Toughness and strength of recycled composites and their virgin precursors

by

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Abstract

With the exponential growth in carbon–fibre use, establishing recycling routes for the composite waste is now imperative. As recycling processes are maturing, it is vital to introduce the recyclates in non-safety–critical structural applications. This work aimed at studying the mechanical response of recycled composites and developing analytical models for predicting their failure, and also that of their virgin precursors.

The effect of recycling on the mechanical response of composites was assessed by comparing virgin and recycled materials with identical woven architectures. The performance depended on the reclamation cycle and loading mode; under optimal recycling conditions, above 75% of strength and virtually 100% of stiffness were recovered.

An experimental study of three state–of–the–art recycled composites revealed complex microstructures, featuring fibres and bundles (held together by residual matrix) of different sizes; this microstructure was key for the fracture process, as bundles significantly toughened the materials. The unique multiscale architecture and mechanical behaviour, while making these recyclates suitable for structural applications, created a need for the development of specific mechanical models for design.

In order to predict the intrinsic properties of composites with such multiscale reinforcement, original models for size effects on the tensile strength and fracture toughness of composite bundles were developed. These models combine statistics, micromechanics and self–similar processes; while their development was originally motivated by recycled composites, they are equally relevant for unidirectional virgin composites.

Subsequently, a micromechanical model for the fracture toughness of recycled composites was developed; this accounts for fracture, debonding and pull–out of reinforcing units with different sizes and orientations, and was successfully validated against the wide range of toughnesses experimentally measured in the recyclates.

This work shows that recycled composites offer an environmentally–friendly and performance–competitive alternative to current structural materials. The models developed can support the optimisation of recycling processes towards damage tolerant materials, as well as their application for eco-design of non-safety–critical structures.
Declaration of originality

The work hereby presented is based on research carried out by the author at the Department of Aeronautics of Imperial College London, and it is all the author’s own work except where otherwise acknowledged. No part of the present work has been submitted elsewhere for another degree or qualification.
Copyright declaration

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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xvii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>xix</td>
</tr>
<tr>
<td>List of Publications</td>
<td>xxi</td>
</tr>
<tr>
<td>Acronyms and Abbreviations</td>
<td>xxv</td>
</tr>
<tr>
<td>Notation</td>
<td>xxvii</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2 Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Carbon fibre recycling processes</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 Technology families</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Pyrolysis</td>
<td>12</td>
</tr>
<tr>
<td>2.2.3 Oxidation in fluidised bed</td>
<td>15</td>
</tr>
<tr>
<td>2.2.4 Chemical recycling</td>
<td>15</td>
</tr>
<tr>
<td>2.3 Composites re-manufacturing</td>
<td>16</td>
</tr>
<tr>
<td>2.3.1 Introduction</td>
<td>16</td>
</tr>
<tr>
<td>2.3.2 Direct moulding</td>
<td>19</td>
</tr>
<tr>
<td>2.3.3 Compression moulding of intermediate non-woven products</td>
<td>21</td>
</tr>
<tr>
<td>2.3.4 Fibre alignment</td>
<td>23</td>
</tr>
<tr>
<td>2.3.5 Woven rCFRP</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Discussion</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1 State of the art and outlook in recycling and re-manufacturing</td>
<td>25</td>
</tr>
<tr>
<td>2.4.2 Forthcoming challenges to the commercialisation of rCFs</td>
<td>26</td>
</tr>
<tr>
<td>2.4.3 Development of structural applications for rCFRPs</td>
<td>28</td>
</tr>
</tbody>
</table>
4.4.2 Mechanical properties ............................................ 64
4.4.3 Tensile fracture toughness .................................... 66
4.4.4 Compressive fracture toughness .............................. 68
4.4.5 Failure and toughening mechanisms ....................... 69

4.5 Discussion .............................................................. 72
4.5.1 Role of the critical fibre length on tensile failure ......... 72
4.5.2 Stable vs. unstable tensile failure ............................ 74
4.5.3 Influence of fibre–bundles on the tensile fracture toughness . 74
4.5.4 Tensile failure of fibre–bundles ............................. 75
4.5.5 Multiscale and fractal features ............................... 75
4.5.6 Compressive failure mode ..................................... 75
4.5.7 Compressive fracture toughness ............................ 77
4.5.8 Comparison with virgin materials ......................... 77
4.5.9 Improvements to the recycling processes ................ 78

4.6 Conclusions ............................................................ 78

5 The influence of micromechanical properties and reinforcement architecture on the mechanical response of recycled composites 81

5.1 Introduction .......................................................... 81
5.2 Materials ............................................................. 82

5.3 Experimental analysis .............................................. 83
5.3.1 Single–fibre analysis ........................................... 83
5.3.2 Composite analysis ............................................ 85

5.4 Results ................................................................. 87
5.4.1 Single–fibre analysis ........................................... 87
5.4.2 Composite analysis ............................................ 92

5.5 Discussion ............................................................ 95
5.5.1 Analysis of recycling processes and reclaimed fibres .... 95
5.5.2 Strength distribution of recycled fibres and size effects . 98
5.5.3 Effect of architecture on stiffness and strength .......... 98
5.5.4 Effect of architecture on toughening mechanisms .... 99
5.5.5 Optimisation of recycling routes ........................... 100

5.6 Conclusions .......................................................... 101

6 Hierarchical scaling law for the strength of composite fibre bundles 103

6.1 Introduction .......................................................... 103
6.2 Model development ................................................ 106
6.2.1 Fibre bundle geometry and shear–lag boundary .... 106
6.2.2 Stress field around a fibre break and definition of the control region
6.2.3 Statistical analysis of level–[1] bundle failure
6.2.4 Hierarchical law for bundle failure
6.2.5 Asymptotic behaviour
6.2.6 Numerical implementation
6.3 Results
6.3.1 Analysis of model predictions
6.3.2 Convergence study
6.3.3 Parametric study on fibre and matrix properties
6.3.4 Asymptotic limits
6.3.5 Validation against experimental results
6.4 Discussion
6.4.1 Physically meaningful model features and experimental validation
6.4.2 Relation between the present model and others in the literature
6.5 Conclusions

7 An analytical model for the translaminar tensile toughness of fibre composites with stochastic fractal fracture surfaces
7.1 Introduction
7.2 Model development
7.2.1 Geometry of quasi-fractal surfaces
7.2.2 Formation of quasi-fractal surfaces
7.2.3 Determination of debonding and pull-out length distributions
7.2.4 Fracture toughness of quasi-fractal surfaces
7.2.5 Numerical implementation
7.3 Results
7.3.1 Analysis of model predictions
7.3.2 Convergence study
7.3.3 Parametric study
7.3.4 Validation against experimental results
7.4 Discussion
7.4.1 Experimental validation
7.4.2 Interpretation of toughening mechanisms
7.4.3 Novel model features and challenging results
7.5 Conclusions

8 Predicting the fracture toughness of multiscale recycled composites
8.1 Introduction
E Generalisation of the weakest link theory to non-uniform stress fields E.1

F Physically-based derivation of the hierarchical scaling law F.1

G Proof of asymptotic behaviour for strength distributions G.1

H Stress concentrations and equilibrium crack length before level-[$i$] failure of a fractal fracture surface H.1

I Mode-II toughness for debonding I.1

J Frictional stresses during pull-out J.1

K Derivation of the level-[$i$] pull-out length distribution in a fractal fracture surface K.1
# List of Figures

2.1 CFRP waste. ................................................................. 7
2.2 Closed life–cycle for CFRPs. ........................................ 9
2.3 Main methodologies for CFRP recycling. .......................... 10
2.4 Scanning–electron microscopy of recycled carbon fibres ........... 12
2.5 Mechanical properties of recycled v.s. virgin carbon–fibres. .... 13
2.6 Re-manufacturing of rCFRPs. ........................................ 17
2.7 Typical unsized, random, low–density–packing (“fluffy”) RCF. .... 17
2.8 Mechanical properties of rCFRPs. .................................. 19
2.9 Intermediate non-woven rCF products for compression moulding. 22
2.10 Examples of demonstrators manufactured with recycled CFs. .... 25

3.1 Fibre reclamation and composite (re-) manufacturing .............. 33
3.2 Reduced compact compression specimens for study of compressive damage. 37
3.3 Fibre yield after pyrolysis (virgin–fibre properties indicated for reference). 38
3.4 Recycled fabrics sheared manually up to the lock-up point. .......... 38
3.5 Scanning–electron micrographs of virgin and recycled carbon fibres. 40
3.6 Tensile strengths of the virgin and recycled fibres. .................. 41
3.7 Thickness and constituent volume fraction of virgin and recycled composites. 42
3.8 Micrographs of cross sections of virgin and recycled composites. .... 43
3.9 Ratio between mean properties of recycled and virgin composites. ... 45
3.10 Typical stress–strain curves for virgin and recycled composites. ..... 46
3.11 Damage morphology in virgin and recycled composites. ............ 47
3.12 Retention of composites’ mechanical properties vs. retention of fibre strength. 50
3.13 Relation between parameters characterising the morphology of recycled weaves and fibre strength retention. ...................... 54

