first failure of the T-joint via interfacial debonding and plastic void growth within the damage process zone. The CNTs,
CNFs and z-pins were also effective at improving the ultimate load and absorbed energy capacity of the T-joint. These were attributed by the intrinsic and extrinsic toughening mechanism invoked by the nanofillers surrounding the crack-tip and the large-scale bridging of the z-pins that suppresses large-scale crack growth. However, substantial improvement was achieved to these properties of the multi-scale reinforced T-joint when combining the CNTs or CNFs with z-pins, where synergistic enhancements were recorded for the absorbed energy capacity.

The results presented in this chapter contribute to the fundamental understanding of the strengthening mechanisms of carbon nanofillers and z-pins on the structural properties of composite joints. Considering that the crack propagation modes along the bond-line for composite T-joints occur under various interlaminar stress-states, finite element analysis of this multi-scale toughening concept on the load-bearing properties of T-joint may help identify the interactions between z-pins and nanofillers. These aspects are right for further inquiry and are recommendations for future study from this PhD project.
Chapter 10: Liquid metal synthesis of 2D aluminium oxide nanoplatelets in toughening epoxy polymers

Abstract

This chapter presents an experimental investigation into the strengthening and toughening properties of two-dimensional platelets of boehmite (γ-AlO(OH)) and alumina (γ-Al2O3). Using a liquid metal alloy reaction process, two-dimensional metal oxide hydroxide and oxide nanoplatelets were synthesised and then used for reinforcing epoxy polymer composites at different weight fractions up to 10%. Both boehmite and alumina platelets significantly increased the tensile modulus, yield stress and fracture toughness of the epoxy polymers. Of the two materials, the boehmite platelets were more effective than the alumina platelets in increasing the tensile modulus (up to 27%) and ultimate strength (up to 14%) of the epoxy. In contrast, the alumina platelets promoted a 50% greater improvement to the mode I fracture energy when compared to using boehmite platelets. The primary mechanisms responsible for the measured property improvements are identified.

The research work presented in this chapter has been published in the following:


10.1 INTRODUCTION

Metal-based oxides, such as aluminium oxides, have a wide range of applications which include uses in pharmaceuticals, medical implants, abrasives and electrical insulators [397-400]. Alumina (Al2O3) is also employed as a filler material to increase the mechanical properties of polymers due to its high stiffness and strength. Spherical or platelet-based Al2O3 nanofillers can increase the
tensile properties, fracture toughness and fatigue strength of epoxy polymers [71, 81, 89-91]. Boehmite (AlO(OH)) nanofillers, which is a hydrated precursor in the processing of alumina, can also improve the mechanical properties of polymers as well as the fire-retardancy properties [82, 401]. The magnitude of the property improvements using either alumina or boehmite particles depend on their morphology, size and concentration [71, 82, 90]. Boehmite particulates, which are used for synthesising various types of aluminium oxides (e.g. α-Al₂O₃, γ-Al₂O₃), have been produced through several processes [82, 402, 403]. These include solid-state decomposition of gibbsite (Al(OH)₃) [404], precipitation from an acidic or basic aluminium salt solution via neutralisation and ageing [405], and sol-gel processing [406].

More recently, a new technique called liquid metal synthesis has been reported as an effective way of producing two-dimensional metal oxide nanosheets [87, 407-412]. Such liquid metaloxides are made by alloying a low melting temperature metal such as gallium with transition and post-transition metals [87, 403, 407, 408, 412]. Galinstan is one such example of a eutectic alloy composed of gallium (68.5 wt%), indium (21.5 wt%) and tin (10 wt%), with a low melting temperature (i.e., 11°C to 19°C) [87, 403, 413]. Zavabeti et al. [87] recently discovered that low-dimensional sub-nanometer thick sheets of metal oxides can be synthesised by alloying various reactive metals, such as hafnium, aluminium and gadolinium, with galinstan. Ultra-thin sheets of metal oxides are then formed at the liquid galinstan surface, which can be exfoliated via a reaction with deionised water [13]. The continuous generation of low-dimensional metal oxide nanoparticles of various shapes (e.g. platelets and rods) can be achieved until eventually all the reactive alloying elements within the galinstan are depleted. An extensional study by Zavabeti et al. [403] also reported that high flux membranes containing sub-nanometre sheets and fibres of γ-AlO(OH) and γ-Al₂O₃ could be produced for water filtration applications using the liquid metal synthesis process. Benefits of this liquid metal approach include the reusability of galinstan for multiple synthesis cycles and low input energy at room temperature [87, 403]. Additionally, two dimensional (2D) nanosheets of aluminium oxides produced by liquid metal synthesis [13] have been reported to exhibit a higher Young’s modulus compared to other aluminium oxide fillers [414, 415]. However, there are no reports into the effect of reinforcing polymers with low-dimensional boehmite or alumina nanoplatelets produced from liquid metals. The filler aspect ratio and two-dimensional morphology may result in higher property improvements compared to oxides.
produced from other processes. Furthermore, it is not clear which of the two types of platelets (i.e. \(\gamma\)-AlO(OH) and \(\gamma\)-Al\(_2\)O\(_3\)) is more effective in strengthening and toughening bulk epoxy polymers.

This chapter presents a study on the effects of low-dimensional \(\gamma\)-AlO(OH) and \(\gamma\)-Al\(_2\)O\(_3\) platelets, synthesised using liquid metal processing, on the mechanical and fracture properties of an epoxy polymers. Boehmite (\(\gamma\)-AlO(OH)) platelets are grown on the surface of liquid metal (galinstan alloyed with aluminium), and then thermally annealed to form \(\gamma\)-Al\(_2\)O\(_3\) platelets. These platelets are added to an epoxy at different weight fractions up to 10%. Tensile and fracture tests are conducted to assess the improvements in the mechanical properties of the epoxy. The improvements to the tensile and fracture toughness properties derived from using the \(\gamma\)-AlO(OH) or \(\gamma\)-Al\(_2\)O\(_3\) platelets are then compared to alumina particles of previous reports to show the enhancement that is achieved from the introduced procedure. Detailed microscopic examinations are conducted to identify the strengthening and toughening mechanisms responsible for the property improvements.