4.1 Nominal geometry of the fracture toughness specimens. ............ 61
4.2 μT and μC tests for investigation of failure and toughening mechanisms. 63
4.3 Microstructural features in the rCFRP. ................................ 63
4.4 Typical stress vs. strain curves from the standard characterisation tests. 64
4.5 Typical failure modes of standard characterisation specimens. .... 65
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>Crack propagation in a typical CT specimen</td>
<td>66</td>
</tr>
<tr>
<td>4.7</td>
<td>All $P(d)$ and $G_T(\Delta a)$ curves from the tensile fracture toughness tests</td>
<td>67</td>
</tr>
<tr>
<td>4.8</td>
<td>Typical result from the longitudinal compressive toughness tests</td>
<td>68</td>
</tr>
<tr>
<td>4.9</td>
<td>Failure mechanisms under stable tensile crack propagation</td>
<td>70</td>
</tr>
<tr>
<td>4.10</td>
<td>Fracture surface of a post-mortem standard tensile specimen</td>
<td>70</td>
</tr>
<tr>
<td>4.11</td>
<td>Typical fracture morphologies in CT specimens</td>
<td>70</td>
</tr>
<tr>
<td>4.12</td>
<td>Failure mechanisms of fibre–bundles under tension</td>
<td>71</td>
</tr>
<tr>
<td>4.13</td>
<td>Sequence of events for stable compressive failure</td>
<td>72</td>
</tr>
<tr>
<td>4.14</td>
<td>Features in compressive shear–bands</td>
<td>73</td>
</tr>
<tr>
<td>4.15</td>
<td>Compressive failure in a region with a thick fibre–bundle</td>
<td>73</td>
</tr>
<tr>
<td>4.16</td>
<td>Multiscale similarity of pull–out failure</td>
<td>76</td>
</tr>
<tr>
<td>4.17</td>
<td>Fractal pattern of defibrillation within a fibre bundle</td>
<td>76</td>
</tr>
<tr>
<td>4.18</td>
<td>Mechanical properties of the recycled CFRPs vs. virgin materials</td>
<td>77</td>
</tr>
<tr>
<td>5.1</td>
<td>Standard mechanical properties of the three rCFRPs</td>
<td>84</td>
</tr>
<tr>
<td>5.2</td>
<td>Geometry of CT specimens for materials T300-rMIT and T800-rMIT</td>
<td>87</td>
</tr>
<tr>
<td>5.3</td>
<td>Fibre diameters of virgin and recycled fibres</td>
<td>87</td>
</tr>
<tr>
<td>5.4</td>
<td>Scanning electron micrographs of virgin and recycled T300 fibres</td>
<td>88</td>
</tr>
<tr>
<td>5.5</td>
<td>Scanning electron micrographs of virgin and recycled T800 fibres</td>
<td>89</td>
</tr>
<tr>
<td>5.6</td>
<td>Strength statistics for virgin and recycled fibres</td>
<td>89</td>
</tr>
<tr>
<td>5.7</td>
<td>Strength distributions of virgin and recycled T300 fibres</td>
<td>90</td>
</tr>
<tr>
<td>5.8</td>
<td>Strength distributions of virgin and recycled T800 fibres</td>
<td>91</td>
</tr>
<tr>
<td>5.9</td>
<td>Fibre–matrix interfacial properties obtained from SFPO tests</td>
<td>92</td>
</tr>
<tr>
<td>5.10</td>
<td>Dry preforms of the T300-rMIT and T800-rMIT materials</td>
<td>93</td>
</tr>
<tr>
<td>5.11</td>
<td>Micrographs of cross sections of the three recycled composites</td>
<td>93</td>
</tr>
<tr>
<td>5.12</td>
<td>Constituent volume fraction of the recycled composites tested</td>
<td>94</td>
</tr>
<tr>
<td>5.13</td>
<td>Characterisation of the architecture of the three rCFRPs</td>
<td>94</td>
</tr>
<tr>
<td>5.14</td>
<td>Results from the CT tests</td>
<td>96</td>
</tr>
<tr>
<td>5.15</td>
<td>Representative mapping of fracture surfaces with R-curves</td>
<td>97</td>
</tr>
<tr>
<td>5.16</td>
<td>Hierarchical bundles in square fibre arrangement</td>
<td>106</td>
</tr>
<tr>
<td>5.17</td>
<td>Shear–lag boundary (assuming preferential interfacial failure)</td>
<td>107</td>
</tr>
<tr>
<td>5.18</td>
<td>Stress fields and length scales in a level–[1] fibre bundle</td>
<td>108</td>
</tr>
<tr>
<td>5.19</td>
<td>Numerical implementation</td>
<td>113</td>
</tr>
<tr>
<td>5.20</td>
<td>Overview of model results</td>
<td>115</td>
</tr>
<tr>
<td>5.21</td>
<td>Numerical convergence of the CoV of strength distributions</td>
<td>116</td>
</tr>
<tr>
<td>5.22</td>
<td>Effect of mean single–fibre strength on bundle strength statistics</td>
<td>116</td>
</tr>
<tr>
<td>5.23</td>
<td>Effect of the CoV of single–fibre strength on bundle strength statistics</td>
<td>117</td>
</tr>
<tr>
<td>5.24</td>
<td>Bundle strength size effect for several shear–lag strengths</td>
<td>117</td>
</tr>
<tr>
<td>5.25</td>
<td>Bundle strength size effect for different values of stress concentrations factor</td>
<td>118</td>
</tr>
<tr>
<td>5.26</td>
<td>Bundle strength size effect considering a WLT approximation for large bundles</td>
<td>119</td>
</tr>
</tbody>
</table>
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Global initiatives contributing to CFRP recycling activities.</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary analysis of different recycling processes.</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Mechanical properties of recycled CFs reclaimed through different processes.</td>
<td>13</td>
</tr>
<tr>
<td>2.4</td>
<td>Summary analysis of different re-manufacturing processes.</td>
<td>18</td>
</tr>
<tr>
<td>2.5</td>
<td>Mechanical properties of rCFRP vs. manufacturing process.</td>
<td>20</td>
</tr>
<tr>
<td>2.6</td>
<td>Overview on manufacturing processes for non-woven intermediate products.</td>
<td>21</td>
</tr>
<tr>
<td>2.7</td>
<td>Estimated values for the cost of carbon fibres [9].</td>
<td>25</td>
</tr>
<tr>
<td>2.8</td>
<td>Demonstrators manufactured with recycled CFs.</td>
<td>27</td>
</tr>
<tr>
<td>2.9</td>
<td>Potential structural applications for rCFRPs [83].</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>Nominal specifications of the virgin composite prepreg [113].</td>
<td>33</td>
</tr>
<tr>
<td>3.2</td>
<td>Nominal specifications of the virgin carbon fibres [114].</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>Identification of materials used.</td>
<td>36</td>
</tr>
<tr>
<td>3.4</td>
<td>Nominal densities of the virgin composite prepreg and its constituents [113].</td>
<td>36</td>
</tr>
<tr>
<td>3.5</td>
<td>Specifications for single–fibre tensile tests.</td>
<td>36</td>
</tr>
<tr>
<td>3.6</td>
<td>Specifications for the standard mechanical characterisation.</td>
<td>36</td>
</tr>
<tr>
<td>3.7</td>
<td>Maximum likelihood Weibull fitting to SFTT strength (for $l = 15$ mm).</td>
<td>39</td>
</tr>
<tr>
<td>3.8</td>
<td>Elastic properties of virgin and recycled composites.</td>
<td>44</td>
</tr>
<tr>
<td>3.9</td>
<td>Strengths of virgin and recycled composites.</td>
<td>44</td>
</tr>
<tr>
<td>3.10</td>
<td>Assessment of typical defects in fibres reclaimed by different pyrolysis cycles.</td>
<td>48</td>
</tr>
<tr>
<td>3.11</td>
<td>Influence of recycled–fibre defects on composite performance.</td>
<td>49</td>
</tr>
<tr>
<td>3.12</td>
<td>Relation between fibre reclamation cycle and manufacturing defects.</td>
<td>52</td>
</tr>
<tr>
<td>4.1</td>
<td>Properties of virgin and recycled carbon-fibres.</td>
<td>59</td>
</tr>
<tr>
<td>4.2</td>
<td>Specifications for the standard mechanical characterisation.</td>
<td>60</td>
</tr>
<tr>
<td>4.3</td>
<td>Volume content of the rCFRP phases.</td>
<td>63</td>
</tr>
<tr>
<td>4.4</td>
<td>Elastic properties of the rCFRP.</td>
<td>64</td>
</tr>
<tr>
<td>4.5</td>
<td>Failure strengths of the rCFRP.</td>
<td>64</td>
</tr>
<tr>
<td>4.6</td>
<td>Extensions at failure of the rCFRP.</td>
<td>64</td>
</tr>
<tr>
<td>4.7</td>
<td>Summary of the tensile fracture toughness measurements.</td>
<td>67</td>
</tr>
<tr>
<td>4.8</td>
<td>Initiation fracture toughness for longitudinal compression.</td>
<td>68</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.1</td>
<td>Recycling route of materials studied</td>
<td>83</td>
</tr>
<tr>
<td>5.2</td>
<td>Specifications for single–fibre tensile tests</td>
<td>84</td>
</tr>
<tr>
<td>5.3</td>
<td>Specifications for single–fibre pull–out tests</td>
<td>85</td>
</tr>
<tr>
<td>5.4</td>
<td>Specifications for architecture characterisation</td>
<td>86</td>
</tr>
<tr>
<td>5.5</td>
<td>Weibull fitting to SFTT strengths</td>
<td>91</td>
</tr>
<tr>
<td>5.6</td>
<td>Architecture characterisation</td>
<td>94</td>
</tr>
<tr>
<td>6.1</td>
<td>Nominal model inputs for parametric studies</td>
<td>114</td>
</tr>
<tr>
<td>6.2</td>
<td>Description of composites for model validation</td>
<td>119</td>
</tr>
<tr>
<td>6.3</td>
<td>Carbon–fibre data for model validation</td>
<td>119</td>
</tr>
<tr>
<td>7.1</td>
<td>Number of fractal levels $i_{\text{max}}$ for difference types of fracture surface</td>
<td>137</td>
</tr>
<tr>
<td>7.2</td>
<td>Nominal model inputs for parametric studies</td>
<td>139</td>
</tr>
<tr>
<td>7.3</td>
<td>Description of composites for model validation</td>
<td>145</td>
</tr>
<tr>
<td>7.4</td>
<td>Fibre properties for model validation</td>
<td>145</td>
</tr>
<tr>
<td>8.1</td>
<td>Mapping of all relevant data for the three material systems studied</td>
<td>161</td>
</tr>
</tbody>
</table>
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xix
List of publications

Parts of the work presented in this thesis have been disseminated through a number of written publications and oral communications; these are listed below, as of April 2013.

Peer–reviewed journal publications


Refereed conference publications


Conference abstracts


Book chapters

### Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-DEP</td>
<td>Three Dimensional Engineering Preforming</td>
</tr>
<tr>
<td>AFRA</td>
<td>Aircraft Fleet Recycling Association</td>
</tr>
<tr>
<td>ATI</td>
<td>Adherent Technologies, Inc.</td>
</tr>
<tr>
<td>BMC</td>
<td>Bulk Moulding Compound</td>
</tr>
<tr>
<td>CC</td>
<td>Compact Compression</td>
</tr>
<tr>
<td>CDF</td>
<td>Cumulative Distribution Function</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon Fibre</td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon Fibre Reinforced Polymer</td>
</tr>
<tr>
<td>CT</td>
<td>Compact Tension</td>
</tr>
<tr>
<td>EoL</td>
<td>End of Life</td>
</tr>
<tr>
<td>FBD</td>
<td>Fluidised Bed Process</td>
</tr>
<tr>
<td>FBM</td>
<td>Fibre Bundle models</td>
</tr>
<tr>
<td>FE</td>
<td>Finite Elements</td>
</tr>
<tr>
<td>FLD</td>
<td>Fibre Length Distribution</td>
</tr>
<tr>
<td>FRP</td>
<td>Fibre Reinforced Polymer</td>
</tr>
<tr>
<td>GFRP</td>
<td>Glass Fibre Reinforced Polymer</td>
</tr>
<tr>
<td>IM</td>
<td>Injection Moulding</td>
</tr>
<tr>
<td>MAPP</td>
<td>Maleic Anhydride grafted PolyPropylene</td>
</tr>
<tr>
<td>MIT</td>
<td>Materials Innovation Technologies</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope / Microscopy</td>
</tr>
<tr>
<td>PP</td>
<td>PolyPropylene</td>
</tr>
<tr>
<td>PS</td>
<td>PolyStyrene</td>
</tr>
<tr>
<td>r-</td>
<td>recycled</td>
</tr>
<tr>
<td>RTM</td>
<td>Resin Transfer Moulding</td>
</tr>
<tr>
<td>RU</td>
<td>Reinforcing Unit</td>
</tr>
<tr>
<td>SCF</td>
<td>SuperCritical Fluids</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope / Microscopy</td>
</tr>
<tr>
<td>SFPO</td>
<td>Single Fibre Pull-Out</td>
</tr>
<tr>
<td>SFRP</td>
<td>Short Fibre Reinforced Polymer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>SFTT</td>
<td>Single Fibre Tensile Test</td>
</tr>
<tr>
<td>SMC</td>
<td>Sheet Moulding Compound</td>
</tr>
<tr>
<td>TFP</td>
<td>Technical Fibre Products</td>
</tr>
<tr>
<td>UD</td>
<td>UniDirectional</td>
</tr>
<tr>
<td>v-</td>
<td>virgin</td>
</tr>
<tr>
<td>WLT</td>
<td>Weakest Link Theory</td>
</tr>
</tbody>
</table>
Notation

Variables (English)

\( a \)  crack length; debonded distance; orientation tensor  
\( a_R \)  aspect ratio  
\( A \)  cross sectional area  
\( c \)  coordination number  
\( C \)  compliance; perimeter  
\( C_K \)  stress–concentrations strength parameter  
\( \text{CoV} \)  coefficient of variation  
\( d \)  displacement  
\( e \)  extension at failure  
\( E \)  Young’s modulus  
\( F \)  Cumulative distribution function; failure probability  
\( \mathcal{F} \)  Extreme cumulative distribution  
\( g \)  shear extension at failure; toughness  
\( G \)  shear modulus  
\( G_c \)  fracture toughness  
\( G \)  fracture toughness  
\( i \)  bundle level  
\( J \)  J-integral  
\( k \)  stress concentrations factor; stiffness of elastic foundation  
\( l \)  length  
\( \ell \)  dimensions of a sample  
\( L \)  length (stochastic variable)  
\( m \)  Weibull shape parameter  
\( n \)  number of elements / fibres  
\( N \)  number of items in a sample  
\( P \)  load  
\( s \)  interfibre spacing  
\( S \)  shear strength; survival probability; complementary cumulative distribution  
\( S \)  extreme compl. cumul. dist.  
\( t \)  thickness  
\( u \)  displacement  
\( U \)  energy absorption  
\( V \)  volume fraction  
\( w \)  width  
\( W \)  energy dissipated  
\( x \)  coordinate  
\( X \)  strength

Variables (Greek)

\( \alpha \)  angle of the fracture surface  
\( \beta \)  angle of the fracture surface  
\( \delta \)  deflection at the anti-symmetry plane  
\( \Delta T \)  change in temperature  
\( \varepsilon \)  deformation  
\( \phi \)  diameter  
\( \gamma \)  true shear deformation  
\( \lambda \)  slope coefficient  
\( \mu \)  friction coefficient
ν  Poisson’s ratio
ρ  density
σ  axial stress
τ  shear stress
τ_µ  friction stress

Superscripts

0  single-fibre
1  in-plane direction 1
2  in-plane direction 2
crit  critical
f  fibre
i  damage initiation
[i]  bundle level
low  lower limit of fracture toughness
m  matrix
RU  reinforcing unit
stbl  variation of fracture toughness
up  upper limit of fracture toughness
v  void
∞  remote

Subscripts

0  initial; Weibull scale parameter
12  in-plane
1  estimated at gauge length l_1
2  estimated at gauge length l_2
A  area
avg  average
bend  bending
B  free edges boundary
c  control length
c  critical
C  compression
crit  critical
deb  interfacial debonding
e  effective recovery length
e  elastic foundation
extens  extensometer
fr  fracture
i  realisation at length l_i
imp  impact
IF  interface
I  mode I; region I
II  mode II; region II
K  linear stress concentrations state
L  pure linear stress state
L  longitudinal
L  length
macro  macroscopic
M  matrix failure path
m  mean value
n  chain of elements
po  pull–out
r  reference length / element
sup  supported by surrounding material
SL  shear–lag
T  tensile; transverse
uns  unsupported
U  uniform stress state
V  volume
W  width
X  strength
∆T  change in temperature

Decorations above

at reference length ˆl
average

xxviii
Chapter 1

Introduction

The exponential growth in the use of Carbon Fibre Reinforced Polymers (CFRPs) observed during the last decades has raised an environmental, economic and legal awareness of the CFRP waste produced. Over the last 15 years, several researchers have been looking intensively for disposal routes alternative to landfilling, by developing recycling processes to recover the Carbon Fibres (CFs) from composite waste.