10.2 MATERIALS AND EXPERIMENTAL METHODOLOGY

10.2.1 Liquid metal synthesis of boehmite and alumina platelets

A liquid metal water-based synthesis process [87, 403] was used for synthesising platelets of boehmite and, following the thermal annealing, alumina. The multi-stage synthesis process is shown in Figs. 10.1, 10.2, 10.3 and 10.4. A eutectic alloy of galinstan was prepared by melting and mixing 68.5 wt% gallium, 21.5 wt% indium and 10 wt% tin at 250°C. These precursor materials had a purity of ~99.99% (Roto Material Inc.). Further details on the preparation of galistan are provided in [87, 403]. The galinstan (in 50 g batches) was then mechanically alloyed with Al rods (>99.99% purity, ~2-3 mm length, 0.58 mm diameter) at ~3.3 wt% by grinding for 20 minutes using a pestle and mortar at room temperature (25°C). The aluminium embrittles and becomes soluble when ground thoroughly with galinstan [416]. The grinding was performed in an inert atmosphere (\(\text{N}_2\) gas, <2 ppm \(\text{O}_2\)) at 25°C to stop oxidation of the aluminium before it dissolved in the galinstan, as shown in Fig. 10.1.
Deionised water was then added to the liquid galinstan-aluminium alloy to synthesise boehmite (see Fig. 10.2) from the reaction process:

$$2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2$$  \hspace{1cm} (1)

**Fig. 10.2.** Schematic depicting the liquid metal synthesis process of $\gamma$-AlO(OH) where (a-b) deionised water is added to a vial containing the galinstan-aluminium liquid metal alloy resulting in the formation of a thin bayerite ($\alpha$-Al(OH)$_3$) layer at the alloy surface. (c) Delamination of bayerite sheets due to nucleation of hydrogen gas bubbles between the liquid metal alloy and water interface.
The liquid metal reaction formed an ultra-thin film of $\alpha$-Al(OH)$_3$ along with H$_2$ gas at the liquid galinstan surface (Fig. 10.2c). Nucleation of H$_2$ bubbles forced the $\alpha$-Al(OH)$_3$ to delaminate as thin sheets into the water phase of the solution. The $\alpha$-Al(OH)$_3$ sheets were extracted from the solution using a pipette (see Fig. 10.3a) and drop-casted onto a glass petri dish. The $\alpha$-Al(OH)$_3$ was then converted into $\gamma$-AlO(OH) at 170°C (see Fig. 10.3b) via the following reaction:

$$\text{Al(OH)}_3 \rightarrow \text{AlO(OH)} + \text{H}_2\text{O}$$  \hfill (2)

The $\gamma$-AlO(OH) platelets were extracted from the petri dish and dried at 200°C for 24 hours (see Fig. 10.3c). As shown in Fig. 10.4, the $\gamma$-AlO(OH) platelets consists of multiple sheets, each measuring ~1.2 – 2 nm as reported in [403].

**Fig. 10.3.** Schematic depicting the liquid metal synthesis process of $\gamma$-AlO(OH) where (a) Bayerite solution extracted via pipette and (b) drop-casted onto petri dish heated at 170°C to convert bayerite to boehmite. (c) Formation of $\gamma$-AlO(OH) flakes after conversion of bayerite.
The γ-Al₂O₃ platelets were synthesised by annealing γ-AlO(OH) at 550°C for 15 hours. The conversion process is:

\[ 2\text{AlO(OH)} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \]  

The mean diameter and thickness of the γ-AlO(OH) and γ-Al₂O₃ platelets, after three-roll milling within the epoxy matrix, were measured using a scanning electron microscope (FEI Nova NanoSEM) and digital image correlation software (ImageJ, NIH, USA). The mean thickness of the platelets was measured from scanning electron micrographs of the fracture surface of the tensile test samples. This process of measuring the particle size was adapted from [371, 373]. The distributions of the diameter and thickness of the two types of platelet are presented in Fig. 10.5. The mean diameter and thickness of the γ-AlO(OH) are both slightly larger than the γ-Al₂O₃. The detailed morphology and crystallinity of the individual γ-AlO(OH) and γ-Al₂O₃ sheets can be found in [403].
10.2.2 Manufacturing of bulk epoxy polymer composites

The $\gamma$-AlO(OH) and $\gamma$-Al$_2$O$_3$ platelets were added to a low-temperature cure epoxy at different weight fractions (0% (i.e. unmodified), 1%, 2%, 5%, 10%). The epoxy was a two-part bisphenol-A and bisphenol-F based resin system (Resin-105 from West System®) [257]. The platelets were initially mixed mechanically into the resin for five minutes using a stirring rod and then further dispersed using a three-roll mill (Dermamill 100). The three-roll milling process is described in Section 3.2.1 (Chapter 3). Following the milling process, the amine hardening agent hardener (Resin 206 from West System®) was added to the mixtures at the weight ratio of 1-to-5 to activate curing. Before curing, the mixtures were degassed in a vacuum chamber for five minutes to remove entrapped air. The liquid mixtures were then cast in moulds to produce coupons for tensile testing, as shown in Fig. 10.6. The double cantilever beam (DCB) test coupons were manufactured using the process described in Section 3.2.3 (Chapter 3). Before testing, the coupons were cured at room temperature following the manufacturers’ guidelines [257], but without an elevated temperature post-cure.
10.2.3 Tensile and fracture toughness testing

The tensile properties of the unmodified epoxy and different types of epoxy polymers were measured using the specimen design (ASTM D638 Type IV configuration) shown in Fig. 10.7a. The tensile tests were conducted using a 10 kN Instron universal testing machine operated at an extension rate of 1 mm/min in accordance with ASTM D638 [311]. The strain was measured using an extensometer (initial gauge length of 25 mm) attached to the gauge section of the tensile sample. A minimum of five samples were tested for each material. The Young’s modulus was calculated using the data up to a 0.2% strain range. The yield stress was measured using the 0.2% strain offset method.

The mode I fracture toughness of the materials was measured using the DCB test. The DCB specimen consisted of a 2 mm thick layer of the epoxy-based material sandwiched between two bonded composite adherends (Fig. 10.7b). Each adherend was made of unidirectional T700 carbon fibre/epoxy composite (VTM264, Lavender Composites, Australia). The pre-crack in a DCB sample was made by initially embedding a polytetrafluoroethylene (PTFE) film measuring 42.5 mm long and 11 µm thick at the mid-plane of the epoxy layer, followed by wedging to sharpen the crack tip and to extend the crack length to 50 ± 2.5 mm. The DCB test involved applying a
monotonically increasing crack opening displacement to the pre-cracked end of the specimen at a rate of 1 mm/min using a 10 kN capacity Instron test machine (ISO 25217 [259]). The crack was forced to grow incrementally along the mid-plane of the epoxy-based layer by loading and unloading. At each increment, the crack opening force, crack opening displacement and crack length were measured, which were then used to calculate the mode I fracture toughness expressed as critical strain energy release rate \( (G_{\text{Ic}}) \) and the critical stress intensity factor \( (K_{\text{Ic}}) \). Five DCB samples were tested for each type of composites.

![Fig. 10.7. Schematic of (a) the tensile test specimen and (b) double cantilever beam (DCB) specimen.](image)

### 10.3 RESULTS AND DISCUSSION

#### 10.3.1 Tensile properties

The effect of \( \gamma \)-AlO(OH) and \( \gamma \)-Al\(_2\)O\(_3\) platelets on the tensile properties of the epoxy polymer is shown in **Fig. 10.8** and **Fig. 10.9**. The Young’s modulus increased with the weight fraction of platelets, with \( \gamma \)-AlO(OH) providing a ~14-33% greater stiffening effect than \( \gamma \)-Al\(_2\)O\(_3\), as shown in **Fig. 10.9a**. The higher moduli of the \( \gamma \)-AlO(OH)/epoxy composites are statistically significant with a 99.8% confidence based on an unpaired \( t \)-test. Zavabeti et al. [403] reported that the DMT
(Derjaquin-Muller-Toporov) modulus of the $\gamma$-AlO(OH) (496 GPa), which is similarly used in the reinforced epoxy polymers studied here, is approximately five times greater than the $\gamma$-$\text{Al}_2\text{O}_3$ (96 GPa) platelets. Using the stiffness values of the boehmite and alumina fillers ($E_f$), a modified Halpin-Tsai analytical model [417] was used to calculate the tensile modulus ($E_c$) of the epoxy polymers containing randomly oriented platelets using the expression below:

$$E_c = \frac{3E_m}{8} \left[ \frac{2w}{t} \left( \frac{E_f}{E_m} \right)^{-1} V_f + 1 \right] + \frac{5E_m}{8} \left[ \frac{4w}{t} \left( \frac{E_f}{E_m} \right)^{-1} V_f + 1 \right]$$

where the tensile modulus of the epoxy matrix and the volume fraction of the platelets are denoted by $E_m$ and $V_f$, respectively. The model used considers the diameter (i.e. width) ($w$) and thickness ($t$) of the platelets presented in Fig 10.5. The analytically calculated tensile modulus are in good agreement with experimentally measured values at filler contents up to 2 wt% (see Fig. 10.9a). However, the analytical model overpredicts the stiffness values of the epoxy polymers containing higher contents (i.e. greater than 2 wt%) of $\gamma$-AlO(OH) or $\gamma$-$\text{Al}_2\text{O}_3$ platelets. This may be attributed to the agglomeration of the platelets caused by inadequate dispersion, which is a common problem with dispersing high concentration of particles [100]. Such agglomeration results in a plateau in the stiffness enhancement observed (see Fig. 10.9a) with filler content.

![Fig. 10.8. Tensile stress-strain curves for the epoxy with different weight contents of (a) $\gamma$-AlO(OH) and (b) $\gamma$-$\text{Al}_2\text{O}_3$ platelets.]
Fig. 10.9. Effect of increasing the concentration of γ-AlO(OH) and γ-Al₂O₃ on the (a) Young's modulus, (b) 0.2% offset yield stress and (c) ultimate tensile strength of the epoxy polymers.

The yield stress of the epoxy increases with the weight percentage of the filler, with the γ-AlO(OH) giving a ~10-13% greater enhancement than the γ-Al₂O₃ (Fig. 10.9b). The ultimate strength of the epoxy increased to ~14% with the γ-AlO(OH) content of up to 5 wt%, but there was a slight loss in the strengthening effect at the highest content of 10 wt% (see Fig. 10.9c). This is also attributed to poor dispersion and agglomeration of the platelets at higher contents [100]. The agglomerated platelets act as localised stress raisers within the polymer matrix [401, 418],

...
causing a reduction in the ultimate strength as well as minimising the stiffening efficacy. The γ-Al₂O₃ had no statistically significant reinforcing effect on the ultimate strength of the composite, even at the highest content. The difference in the strengthening effect between the two types of platelet is attributed to differences in their bonding to the epoxy matrix. Fractographic examination of the fractured tensile test specimens revealed that a large proportion of γ-AlO(OH) platelets ruptured (see Fig. 10.10a) whereas the γ-Al₂O₃ platelets debonded and pulled-out (see Fig. 10.10b) from the epoxy matrix. Fracture of the γ-AlO(OH) is indicative of its strong bonding to the epoxy, which is promoted by the hydroxyl groups covalently bonding to amine and tertiary hydroxide groups of the epoxy during the curing process [401, 419-421]. The covalent bonding promotes stress transfer across the platelet-matrix interface and thereby increased the yield and ultimate tensile strength of the composites.