The technologies for CFRP recycling are reaching a mature stage; recycled (r-) fibres have now similar performances to their virgin precursors, and are being commercialised by a few specialised companies. In addition, manufacturing processes have been adapted to reimpregnate reclaimed fibres and produce recycled composites, which in many cases have a mechanical performance comparable to that of glass–fibre composites and aluminium.

These developments make it technologically feasible to use rCFRPs in non-critical structural applications, and some components have been produced as demonstrators. However, there are barely any studies on the mechanical response of these materials; this makes engineers and designers reluctant to use a new material for which the failure mechanisms are unknown and the simulation tools are nonexistent.

Recycled composites are inherently more complex than their virgin precursors, both due to variation of fibre properties and transformation of the reinforcement architecture. Consequently, it is necessary to understand the specificities of the response of rCFRPs and to develop suitable design methods. This will assist the establishment of a market for the recyclates and close the loop in the CFRP life-cycle.

This research aims therefore at developing an in-depth understanding of the mechanical behaviour of recycled composites and creating the first modelling tools for these novel materials. This requires addressing the following challenges:
Chapter 1

- To identify potential suppliers of recycled materials, and to understand which are the drivers for introducing the recyclates in structural applications;
- To investigate and characterise the mechanical response of state–of–the–art recycled fibres composites, and how this is affected by the recycling process;
- To develop analytical models for predicting the response and failure of recycled composites, which can then guide material optimisation and mechanical design;
- To use recycled composites as a platform for research in other related fields.

In this context, Chapter 2 reviews the literature on the whole CFRP recycling chain, including (i) motivation for recycling, (ii) fibre–reclamation processes, (iii) remanufacturing techniques and (iv) market outlook for recycled composites. This work was fundamental to establishing contact with some of the main players in the CFRP recycling field, who kindly provided materials for investigation in the scope of this project.

The experimental analysis of recycled fibres and composites is presented in Chapters 3 to 5. At first, this study focuses on understanding how the recycling process affects the mechanical performance of recycled fibres and composites (Chapter 3); to ensure a fair comparison at the macroscale, the original architecture of the virgin composite was preserved during fibre reclamation and composite re-manufacturing.

Subsequently, the mechanical response of a state–of–the–art rCFRP is analysed in–depth. Chapter 4 reveals a composite with very complex microstructure, with discontinuous and randomly–oriented fibres and bundles — held together by residual matrix not removed during fibre reclamation — of different sizes. A comprehensive characterisation of mechanical properties shows that such multiscale architecture has a significant impact on the fracture toughness of the recyclates. This behaviour is further confirmed in Chapter 5 for the other two rCFRPs, proving that bundles dramatically toughen the recyclates, even when micromechanical properties are not significantly different.

The experimental findings motivated the development of predictive models for the fracture toughness of recycled composites. Because the properties governing the failure of fibre bundles are size dependent, Chapters 6 and 7 present original models for predicting the intrinsic tensile strength and translaminar fracture toughness of composite fibre bundles, as well as the associated size effect. Both models are based on the stochastic fibre–strength distribution and properties of the matrix and interface, assuming a hierarchical self–similar failure process. These model are key for predicting the fracture toughness of recycled composites; moreover, they also push forward the state of the art in modelling unidirectional virgin composites, as shown by an extensive validation against literature results.
A micromechanical model for the fracture toughness of recycled composites is then developed in Chapter 8; this considers the works of fracture, debonding and pull-out of reinforcing units. The orientation of each fibre or bundle and its influence on the pull–out process was taken into account by allowing them to bend within the bridging region. The predictions of the analytical model were compared against the experimental toughness measurements, which successfully validates the model for the different rCFRPs with a wide range of toughnesses.

The overall conclusions of this work are summarised in Chapter 9. Finally, the scope for further extensions is outlined in Chapter 10.
Chapter 2

Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook

2.1 Introduction

The increasing use of carbon fibre reinforced polymers (CFRPs) has raised an environmental and economic awareness for the need to recycle the CFRP waste. The latest governmental UK strategy for composites [1] identifies “Increasing Sustainability and Recycling” as one of the three major goals for the composites industry. In this chapter, the current status of recycling processes for CFRP and the forthcoming challenges for the introduction of the recyclates in structural applications are reviewed.

The world-wide demand for carbon fibres (CFs) reached approximately 35,000 ton in 2008; this number is expected to double by 2014, representing a growth rate of over 12% per year [2]. CFRP is now used in a widening range of applications, and in growing content in most of them [3]: the aircraft industry is one of the most impressive examples, with the new Boeing 787 and Airbus A350 having up to 50% of their weight in CFRP, and military aircraft showing a similar trend [4].

Despite all advantages associated with CFRPs, the increasing use generates an also increasing amount of CFRP waste. Common sources of waste include out–of–date pre–pregs, manufacturing cut–offs, testing materials, production tools and end–of–life (EoL) components (Figure 2.1 [5,6]): manufacturing waste is approximately 40% of all the CFRP waste generated [7] (woven trimmings contribute with more than 60% to this
number \[8\]). Continuing with the aeronautics sector as example, the first aircraft with structural CFRP components will soon be decommissioned \[4\]; within 30 years, the same will happen to the new composite–generation aircraft (8,500 commercial planes will be retired by 2025 \[9\]), with each vehicle representing more than 20 ton of CFRP waste \[10\]. Within a similar time frame, the wind industry will be another great source of CFRP waste \[11\].

Recycling composites is inherently difficult because of (i) their complex composition (fibres, matrix and fillers), (ii) the cross–linked nature of thermoset resins (which cannot be remoulded), and (iii) the combination with other materials (metal fixings, honeycombs, hybrid composites, etc.). Presently, most of the CFRP waste is landfilled \[12\]; the airframe of EoL vehicles is usually disposed in desert graveyards, airports, or by landilling \[9,13\]. However, these are unsatisfactory solutions for several reasons:

- Environmental impact: the increasing amount of CFRP currently produced raises concerns on waste disposal and consumption of non-renewable resources \[12\].
- Legislation: recent European legislation is enforcing a strict control of composite disposal; the responsibility of disposing EoL composites is now on the component’s manufacturer, legal landfilled of CFRP is limited, and for instance it is required that automotive vehicles disposed after 2015 are 85% recyclable \[14–16\].
- Production cost: CFs are expensive products, both in terms of energy consumed during manufacturing (up to 165 kWh/kg) and material price (up to 40 £/kg) \[9\].
- Management of resources: demand of virgin (v-) CFs usually surpasses supply–capacity \[10\], so recycled (r-) CFs could be re-introduced in the market for non-critical applications \[17,18\].
- Economic opportunity: disposing CFRP by landfiling, where not illegal, can cost approximately 0.20 £/kg \[19\]; recycling would convert an expensive waste disposal into a profitable reusable material \[17\].

It is clear that turning CFRP waste into a valuable resource and closing the loop in the CFRP life–cycle (Figure \[2.2\]) is vital for the continued use of the material in some applications, e.g. the automotive industry \[12\]. This need has driven not only a great amount of research on recycling processes for CFRPs over the last 15 years, but also the formation of several collaborative entities working on a more commercial / industrial level (Table \[2.1\]).

Some review papers on carbon–fibre recycling are available in the literature, focusing either on established recycling processes \[12,20\] or on their implementation at commercial scales \[11,21\]. However, there is a strong connection between recycling,
re-manufacturing processes and the final performance of the recyclates \cite{22}; this clearly affects the type of markets in which rCFs can be introduced, which has a great impact for any commercial recycling operation \cite{23}. Processes, performance, commercialisation and markets must therefore be considered altogether if a comprehensive analysis of CFRP recycling operations is pursuit.

This chapter aims to fill this need: on the one hand, it encompasses the latest technical developments and the forthcoming commercialisation challenges; on the other, it relates the existing recycling and re-manufacturing processes to the final recyclates and their respective potential market applications.