**Fig. 10.10.** SEM micrographs from the fracture surface of the tensile test specimens for an epoxy composite containing (a) 5 wt% γ-AlO(OH) and (b) 5 wt% γ-Al₂O₃.

By contrast, interfacial debonding followed by pull-out (without fracture) of the γ-Al₂O₃ platelets is indicative of its weaker bonding and consequently disbonding before rupture. These platelets do not covalently bond to epoxy, and instead bonded to the matrix via van der Waals forces. Opelt et al. [91] also reported that weak bonding exists between alumina particles and epoxy polymer due to the absence of functional groups to promote covalent bonding. For this reason, the γ-Al₂O₃ does not significantly increase the ultimate tensile strength of the epoxy when
compared to the $\gamma$-AlO(OH). The ultimate tensile strength ($\sigma_c$) of the epoxy polymers containing $\gamma$-Al$_2$O$_3$ was predicted using the rule-of-mixtures expression below:

$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f)$$  \hspace{1cm} (5)

based on the ultimate tensile strength of the alumina fillers ($\sigma_f = 300$ MPa [364]) and of the unmodified epoxy ($\sigma_m$) presented in Fig. 10.9c. The rule-of-mixtures model above assumes that the $\gamma$-Al$_2$O$_3$ platelets are well bonded (e.g. covalently) with the epoxy matrix up to the point of failure when both the platelets and the epoxy matrix fail simultaneously. Due to this incorrect assumption, the predicted ultimate tensile strengths of the $\gamma$-Al$_2$O$_3$/epoxy polymers from the model (see Fig. 10.9c) significantly exceeds the experimentally measured values. The analytical predictions for the epoxy polymers containing $\gamma$-AlO(OH) could not be conducted as no published reports on the ultimate tensile strength of boehmite could be found.

Table 10.1 and Fig. 10.11 present a comparison of the values and relative improvements to the Young’s modulus and ultimate tensile strength from the present study with data reported in the literature with AlO(OH) or Al$_2$O$_3$ fillers at various sizes, morphologies and contents [71, 81, 90, 401]. The tensile property values for the composites measured herein are compared with published values for other epoxy polymers containing AlO(OH) or Al$_2$O$_3$ with either a spherical (0D) or platelet (2D) morphology. It is important to note the types of epoxy used from the present study and other reports from the literature are not the same (i.e. different type of epoxy and curing conditions). Therefore, the percentage improvements in the tensile property values presented in Fig. 7 are normalised based on the type of unmodified epoxy used within the present work and reported in the literature [71, 81, 90, 401]. With the addition of the aluminium oxide particles, there is a general improvement in the Young’s modulus of the composite by up to 40%. However, the greatest relative improvements in the tensile properties correspond to when the AlO(OH) platelets are employed, which were obtained using the liquid metal synthesis process. However, the ultimate tensile strengths measured in the present work when using either the $\gamma$-AlO(OH) or $\gamma$-Al$_2$O$_3$ platelets in the epoxy polymers are relatively modest compared to the values reported by Wu et al. [10], Lim et al. [5] and Zhang et al. [6]. A major reason for this is clearly that their type of unmodified epoxy polymers had a significantly greater ultimate tensile strength than the one employed in the present chapter.
Table 10.1: Comparisons of tensile and fracture toughness properties for the aluminium oxide reinforced epoxy polymers in the present study with reported values from the literature. (Note: The legend contains information presented in the order: (i) morphology of nanofiller (i.e. 0D and 2D is a spherical particulate and a platelet, respectively), and (ii) key dimensions.)

<table>
<thead>
<tr>
<th>Source</th>
<th>Fillers content and type</th>
<th>Young’s modulus, $E_\text{r}$ (GPa)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Critical strain energy release rate, $G_\text{ic}$, (J/m$^2$)</th>
<th>Critical stress intensity factor, $K_\text{ic}$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Present study</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2D, ~6.10 μm dia, 1.17 μm thickness and density of 3050 kg/m$^3$)</td>
<td>Unmodified Epoxy 2.67</td>
<td>2.67</td>
<td>48.5</td>
<td>136</td>
<td>0.49*</td>
</tr>
<tr>
<td></td>
<td>1.0 wt% AlO(OH) 3.11</td>
<td>3.11</td>
<td>52.0</td>
<td>215</td>
<td>0.67*</td>
</tr>
<tr>
<td></td>
<td>2.0 wt% AlO(OH) 3.32</td>
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<td>0.79*</td>
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<tr>
<td></td>
<td>5.0 wt% AlO(OH) 3.49</td>
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<td>53.4</td>
<td>384</td>
<td>0.94*</td>
</tr>
<tr>
<td></td>
<td>10.0 wt% AlO(OH) 3.73</td>
<td>3.73</td>
<td>51.0</td>
<td>501</td>
<td>1.12*</td>
</tr>
<tr>
<td>(2D, ~5.30 μm dia, 0.99 μm thickness and density of 3650 kg/m$^3$)</td>
<td>1.0 wt% Al$_2$O$_3$ 3.00</td>
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<td>0.80*</td>
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<td>48.7</td>
<td>574</td>
<td>1.13*</td>
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<tr>
<td></td>
<td>10.0 wt% Al$_2$O$_3$ 3.61</td>
<td>3.61</td>
<td>48.6</td>
<td>462</td>
<td>1.05*</td>
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<tr>
<td>Wu et al. [401]</td>
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<td>-</td>
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<td></td>
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<td>-</td>
<td>78.2</td>
<td>-</td>
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<tr>
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<td>-</td>
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</tr>
<tr>
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<td>3.06</td>
<td>84.1</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>Zhang et al. [81]</td>
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<td>2.61</td>
<td>65.2</td>
<td>124</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>3.6 wt% Al$_2$O$_3$ 2.78</td>
<td>2.78</td>
<td>65.4</td>
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<td>0.67</td>
</tr>
<tr>
<td></td>
<td>7.0 wt% Al$_2$O$_3$ 2.92</td>
<td>2.92</td>
<td>76.3</td>
<td>160</td>
<td>0.73</td>
</tr>
<tr>
<td>Duan et al. [90]</td>
<td>Unmodified Epoxy 2.02</td>
<td>2.02</td>
<td>44.2</td>
<td>-</td>
<td>0.82</td>
</tr>
<tr>
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<td>1 wt% Al$_2$O$_3$ 2.19</td>
<td>2.19</td>
<td>42.6</td>
<td>-</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>3 wt% Al$_2$O$_3$ 2.39</td>
<td>2.39</td>
<td>46.0</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>5 wt% Al$_2$O$_3$ 2.44</td>
<td>2.44</td>
<td>46.5</td>
<td>-</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>7 wt% Al$_2$O$_3$ 2.38</td>
<td>2.38</td>
<td>46.0</td>
<td>-</td>
<td>1.12</td>
</tr>
</tbody>
</table>