The chapter is organised as follows: Section \ref{sec:state_of_art} establishes the state of the art in carbon fibre recycling. Section \ref{sec:re-manufacturing} analyses re-manufacturing of recycled composites using rCFs. Section \ref{sec:current_issues} discusses achievements and current issues with recycling operations, including technical, commercial and marketing considerations, all in the scope of structural applications. Finally, the main conclusions are summarised in Section \ref{sec:conclusions}.
<table>
<thead>
<tr>
<th>Initiative</th>
<th>Scope</th>
<th>Contributors</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFRA, Aircraft Fleet Recycling Association (2006)</td>
<td>“Sustainable management of EoL airframes and engines” [29]</td>
<td>· Aircraft manufacturers&lt;br&gt;· Material recyclers&lt;br&gt;· Technology developers&lt;br&gt;· Others (currently over 40 members) [29,30]</td>
<td>· Publishing standards for aircraft recycling [31] · Accrediting companies with eco–friendly certificate [29] · Retiring aircraft (7,000 since 2006) [29] · Supporting CFRP recycling activities</td>
</tr>
<tr>
<td>Increasing Sustainability and Recycling Consortium (2009)</td>
<td>To “ensure the sustainability of [composites] industry, increase uptake and secure the future use of advanced composites” [1]</td>
<td>· BIS (UK Dept. for Business, Innovation &amp; Skills)&lt;br&gt;· CFRP producers &amp; users&lt;br&gt;· CF recyclers&lt;br&gt;· Universities</td>
<td>· Supporting the improvement and development of recycling processes [10] · Establishing applications for the recyclates [10] · Providing a link between industry and researchers</td>
</tr>
<tr>
<td>Carbon Fibre Recycling and Reuse Conference (2009) [33]</td>
<td>The world’s first Conference exclusively dedicated to CFRP recycling</td>
<td>· CF recyclers&lt;br&gt;· (r)CFRP producers &amp; users&lt;br&gt;· (r)CF and (r)CFRP researchers</td>
<td>· Overview on advances in recycling and re-manufacturing [34] · Discussion on commercialisation of processes and recyclates [34] · Analysis of (r)CFRPs and market outlook [34]</td>
</tr>
</tbody>
</table>
Recycling carbon fibre reinforced polymers for structural applications

References:
(i) from Connor (2008) [35]
(ii) from NASA (F-18 aircraft) [36]
(iii) from Marsh (2008), at Recycled Carbon Fibre Ltd. [4]
(iv) from Connor (2008) [35]
(v) from Janney et al. (2009), at Materials Innovation Technologies LLC. [37]

Figure 2.2: Closed life-cycle for CFRPs.

2.2 Carbon fibre recycling processes

2.2.1 Technology families

2.2.1.1 Overview

Two technology families have been proposed to recycle CFRPs (Figure 2.3): mechanical recycling and fibre reclamation. Both are addresses below, and a critical comparison is summarised in Table 2.2. Most efforts have been focusing on thermoset composites (e.g. carbon–epoxy systems), as their cross–linked matrix cannot be reprocessed simply by remelting [12].
2.2.1.2 Mechanical recycling

Mechanical recycling involves breaking down the composite by shredding, crushing, milling, or other similar mechanical process; the resulting scrap pieces can then be segregated by sieving into powdered products (rich in resin) and fibrous products (rich in fibres) [12,38].

Typical applications for mechanically-recycled composites include their re-incorporation in new composites (as filler or reinforcement) and use in construction industry (e.g. as fillers for artificial woods or asphalt, or as mineral-sources for cement) [12,39]. However, these products represent low-value applications; mechanical recycling is therefore mostly used for glass fibre reinforced polymers (GFRPs) [12], although applications to CFRPs can be found as well (especially with thermoplastic resins) [12,24,40,42]. Because mechanical recycling does not recover individual fibres, the mechanical performance of the recyclates is evaluated at the composite level (Table 2.5 in Section 2.3).

2.2.1.3 Fibre reclamation

Fibre reclamation consists on recovering the fibres from the CFRP, by employing an aggressive thermal or chemical process to break-down the matrix (typically a thermoset); the fibres are released and collected, and either energy or chemical feedstock can be recovered from the matrix. Fibre reclamation may be preceded by preliminary operations e.g. cleaning and mechanical size-reduction of the waste.
<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>- Simplicity of processes</td>
<td>- Significant degradation of mechanical properties</td>
<td>ECRC</td>
</tr>
<tr>
<td></td>
<td>- Recovery of both fibres and resin</td>
<td>- Unstructured, coarse and non-consistent fibre architecture</td>
<td>Kouparitsas et al. [40]</td>
</tr>
<tr>
<td></td>
<td>- No use or production of hazardous materials</td>
<td>- Limited possibilities for re-manufacturing</td>
<td>Ogi et al. [42]</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>- High retention of mechanical properties</td>
<td>- Possible deposition of char on fibre surface</td>
<td>RCF-Ltd</td>
</tr>
<tr>
<td></td>
<td>- Potential to recover chemical feedstock from the resin</td>
<td>- Sensitivity of properties of recycled fibres</td>
<td>JCMA</td>
</tr>
<tr>
<td></td>
<td>- No use of chemical solvents</td>
<td>- Environmentally hazardous off-gases</td>
<td>MIT-RCF</td>
</tr>
<tr>
<td>Fluid. bed proc.</td>
<td>- High tolerance to contamination</td>
<td>- Strength degradation between 25% and 75%</td>
<td>HADEG</td>
</tr>
<tr>
<td>Chemical</td>
<td>- Very high retention of mechanical properties and fibre length</td>
<td>- Common reduced adhesion to polymer</td>
<td>ATI, 1998, under continuous development</td>
</tr>
<tr>
<td></td>
<td>- High potential for material recovery from chemically bonded matrix</td>
<td>- Stronger degradation of properties of recycled fibres</td>
<td>Pickering et al., University of Nottingham [12,43,53–58]</td>
</tr>
</tbody>
</table>

Key for Process scale: P: pilot-scale plant; L: laboratory scale; C: commercial-scale plant; u/p: upgrade planned.
Fibre reclamation processes are particularly suitable to CFRPs: carbon fibres have high thermal and chemical stability [12], so usually their excellent mechanical properties are not significantly degraded (especially regarding stiffness). Generally, the rCFs have a clean surface (Figure 2.4(a)) and mechanical properties comparable to the virgin (v-) precursors (Figure 2.5); nevertheless, some surface defects (pitting, residual matrix and char, Figure 2.4(b)) and strength degradation (especially at longer gauge lengths) are also reported [75].

After reclamation, the recycled fibres are usually re-impregnated with new resin to manufacture recycled CFRPs (rCFRPs, Section 2.3). In addition, rCFs have also been used in non-structural applications (Section 2.4.3).

An overview on fibre reclamation processes is given in Sections 2.2.2 to 2.2.4. A critical comparison between them is established in Table 2.2, while Figure 2.5 and Table 2.3 present the mechanical properties of recovered fibres.

2.2.2 Pyrolysis

Pyrolysis, the thermal decomposition of organic molecules in an inert atmosphere (e.g. N$_2$), is one of the most widespread recycling processes for CFRP. During pyrolysis, the CFRP is heated up to 450$^\circ$C to 700$^\circ$C in the (nearly) absence of oxygen; the polymeric matrix is volatilised into lower–weight molecules, while the CFs remain inert and are eventually recovered [4, 47]. Advantages, drawbacks and current implementations of pyrolysis are summarised in Table 2.2; mechanical properties of reclaimed fibres are presented in Table 2.3.

![Figure 2.4](image-url)

(a) Clean recycled fibres. (b) Recycled fibres with char residue.

Figure 2.4: Scanning–electron microscopy of recycled (through pyrolysis) carbon fibres [76].
Recycling carbon fibre reinforced polymers for structural applications

Table 2.3: Mechanical properties of recycled CFs reclaimed through different processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Recycler(^{(*)})</th>
<th>Fibre type</th>
<th>(E^f) (GPa)(^{(1)})</th>
<th>(X_T^f) (GPa)(^{(1)})</th>
<th>(S_{IF}) (MPa)(^{(1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>RCF-Ltd [35]</td>
<td>Hexcel AS4</td>
<td>231(+0.4%)</td>
<td>3.69(+2%)</td>
<td>42(−2%)</td>
</tr>
<tr>
<td></td>
<td>Meyer et al. [47]</td>
<td>Toho HTA</td>
<td>3.57(−4%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Karborek S.p.a. [75]</td>
<td>Toray T800</td>
<td>222(−12%)</td>
<td>4.62(−10%)</td>
<td>99(+41%)</td>
</tr>
<tr>
<td></td>
<td>Lester et al. [52]</td>
<td>Grafil 34-700</td>
<td>210(−13%)</td>
<td>3.26(−20%)</td>
<td></td>
</tr>
<tr>
<td>Fluid. bed</td>
<td>Pickering et al. [53,57]</td>
<td>Toray T600S</td>
<td>218(+4%)</td>
<td>3.18(−34%)</td>
<td>62(+3%)</td>
</tr>
<tr>
<td>Chemical</td>
<td>ATI [67]</td>
<td>Hexcel AS4</td>
<td>3.37(−9%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pinero-Hernanz et al. [71]</td>
<td>Toray T600S</td>
<td>205(−15%)</td>
<td>4.00(−2%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jiang et al. [61]</td>
<td>Toray T700S</td>
<td>225(−2%)</td>
<td>5.20(−0.3%)</td>
<td>62(−9%)</td>
</tr>
</tbody>
</table>

\(^{(*)}\) See Sections 2.2.2 (pyrolysis), 2.2.3 (fluidised bed process), and 2.2.4 (chemical recycling).

\(^{(1)}\) Values between brackets represent variation relatively to virgin fibre.

Recycled Carbon Fibre Ltd. (RCF-Ltd) (Milled Carbon Group) [4–6] is “the world’s first commercial scale continuous recycled carbon fibre operation”. Milled Carbon Group started developing a pyrolysis process for CFRP in a pilot-plant in 2003, and finally upgraded to commercial scale and formed Recycled Carbon Fibre Ltd. (based in the West Midlands, UK).

![Graphs: Young’s modulus, Strength, Interfacial shear strength with epoxy resin.](image)

Figures 2.5: Mechanical properties of recycled carbon-fibres and their virgin precursors [5,53,61], see Sections 2.2.2 (pyrolysis), 2.2.3 (fluidised bed process), and 2.2.4 (chemical).
RCF-Ltd has successfully reclaimed fibres from virtually all types of waste (including EoL military aircraft, hybrid pressure vessels, large production tools, and manufacturing waste, Figure 2.1). Their process is implemented as a semi–open continuous–belt furnace, with controlled atmosphere to avoid char formation. It complies with all the relevant legislation regarding the treatment (post-combustion) of off-gases; the energy from the matrix is recovered and fed back in the process (material recovery from the polymer is not economically viable) [45].

The large dimensions and continuity of the furnace belt allow for entire out–of–date pre-preg rolls to be recycled while maintaining the architecture of the reinforcement. Nevertheless, most of RCF-Ltd’s products are sold as milled or chopped fibres [4] or pellets; the company recently launched Green Carbon Fibre Ltd. for commercialisation of these products [77]. The Milled Carbon Group has been active in research projects with Boeing (one of their feedstock providers) and many Universities [6].

Japan Carbon Fiber Manufacturers Association (JCMA) [1, 32] started working on CFRP recycling in 2006. JCMA currently runs a pyrolysis plant, but details on the process itself and mechanical properties of fibres have not been disclosed.

Materials Innovation Technologies RCF (MIT-RCF) [48] was created by MIT-LLC, an “advanced–materials solutions–developer” company, based at North Carolina, USA. MIT-LLC started recycling CFRP in 2008, using an undisclosed pyrolysis process [37]. Their approach includes a preliminary step of chopping the feedstock to a consistent length; after pyrolysis, an in–house developed manufacturing process (three dimensional engineered preforming, 3–DEP) proved to be particularly suitable for re-manufacturing (Section 2.3).

CFK Valley Stade Recycling GmbH & Co. KG [49] is a German CFRP–recycling company. CFK uses a pyrolysis process (complemented with an oxidation step for char removal) developed together with the Technical University of Hamburg–Harburg [19] and ReFiber ApS.

CFK’s pyrolysis is implemented in a continuous process, and it is suitable for several types of CFRP waste; the main products comprise milled fibres, chopped fibres, and textile products. The company collaborates with Airbus Hamburg [21, 49].

Karborek S.p.a. [50] is an Italian CFRP–recycling company. Karborek uses a combined pyrolysis and upgrading (in oxygen) patented process to recycle the fibres and avoid char formation [46]; although fibre–length is preserved during reclamation, Karborek’s main products are milled and chopped rCF, as well as blended non-woven veils with carbon and thermoplastic fibres (Section 2.3.3). The company collaborates with Boeing and Alenia [50].
Firebird Advanced Materials, Inc. [8] is another company based in North Carolina, USA; their pyrolysis uses a continuous microwaves process, which avoids char formation [8,52].

HADEG Recycling Ltd. [51] is a German company working in collaboration with the Technical University of Hamburg–Harburg. HADEG’s products include not only fibres reclaimed by pyrolysis, but also unprocessed manufacturing remainings (dry CF rovings / fabrics and uncured pre-preg cut-offs).

2.2.3 Oxidation in fluidised bed

Oxidation is another thermal process for CFRP recycling; it consists in combusting the polymeric matrix in a hot and oxygen–rich flow (e.g. air at 450°C to 550°C). This method has been used by a few researchers [78], being the fluidised bed process (FBP) the most well–known implementation [12,54].

FBP has been developed and implemented by Pickering et al. at the University of Nottingham for more than 10 years [54]. Advantages and drawbacks of FBP are summarised in Table 2.2; mechanical properties of the reclaimed fibres are presented in Table 2.3.

During recycling, CFRP scrap (reduced to fragments approximately 25 mm large) is fed into a bed of silica on a metallic mesh. As the hot air stream passes through the bed and decomposes the resin, both the oxidised molecules and the fibre filaments are carried up within the air stream, while heavier metallic components sink in the bed; this natural segregation makes the FBP particularly suitable for contaminated EoL components [12, 43]. The fibres are separated from the air stream in a cyclone, and the resin is fully–oxidised in an afterburner; energy–recovery to feed the process is feasible [7,12,54,55].

2.2.4 Chemical recycling

Chemical methods for CFRP recycling are based on a reactive medium — e.g. catalytic solutions [67], benzyl alcohol [62], and supercritical fluids [61,71,72,79] — under low temperature (typically < 350°C). The polymeric resin is decomposed into relatively large (and therefore high value) oligomers, while the CFs remain inert and are subsequently collected [63].

Advantages, drawbacks and current applications of chemical recycling are summarised in Table 2.2; mechanical properties of reclaimed fibres are presented in Table 2.3.
Adherent Technologies, Inc. (ATI) is an R&D centre (New Mexico, USA), where Allred et al. developed a “catalytic tertiary recycling process” for CFRP over the past 10 years. The standard method consists on a proprietary low-temperature liquid catalysis; in addition, a dry pyrolytic process was also implemented to overcome problems with contaminated waste. Due to its scrap preparation and post-treatment units, the whole process is automated and runs continuously.

ATI recycles both manufacturing waste and EoL components. The rCFs are marketed either milled or chopped; resin products are also recovered as fuels or chemical feedstock. The centre collaborates with Boeing, North Carolina State University and the US government.

Hitachi Chemical Co., Ltd. is a Japanese chemical manufacturer and R&D centre, where Nakagawa et al. developed a CF–epoxy recycling process using benzyl-alcohol and a catalyst in a N\textsubscript{2} atmosphere. The plant includes a distillation system for cleaning the reaction fluid (which is then re-introduced in the system) and recovering resin-based products. Nakagawa et al. have reclaimed CFs from EoL components of sports and aeronautics industry.

Supercritical fluids (SCFs) are fluids at temperatures and pressures (typically just) above the critical point; at this stage, the fluid presents itself in one single supercritical phase, while having combined characteristics: liquid-like density and dissolving power, and gas-like viscosity and diffusivity. SCFs can therefore penetrate porous solids and dissolve organic materials, while still being relatively innocuous under atmospheric conditions.

Several types of SCF (usually coupled with alkali catalysts) have been used for CF recycling, such as water, methanol, ethanol, acetone, and propanol, being the latter considered the best option.

Chemical recycling with SCFs is a more recent approach; it is nevertheless already recognised for producing rCFs with virtually no mechanical degradation, and for allowing recovering useful chemicals from the matrix.

2.3 Composites re-manufacturing

2.3.1 Introduction

The second phase of CF reclamation processes (overview in Figure 2.3(b)) consists on re-impregnating the reclaimed fibres with a new matrix (Figure 2.6).
The rCFs are usually fragmented into short lengths, as a result of (i) size reduction of CFRP waste before reclamation, (ii) fibre breakage during reclamation, and (iii) chopping of the fibres after reclamation. In addition, all fibre reclamation processes remove the sizing from the fibres, so the recyclate is in a filamentised, random, low-density-packing (fluffy) form (Figure 2.7) [43]. Therefore, the existing manufacturing processes — developed for virgin materials, typically available as sized tows — must be adapted to the unique recycled-fibre form [43,59].

An overview on re-manufacturing processes is given in Sections 2.3.2 to 2.3.5. A critical comparison between them is established in Table 2.4; Figure 2.8 and Table 2.5 present the mechanical properties of the different types of rCFRP.

Figure 2.6: Re-manufacturing of rCFRPs.

Figure 2.7: RCFs in a typical unsized, random, low-density-packing (“fluffy”) form [43].
Table 2.4: Summary analysis of different re-manufacturing processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct moulding</td>
<td>Implementation manufacturer already known</td>
<td>Mechanical performance compatible with low-/medium-end structural applications</td>
</tr>
<tr>
<td>Compr. mould. of non-woven products</td>
<td>Development of processes needed for improvement of mechanical properties</td>
<td>Common fibre damage during compression moulding</td>
</tr>
<tr>
<td>Compr. mould. of aligned mats</td>
<td>Improved uniaxial mechanical properties</td>
<td>Need for nearly perfect alignment to improve packability</td>
</tr>
<tr>
<td>Impregnation of woven mat</td>
<td>Structured architecture with continuous fibres</td>
<td>Applicability currently reduced</td>
</tr>
</tbody>
</table>

Key for Focus: (P): process development; (T): mechanical testing; (D): demonstrator manufacturing (see Table 2.8).