* Assuming a Poisson ratio (ν) of ~0.35, the $K_\text{ic}$ values for the present study were calculated using $K_\text{ic} = \sqrt{G_\text{ic} \times E \times (1 - \nu)}$, where $E$ is the Young’s modulus and $G_\text{ic}$ is the mode I fracture energy (critical strain energy release rate) for the corresponding epoxy composite samples.
Fig. 10.11. Percentage improvements (compared to the unmodified epoxy) to the (a) Young’s modulus and (b) ultimate tensile strength of the composites studied in the present work and other types of epoxy polymers containing AlO(OH) or Al₂O₃ nanoparticles reported in [71, 81, 90, 401].

10.3.2 Fracture toughness properties

The mode I fracture energy ($G_{Ik}$) measured for the unmodified epoxy and the reinforced epoxy polymers are given in Fig. 10.12. The $G_{Ik}$ values of the epoxy increase with the $\gamma$-AlO(OH) content, and at the highest weight fraction (i.e. 10%) the toughness is improved by $\sim$270%. The $G_{Ik}$ values also increase with the weight fraction of $\gamma$-Al₂O₃ platelets, although the highest toughness (with an improvement of up to $\sim$320%) corresponds to a content of 5 wt%. Up to this platelet content, the $\gamma$-Al₂O₃ fillers is $\sim$50% more effective than the $\gamma$-AlO(OH) at increasing the $G_{Ik}$ value. However, the toughening induced by $\gamma$-Al₂O₃ platelets decreases at the highest content and the reasons for this are described below. The platelets not only improved the $G_{Ik}$ value but also improved the stability of the crack growth process in some of the epoxy polymers.
Fig. 10.12. Effect of γ-AlO(OH) and γ-Al₂O₃ contents on the mode I fracture toughness (critical strain energy release rate) of the epoxy polymer.

Typical load versus crack opening displacement (P-δ) curves measured during DCB testing of the epoxy polymers containing different weight fractions of γ-AlO(OH) or γ-Al₂O₃ platelets are shown in Fig. 10.13. The P-δ curve for the unmodified epoxy polymer shows a series of large and abrupt drops in the crack opening force with increasing displacement, which is indicative of unstable (slip-stick) crack growth. Unstable cracking is commonly observed in unmodified epoxies due to their intrinsically low toughness. Unstable cracking also occurred in the epoxy polymers reinforced with γ-AlO(OH), as characterised by the slip-stick behaviour of the crack growth process. More stable crack growth, indicated by the absence of large and sudden load drops in the P-δ curve can be observed in the epoxy reinforced with γ-Al₂O₃, except at the lowest content. The crack growth process transitioned from unstable to stable when the γ-Al₂O₃ content was above 1 wt%. 
The γ-AlO(OH) or γ-Al₂O₃ platelets induced intrinsic toughening mechanisms in the process zone at the crack tip and extrinsic toughening mechanisms in the crack wake, as illustrated schematically in Fig. 10.14. Both γ-AlO(OH) and γ-Al₂O₃ platelets induced localised plastic shear yielding of the matrix, contributing to the intrinsic toughening. Micro-void growth in the epoxy matrix was also observed around γ-Al₂O₃ platelets. Localised plastic yielding of the epoxy matrix occurred adjacent to the γ-AlO(OH) and γ-Al₂O₃ platelets due to the stress concentrations induced by their high stiffness (see Figs. 10.15a and 10.15b), and this contributed to the increased $G_{IC}$ value for both types of composites. The γ-Al₂O₃ platelets tend to fully debond from the epoxy matrix under the triaxial (i.e. hydrostatic) stress field concentrated within the crack tip process zone (Fig. 10.15b) because these platelets were only weakly bonded to the epoxy. Particle-matrix debonding is an effective toughening process in some composite materials [122, 337]. The γ-AlO(OH) platelets, which were more strongly bonded to the matrix, showed very limited debonding (Figs. 10.15a and 10.16a) and therefore were less effective than γ-Al₂O₃ at increasing the fracture energy. The plastic shear yielding of the epoxy adjacent to the debonded γ-Al₂O₃ platelets led to the initiation and growth of microvoids (Fig. 10.15c). However, γ-AlO(OH) platelets did not generate microvoiding (or cavitation) because their strong bonding to the matrix inhibited complete
debonding. Void formation is an effective intrinsic toughening process in polymers [124, 337, 422], and its absence in the $\gamma$-AlO(OH) composites accounts, in part, for their lower $G_{Ic}$ values compared to the $\gamma$-Al$_2$O$_3$ composites. The density of microvoids within the process zone increased with $\gamma$-Al$_2$O$_3$ content, which correlates to the rapid increase in the $G_{Ic}$ value up to a content of 5 wt%. The maximum size of the voids (~15-25 $\mu$m) was measured using scanning electron microscopy to be 3 to 5 times the size of the $\gamma$-Al$_2$O$_3$ platelets. At a given filler content, optimal toughening occurs in composites when the spacing between inclusions/particles is sufficiently large, and the fillers are evenly dispersed so that they do not impede the plastic flow of the epoxy matrix needed for void growth to occur [65, 70]. The growth of microvoids was impeded at the highest $\gamma$-Al$_2$O$_3$ content (i.e. 10 wt%) due to (i) the relatively close spacing and increased the packing density of the platelets and (ii) the tendency of the platelets to form agglomerates at this relatively high content (Fig. 10.15d).

**Fig. 10.14.** Schematic representations of the fracture toughening mechanisms exhibited by the composites containing (a) $\gamma$-AlO(OH) and (b) $\gamma$-Al$_2$O$_3$ platelets.
Fig. 10.15. SEM images of the fracture surface of the epoxy polymers containing (a) 5 wt% AlO(OH), (b-c) 5 wt% Al₂O₃, (d) 10 wt% Al₂O₃.

Fig. 10.16. SEM images of the fracture surface behind the crack tip of the epoxy polymer containing (a and b) γ-AlO(OH) and (c) γ-Al₂O₃.
Multiple extrinsic toughening mechanisms were operative over a very short distance (~35 μm) behind the main crack front in the composites, including rupture of the γ-AlO(OH) platelets and pull-out of the γ-Al₂O₃ platelets. Platelets that were orientated in a near-normal direction to the direction of crack growth were able to bridge the crack. This bridging action generates a traction load that reduces the stress exerted on the crack tip, thereby increasing the fracture energy. Under increasing crack opening, the γ-AlO(OH) platelets bridging the crack wake ruptured along the crack propagation plane (Figs. 10.16a and 10.16b) whereas the bridging γ-Al₂O₃ platelets were pulled-out (usually without breaking) (Figs. 10.15b and 10.16c). The strong bonding of the γ-AlO(OH) platelets to the epoxy restricted their pull-out, so they ruptured instead. With a weaker bonding to the matrix, the γ-Al₂O₃ platelets debonded from the epoxy in the crack tip process zone and underwent pull-out under increasing crack opening. The interfacial shear friction traction stress generated during particle pull-out promotes a stronger toughening effect than when the particles fracture [287]. Therefore, the additional toughening mechanism of particle pull-out, together with the other processes of interfacial debonding and microvoid formation, are responsible for γ-Al₂O₃ being more effective as a filler than γ-AlO(OH) platelets for increasing the \( G_{IC} \) value of the epoxy polymer. It is likely that these additional mechanisms, and the resultant increase in fracture energy, are also responsible for the more stable (i.e. less slip-stick) crack growth process in the epoxy polymers reinforced with γ-Al₂O₃.

The platelets obtained using the liquid metal reaction method are more effective at increasing the mode I fracture toughness or critical stress intensity factor \( (K_{IC}) \) of epoxy when compared to other types of aluminium oxides. Assuming a Poisson ratio \( (\nu) \) of ~0.35, the \( K_{IC} \) values for the present study were calculated using,

\[
K_{IC} = \sqrt{G_{IC} \times E \times (1 - \nu)}
\]

where \( E \) is the Young’s modulus and \( G_{IC} \) is the mode I fracture energy (critical strain energy release rate) for the corresponding epoxy composite samples. A comparison of the toughness values and improvements of epoxy polymers containing aluminium oxide particles or platelets is presented in Table 10.1 and Fig. 10.17. It is clear that the γ-AlO(OH) and γ-Al₂O₃ platelets synthesised using the liquid metal processing technique are more effective in toughening epoxies, particularly at higher contents, than aluminium oxides obtained from other processing routes. It is well known that the magnitude of the toughening induced by particles and platelets is dependent on several
factors, with the dominant factors being their aspect ratio [90], size or length [71], shape [90], and surface chemical functionality [89, 91]. The γ-AlO(OH) platelets prepared in this study are much larger (i.e. ~6.1 μm) in diameter than those reported in other studies (with an average size ~20-200 nm). Consequently, the aspect ratio of the platelets synthesised using the liquid metal process is much greater. The large size of the γ-AlO(OH) aids both the intrinsic (e.g. void growth) and extrinsic (e.g. crack bridging) processes in toughening the epoxy polymer. Similarly, the alumina platelets γ-Al₂O₃ used in this study were also in the form of platelets (~5.3 μm in diameter). In contrast, other studies have employed alumina particles in the shapes of spherical particulates or platelets at much smaller dimensions (see Table 10.1).

![Graph showing percentage improvement in critical stress intensity factor (Klc) with filler content.](image)

**Fig. 10.17.** Percentage improvement (compared to the unmodified epoxy) to the mode I critical stress intensity factor (Klc) of the composites studied in the present work and other types of epoxy polymer containing AlO(OH) or Al₂O₃ nanoparticles reported in [71, 81, 90, 401].

### 10.4 CONCLUSION

The tensile modulus, yield stress and fracture toughness of an epoxy polymer have been greatly improved by incorporating low-dimensional boehmite γ-AlO(OH) and alumina γ-Al₂O₃ nanoplatelets. The boehmite platelets were synthesised via a liquid metal reaction technique, and
the alumina γ-Al₂O₃ platelets were obtained by annealing the boehmite γ-AlO(OH) platelets. The Young’s modulus and yield stress of the epoxy increased with increasing boehmite or alumina content, with the boehmite platelets providing a slightly stronger reinforcing effect due to their higher elastic modulus. The ultimate tensile strength of the epoxy polymers also increased, at least initially, with increasing boehmite content, while the alumina platelets resulted in no significant increase. The reason for the higher effectiveness of the boehmite was that this type of platelet covalently bonds with the epoxy matrix to give a relatively strong interface between the γ-AlO(OH) platelets and the epoxy matrix. The mode I fracture toughness increased with the content of the boehmite γ-AlO(OH) or alumina γ-Al₂O₃ platelets, with the alumina providing a higher toughness up to a limiting concentration of 5wt%. The toughness of the epoxy nanocomposite was increased by the boehmite due to this type of platelet (i) inducing more localised plastic flow at the crack tip and (ii) bridging across the crack faces in the wake of the advancing crack. The alumina, due to its weaker bonding to the epoxy, increased the toughness via (i) interfacial debonding, plastic yielding and microvoid formation at the crack tip and (ii) bridging and pull-out in the crack wake. These additional intrinsic and extrinsic toughening mechanisms initiated by the presence of the alumina platelets are responsible for the alumina being more effective than boehmite at increasing the toughness.