Key for Matrix: (r)PP: (recycled) polypropylene; PC: polycarbonate; EP: epoxy resin; VE: vinylester resin; UP: unsaturated polyester; un.: unknown.

---

**Process**

- Direct moulding
- Compr. mould. of non-woven products
- Compr. mould. of aligned mats
- Impregnation of woven mat
2.3.2 Direct moulding

2.3.2.1 Overview

Injection moulding (IM) and bulk moulding compound (BMC) compression are two direct methods of remoulding rCFs into recycled composites. Advantages, drawbacks and applications of these processes are summarised in Table 2.4, and the mechanical properties of the composites are presented in Table 2.5.

2.3.2.2 Injection moulding

During IM, a mixture of resin (typically a thermoplastic), rCFs (short or milled) and fillers / additives is pre-compounded into pellets, which are subsequently injected into a mould (at 10 MPa to 100 MPa) [81].

Wong et al. (University of Nottingham) [82] injected rCFs (from FBP) with polypropylene (PP). The addition of coupling agents (maleic anhydride grafted polypropylene, MAPP) improved fibre–matrix adhesion and thus the overall mechanical properties (Table 2.5).
Chapter 2

Table 2.5: Mechanical properties of recycled CFRPs manufactured through different processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Manufacturer</th>
<th>Matrix</th>
<th>$V_f$ (%)</th>
<th>$E_T$ (GPa)</th>
<th>$X_T$ (MPa)</th>
<th>$U_{imp}$ (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical recycling</td>
<td>Takahashi et al. [41]</td>
<td>PP</td>
<td>24</td>
<td>21 (a)</td>
<td>101 (a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ogi et al. [42]</td>
<td>ABS</td>
<td>24</td>
<td>12</td>
<td>102</td>
<td>19</td>
</tr>
<tr>
<td>Injection moulding</td>
<td>Wong et al. [82]</td>
<td>PP (b)</td>
<td>19</td>
<td>16</td>
<td>126</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Connor et al. [35]</td>
<td>PC</td>
<td>16</td>
<td>14</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>BMC compr.</td>
<td>Turner et al. [58]</td>
<td>EP (c)</td>
<td>10</td>
<td>20</td>
<td>71</td>
<td>8</td>
</tr>
<tr>
<td>Compr. mould. of non-woven products</td>
<td>Wong et al. [76]</td>
<td>EP</td>
<td>30</td>
<td>25</td>
<td>207</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nakagawa et al. (d)</td>
<td>UP</td>
<td>16</td>
<td>5.5</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Janney et al. [37]</td>
<td>EP</td>
<td>34</td>
<td>23 (e)</td>
<td>400 (e)</td>
<td></td>
</tr>
<tr>
<td>Compr. mould. of aligned mats</td>
<td>Turner et al. [58]</td>
<td>EP</td>
<td>44</td>
<td>80</td>
<td>422</td>
<td>35</td>
</tr>
</tbody>
</table>

(*) See Sections [2.2.1.2](#), [2.3.2.2](#), [2.3.2.3](#), [2.3.3](#), and [2.3.4](#).
(a) Along preferential fibre direction.
(b) With 5% (over fibre weight fraction) of G3003 MAPP coupling agent.
(c) Filled with calcium carbonate, moulded at 2 MPa.
(d) Recycled–CF feedstock with $l_f = 25$ mm.
(e) Flexural properties.

Connor et al. (North Carolina State University) [35] manufactured and compared the performance of two injected CFRPs: one with virgin and another with recycled (from RCF-Ltd) carbon fibres. The recyclate (Table 2.5) was 25% less stiff than the virgin control; strength reduction was less pronounced (12%), likely due to an improved fibre–matrix adhesion in the recyclate. The same process was not successful with ATI fibres, because of their more dispersed structure and poorer fibre–matrix adhesion.

2.3.2.3 BMC compression

BMCs are intermediate products made by mixing resin (typically a thermoset), rCFs, fillers and curing agents into bulky charges; this premix is subsequently compression moulded (under 3.5 MPa to 35 MPa) into an rCFRP component [81,90].

Pickering, Turner et al. (University of Nottingham) moulded several BMCs with rCFs from the FBP [7,58] and SCFs [58]. The formulation of the BMC was tuned so as
to overcome the poor flow properties of the resin and the filamentised and entangled form of the fibres.

The main factors affecting the mechanical performance of the rCFRPs (especially the strength) were the fractions of fillers and of rCFs. The mechanical performance of the rCFRPs (optimised properties in Table 2.5) is superior to that of commercial glass BMCs; however, it is not clear whether rCFRPs can compete in price.

2.3.3 Compression moulding of intermediate non-woven products

The production and subsequent re-impregnation of 2D or 3D rCF non-woven dry products (with a short and random reinforcement architecture, Figure 2.9(a)) is one of the most widely used manufacturing processes for rCFRPs.

Several methods to produce the intermediate dry non-woven products are summarised in Table 2.6; the potential for fibre alignment (detailed in Section 2.3.4) is highlighted. Most techniques are similar to the production of Chopped Strand Mats (mostly applied to vGFRP) or paper.

The 2D or 3D non-woven dry products are then either compression moulded with resin layers, or re-impregnated through a liquid process. Advantages, drawbacks and applications of these processes are summarised in Table 2.4; mechanical properties of the rCFRPs are presented in Table 2.5.

Table 2.6: Overview on manufacturing processes for non-woven intermediate products.

<table>
<thead>
<tr>
<th>Process</th>
<th>Manufacturer</th>
<th>Overview (see Section 2.3.3)</th>
<th>Fibre alignment (see Section 2.3.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper-making technique</td>
<td>TFP and Pickering et al.</td>
<td>Industrial wet papermaking process (with bundle filamentation step)</td>
<td>Controllable preferential alignment along moving belt</td>
</tr>
<tr>
<td>Wet dispersion</td>
<td>Szpieg et al.</td>
<td>In-house developed wet mixer</td>
<td>Not possible in current configuration</td>
</tr>
<tr>
<td>Carding process</td>
<td>Cornacchia et al.</td>
<td>Dry carding of rCF and thermoplastic fibre hybrid mats</td>
<td>Unknown</td>
</tr>
<tr>
<td>Carding process</td>
<td>Nakagawa et al.</td>
<td>Dry carding of rCF mats</td>
<td>Unknown</td>
</tr>
<tr>
<td>3-DEP process</td>
<td>MIT-LLC</td>
<td>Deposition of chopped fibres on a 3D forming screen</td>
<td>Controllable alignment using multi-motions deposition tool</td>
</tr>
</tbody>
</table>
Figure 2.9: Intermediate non-woven rCF products for compression moulding.

Pickering, Wong, Turner, et al. (University of Nottingham, in collaboration with Technical Fibre Products, TFP 87,88) produced 2D mats with rCFs reclaimed through several processes (FBP 7,57, pyrolysis 76 and SCF 58).

The random and filamentised form of the rCFs yielded mats with high loft and low permeability; this increased the moulding pressures, which consequently damaged the fibres during manufacture. For instance, achieving $V_f = 40\%$ required compression at 14 MPa, leaving only 10\% of fibres longer than the critical length 76; therefore, and despite the good fibre–matrix adhesion, the rCFRP tensile strength saturated at $V_f = 30\%$ 57,76.

The specific stiffness and strength of the optimised rCFRP compared favourably with virgin materials (Table 2.5 and Figure 2.8) 57,89. Current work focuses on improving the mat–flow properties (e.g. by using thin mats down to 10 g/m², performing pre-compaction, reducing binder levels, filling the resin) 58,59, and studying alternatives to compression moulding (e.g. autoclave and out–of–autoclave curing) 43,58,59.

Materials Innovation Technologies, LLC. (MIT-LLC) developed the three dimensional engineered (3-DEP) preforming process (originally for virgin SFRPs) 85, which consists on the deposition of chopped fibres (dispersed in water) on a porous forming screen mounted on a deposition tool, through application of vacuum 37,48. The multiple–motions of the deposition tool enabled manufacturing of complex 3D parts (Figure 2.9(a)), with controlled fibre placement and orientation if required (detailed in Section 2.3.4).

MIT-LLC’s researchers found that using constant fibre–lengths within each plate improved the permeability of the preforms during compression moulding (at 1.7 MPa) and, consequently, the mechanical performance of the rCFRP (Figure 2.8 and Table 2.5).
Nakagawa et al. (from Hitachi Chemical Co., Ltd.) \cite{62,69} manufactured sheet moulding compounds (SMCs) by carding the rCFs. The composite’s tensile strength (Table 2.5) increased with the length of the rCFs fed to the carding machine up to a saturation point at $l_f \approx 40 \text{ mm}$.