In adopting the liquid metal synthesis process to produce low-dimensional aluminium oxides to improve the mechanical properties of polymer composites, this chapter has demonstrated the efficacy of boehmite and alumina nanoplatelets. It is feasible that these platelets could also be beneficial in enhancing other properties of polymers such as fire resistance, dielectric properties, thermal conductivity and thermo-mechanical properties [82], and these aspects can be considered as a future work from the present thesis.
Chapter 11: Conclusions

11.1 SUMMARY OF MAJOR FINDINGS

The work presented in this PhD project has contributed towards the understanding of improving the fracture toughness of polymers and delamination resistance of fibre reinforced polymer composites using reinforcements at multiple dimensional scales. The current techniques to enhance the fracture toughness properties of polymers and composites are reviewed. Research gaps were identified within the scope of multi-scale toughened materials containing a combination of nano-, micron- and macro-scale reinforcements that exhibit synergistic (i.e. greater-than-additive) toughness properties.

The mode I fracture toughness properties of multi-scale reinforced epoxy polymers containing randomly oriented or aligned carbon nanofibres (CNFs) and short carbon fibres (SCFs) were investigated in Chapters 3 and 4. It was found that the CNFs and SCFs, when used separately or together, can be rapidly aligned in the liquid epoxy during curing in the direction of the applied AC electric field. On a weight fraction basis, the toughening efficacy was much greater for CNFs when compared to SCFs. Combining the CNFs and SCFs together to create multi-scale reinforced epoxy polymers has an additive toughening effect. This additive toughness effect was further enhanced by using the electric field to align the fillers normal to the crack growth direction. In comparison to the unmodified epoxy, the $G_{IIc}$ value of the multi-scale reinforced epoxy polymers was increased up to about 20-fold using a combination of electrically aligned CNFs and SCFs. Based upon the identified intrinsic and extrinsic toughening mechanisms, an analytical model has been developed to successfully predict the $G_{IIc}$ values and the individual toughening contribution of the multi-scale reinforced polymers.

Chapter 5 presented an experimental investigation into the delamination toughening and impact damage tolerance carbon fibre reinforced epoxy composites containing CNFs and SCFs within the polymer matrix. The impact damage resistance and compression after impact strength of carbon-epoxy composites can be enhanced significantly with the addition of CNFs and/or SCFs. The modes I and II interlaminar fracture toughness can be improved by blending CNFs and SCFs, when used separately, into the epoxy matrix. The CNFs were much more effective at improving
the mode I and mode II interlaminar when compared to using SCFs. Improvements observed towards the interlaminar fracture toughness properties were due to the intrinsic and extrinsic toughening mechanism invoked by the fillers. Synergistic improvements (72%) were observed on the mode II interlaminar fracture toughness properties of the multi-scale reinforced composite containing both CNFs and SCFs. Subjecting the laminates to a low-velocity impact loads resulted in delamination growth and fibre damage. The addition of CNFs and/or SCFs reduced the impact damage area with the increase in the incident impact energy. As a result, improving the compression after impact strength by up to 30%. Reduction to the damage area from the toughened composite was due to the increased interlaminar fracture toughness properties, with the multi-scale reinforced composites being the most effective at improving the impact damage tolerance.

Chapters 6 and 7 presented a compressive experimental and numerical study into the synergistic toughening of multi-scale carbon fibre reinforced epoxy composites containing both CNFs and z-pins. Combining CNFs and z-pins within the same material induces a synergistic improvement to the modes I and II toughness that was greater either of the reinforcements, when used separately. The magnitude of the synergistic toughening increases with the volume contents of both CNFs and z-pins, where the highest synergistic improvement of 70% and 26% was measured for the mode I and mode II fracture toughness, respectively. The synergistic toughening effect is induced by the CNFs present along the z-pin/laminate interface, thereby increasing the modes I and II crack bridging traction properties of the z-pins. The crack growth resistance response and fracture toughness properties of the multi-scale reinforced laminates were successfully predicted using a finite element (FE) model that considers interlaminar toughening due to the CNFs, and the modes I and II traction properties of the z-pins. Using the FE model, it was found that the magnitude of synergistic toughening effect increases with the delamination length due to a greater number of z-pins becoming operative within the crack bridging zone until the steady-state crack growth condition is reached. Chapter 8 extended on the previous two chapters with an experimental investigation on the synergistic toughening effect of hybridizing CNF, carbon nanotubes (CNTs) or graphene nanoplatelets (GNPs) with z-pins on the interlaminar fracture toughness of carbon fibre epoxy composites. On weight fraction basis, the CNTs and CNFs promoted a greater synergistic toughening effect for the mode I (~38%) and mode II (~20%) interlaminar fracture toughness, respectively. Fractography revealed that the CNTs and CNFs increased the bridging traction energy of z-pins during the delamination crack growth. The
diameter of the z-pins also influenced the magnitude of the mode I and mode II synergistic delamination toughening effect with CNFs. The greater-than additive toughening effect was greater using thin z-pins (~23-25%) because their total surface area per unit area of delamination crack was higher than thick z-pins (~12-18%). Additive improvements were only observed for the multi-scale reinforced composites containing GNPs and z-pins. Synergistic toughening enhancements on the interlaminar fracture toughness of carbon fibre reinforced epoxy composites reported in Chapters 5, 6, 7 and 8 are greater that the relative percentage synergy values reported in [49, 68, 230] (see Chapter 2 – Table 2.5).

The pull-off structural properties of the multi-scale toughened composite T-joints containing carbon nanofillers (i.e. CNTs, CNFs or GNP) and z-pins was experimentally investigated in Chapter 9. The CNTs, CNFs and GNP were effective at increasing the load-at-first failure of the unpinned and z-pinned T-joints by suppressing early onset of cracks within the delta fillet region due to increase mode I initiation interlaminar fracture toughness reported in Chapter 8. The CNTs, CNFs and z-pins, when used separately, were also effective at improving the ultimate load and absorbed energy capacity of the T-joint. The CNFs were the most effective at improving the initiation failure load, ultimate failure load and absorbed energy capacity by up to 70%, 46% and 200%, respectively. However, substantial improvement was achieved to these properties of the T-joints when combining the CNTs or CNFs with z-pins, where synergistic enhancement were achieved on the absorbed energy capacity values.

Chapter 10 presented an experimental investigation into the strengthening and toughening properties of epoxy polmyers using two-dimensional platelets of boehmite (γ-AlO(OH)) and alumina (γ-Al2O3). Using liquid metal alloy reaction process, two-dimensional metal oxide hydroxide and oxide nanoplatelets were synthesised and then used for reinforcing epoxy polymers. Both boehmite and alumina platelets significantly increased the tensile modulus, yield stress and fracture toughness of the epoxy composites. Of the two materials, the boehmite platelets were more effective than the alumina platelets in increasing the tensile modulus (up to 27%) and ultimate strength (up to 14%) of the epoxy. The hydroxide groups present on the bohemite platelets covalently bonds with the epoxy. In contrast, the alumina platelets promoted a 50% greater improvement to the mode I fracture energy when compared to using boehmite platelets. The poor bonding between alumina platelets and epoxy imparted additional toughening mechanisms (i.e.
void growth and pull-out), thereby promoting a much greater fracture toughness improvement when compared to the boehmite platelets.

**11.2 FUTURE RESEARCH CONSIDERATIONS**

Significant progress has been achieved within this PhD project in discovering new methods in engendering synergies on the (i) fracture toughness properties of bulk epoxy polymers and (ii) delamination resistance and structural properties of carbon fibre reinforced epoxy composites. However, further experimental and analytical research is required to expand the current research presented within this PhD thesis.

**11.2.1 Electric field alignment of multi-scale carbon reinforcements in epoxy polymers**

*Chapters 3 and 4* reported that hybridizing and aligning both CNFs and SCFs can substantially improve the quasi-static mode I fracture toughness of epoxy polymers by up to 20-fold. Further investigation can be considered on investigating the mode I fatigue damage resistance of these multi-scale reinforced epoxy polymers subjected to cyclic loads. In *Chapter 3*, it was found that both CNFs and SCF can be aligned in a liquid epoxy along the direction of an applied electric. Astonishingly, a small proportion CNFs were deposited onto the SCFs along with chaining during application of the electric field due to the localized charging on the SCFs. This is first demonstration of using an electric field to coat CNFs onto short fibres. This technique can also be used to deposit other nanofillers such as CNTs or GNPs onto SCFs, and may prove to effective at synergistically enhancing the electrical conductivity and damage detection properties of epoxy polymers at relatively low contents of fillers. These aspects discussed above are considerations for future studies.

**11.2.2. Multi-scale toughening of carbon fibre reinforced composites using carbon nanofillers and z-pins**

The results presented in *Chapters 6, 7* and *8* contribute to fundamental understanding of the synergistic interlaminar fracture toughening mechanism of hybridising carbon nanofillers (i.e. CNTs, CNF and GNPs) with z-pins. The synergistic toughening gained by CNFs have to the benefit of making z-pinned laminates, even more, delamination resistant or allowing a reduction
in the volume content of z-pins while maintaining a high level of delamination toughness. Chapter 9 reported that this multi-scale toughening methodology is effective at improving structural properties of composite T-joints. However, it is well known that z-pins can reduce the stiffness, failure stress, fatigue life and other in-plane mechanical properties of composite materials, and the magnitude of these property reductions increase with the z-pin content [36, 212, 213, 423, 424]. By adding nanofillers, it is possible to lower the z-pin content (and hence reduce the loss to the in-plane mechanical properties) without a corresponding reduction to the interlaminar toughness properties. Further considerations would be to investigate the compression and flexural properties of 3D reinforced composite containing nanofiller reinforced polymer matrix. Results on mode I and mode II interlaminar toughening suggests that synergistic toughening may also occur in the multi-scale reinforced composites under mixed-mode I/II quasi-static or cyclic loading. The impact damage tolerance assessment of these class of multi-scale reinforced composites should be considerations for future work. It is also possible other types nanofillers, such as silica nanoparticles or aluminum oxides, along with other types of 3D reinforcements of a similar length scale and toughening action to z-pins, such as woven z-binders or stitches, may promote this greater-than-additive toughening effect when used in combination. These aspects discussed above are right for further scientific inquiry in future investigation.

11.2.3. Liquid metal synthesis of aluminum metal in enhancing the functional properties of polymers

In adopting the liquid metal synthesis process to produce low-dimensional aluminium oxides to improve the mechanical properties of epoxy polymers, this work has demonstrated the efficacy of boehmite and alumina platelets to improve the tensile and fracture toughness properties of epoxy polymers. It is feasible that these platelets synthesized from the liquid metal synthesis process could also be beneficial in enhancing other properties of polymers such, dielectric properties, thermal conductivity, gas permeability and thermo-mechanical properties as these aspects are considerations for future investigations. Considering that boehmite covalently bonds with the epoxy, properties such as the interlaminar fracture toughness, interlaminar shear strength and fire resistance of carbon fibre reinforced composites toughened by these aluminum particles can be considered for future studies.
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261


266


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