Spiezg et al. (from Swerea SICOMP and Lulea University of Technology) produced fully-recycled composites \cite{94}, with milled rCFs (supplied by HADEG Recycling Ltd., $l_{mf} \approx 200 \mu\text{m}$ \cite{51}) and reprocessed PP PURE (commercialised by Lankhorst Pure Composites b.v.) manufacturing scrap \cite{95}.

Overall fibre content was $25\% < V^f < 30\%$, but resin rich regions were present; nevertheless, void content was only $1\%$ \cite{86}. Non-linear visco-elastic and plastic effects have been studied \cite{94}; current work focuses on improving mechanical performance.

Cornacchia et al. (from Karborek S.p.a.) \cite{46,50} manufactured hybrid non-woven mats with their in-house recycled CFs and PP fibres, using a carding process and subsequent compression moulding (at 8 MPa for $V^f = 30\%$).

### 2.3.4 Fibre alignment

Fibre alignment (Figure 2.9(b)) is a key-point to improve the mechanical performance of composites manufactured with discontinuous rCFs \cite{43}: not only the composite’s mechanical properties improve along preferential fibre direction, as manufacturing requires lower moulding pressures (Figure 2.9(c)) and smoother fibre–to–fibre interactions \cite{58,89}.

Advantages, drawbacks and applications of compression moulding of aligned mats are summarised in Table 2.4; mechanical properties of the rCFRPs are presented in Table 2.5.

The modified papermaking technique (developed by Pickering et al., at the University of Nottingham, and TFP) is a proprietary adaptation of the manufacturing process for random non-woven 2D mats. Currently, up to 80\% of the theoretical UD alignment is reached (Figure 2.9(b)), using shorter rCFs and thin mats (down to 10 g/m²) \cite{43,58,59,88}.

This method yielded rCFRPs with the highest mechanical properties ever reported (Figure 2.8 and Table 2.5); however, the filamentised rCF form reduces the impact energy to half of that typically measured for GFRP SMCs \cite{58}. Ongoing work focuses on improving packability of mats and through-the-thickness uniformity of alignment \cite{58,59,89}.
The 3-DEP process \cite{85} developed by MIT-LLC (Section 2.3.2), was used to produce a vCFRP cone with fibres preferentially aligned circumferentially; this was achieved by adjusting the position and motion of the deposition tool.

A centrifugal alignment rig \cite{89} was developed by Pickering et al. at the University of Nottingham; it uses a rotating drum equipped with a convergent nozzle, which aligns a highly–dispersed suspension of rCFs. The use of shorter fibres (down to $l^f \approx 5$ mm) improved the rCFRP alignment obtained (up to 90%).

A yarn spinning technique is under development by Pickering et al. (University of Nottingham and others), and within the FibreCycle project \cite{4, 5, 63}. Wet–dispersions of rCFs are transported through a pipe with an induced vortex; under optimised conditions, spun yarns with 50 filaments and 60 mm long are produced \cite{89}.

### 2.3.5 Woven rCFRP

As some recycling processes can preserve the reinforcement architecture of the waste (Section 2.2), it is possible to recover the structured weave from large woven items, e.g. out–of–date pre-preg rolls, EoL aircraft fuselage, or pre-preg trimmings from large components; re-impregnating (through e.g. resin transfer moulding (RTM) or resin infusion) the recycled weave fabrics then produces woven rCFRPs. With currently available recycling processes, stiffness and strength could theoretically reach more than 70 GPa and 700 MPa respectively; moreover, fabrics reclaimed from pre-preg rolls would be fully traceable. Advantages, drawbacks and applications of this process are summarised in Table 2.4.

Allen et al. \cite{90} (North Carolina State University) used woven fabrics from undisclosed recyclers; the mechanical properties of the rCFRPs were poor when compared to similar vCFRPs (especially tensile strength), due to fibre degradation during recycling.

Meredith et al. \cite{91} (Warwick University) used woven rCFRP in non–critical parts of an environmentally sustainable Formula-3 car (Figure 2.10(c)); the car also uses other recycled and natural materials (e.g. potato starch) and bio-fuels (e.g. derivatives from chocolate oil).

Janicki Industries \cite{93} collaborated with Boeing to manufactured a rCFRP tool for composite lay–up \cite{92}.
Recycling carbon fibre reinforced polymers for structural applications

(a) Wing mirror covers (by BMC compression, from Warrior et al. (2009) [59]).

(b) Aircraft seat arm-rest (by 3-DEP process, from George (2009) [92]).

(c) Rear or WorldFirst F3 car (by woven re-impregnation, from Meredith (2009) [91]).

Figure 2.10: Examples of demonstrators manufactured with recycled CFs.

2.4 Discussion

2.4.1 State of the art and outlook in recycling and re-manufacturing technologies

Three methods for recovering clean fibres from CFRP waste were identified: pyrolysis, oxidation in fluidised bed, and chemical recycling (Table 2.2). Pyrolysis is currently the only process with commercial-scale implementations [6,32,48]; some chemical methods are advantageous regarding the mechanical performance of the rCFs [59,61], while the fluidised bed process is particularly interesting for EoL components and contaminated waste [12].

Mechanical degradation is usually minor in all processes apart from the fluidised bed (Figure 2.5 and Table 2.3), although it depends on fibre type and length [75]. Current estimatives [9] suggest that reclaiming rCFs requires only a small fraction of the resources for producing vCFs (Table 2.7), so recycling CFRP appears to be economically and environmentally viable. The main technical challenges relate now to waste preparation, recycling of EoL parts, and quality control of rCFs [8,23,43].

Research on rCFRP manufacturing is still on-going, as the entangled and unsized rCF form requires existing methods to be adapted. Re-impregnating non-woven mats is one of the most effective methods in terms of the mechanical performance of the

Table 2.7: Estimated values for the cost of carbon fibres [9].

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Manufacturing energy (kWh/kg)</th>
<th>Price (£/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vCF</td>
<td>55 – 165</td>
<td>20 – 40</td>
</tr>
<tr>
<td>rCF</td>
<td>3 – 10</td>
<td>11 – 16</td>
</tr>
</tbody>
</table>
composites \[37, 48, 59, 76\]: properties are at the level of structural virgin materials e.g. GFRPs, short–fibre CFRPs and aluminium (Figure 2.8 and Table 2.5).

Further technical developments in re-manufacturing technologies are still needed, especially regarding inducing fibre alignment, increasing fibre content, and decreasing fibre damage during processing \[22, 43\] (see Chapter 4). The performance of most rCFs is similar to that of virgin fibres, so recycled composites could in principle reach the properties of vCFRPs with comparable architectures if suitable manufacturing processes were developed.

A few structural components have been manufactured with rCFRPs as technology demonstrators: crashworthy and secondary components for the automotive industry, components for aircraft interiors, and tooling (Figure 2.10 and Table 2.8).

2.4.2 Forthcoming challenges to the commercialisation of rCFs

In addition to the technical challenges identified in the previous section, the major current challenge to CFRP recycling operations is the establishment of a sound CFRP recycling chain supporting the effective commercialisation of recycling processes and products \[1, 8, 11, 21, 23, 43, 92\]. The main issues to overcome, as identified by academics, recyclers, end-users and governments, are:

- Global strategy: organised networks for CFRP recycling (Table 2.1) — bringing together suppliers / users (composite–related industries), recyclers and researchers — must be created, so as to understand the current state of the art and plan for future developments on the topic according to industrial needs.

- Incentives for recycling: governments should support the option of recycling; this could involve not only penalties for non-recyclers (e.g. landfilling taxes) but also direct privileges (e.g. carbon credits) for companies recycling their CFRP waste \[23\].

- Implementing suitable legislation: there is currently a void in specific legislation covering the CFRP recycling operations. For instance, the classification of pyrolysis processes for CFRP recycling should be distinguished from that of traditional pyrolysis processes \[45\]; a suitable classification of CFRP waste for international transport to recycling units needs to be approved.

- Logistics and cooperation in the supplying chain: waste suppliers must cooperate with recyclers, which includes supplying the waste in a continued and suitable form \[4, 8\] and providing the recyclers with material certificates whenever possible.
Table 2.8: Demonstrators manufactured with recycled CFs.

<table>
<thead>
<tr>
<th>rCFRP demonstrator</th>
<th>Virgin component</th>
<th>CF recycler (Section 2.2)</th>
<th>rCFRP manufacturer (Section 2.3)</th>
<th>rCFRP matrix(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wing mirror cover [59]</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Pickering et al. (using BMC compression)</td>
<td>UP</td>
</tr>
<tr>
<td>Car door panel [59]</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Pickering et al. (using CM non-woven mats)</td>
<td>EP</td>
</tr>
<tr>
<td>Corvette wheelhouse [37]</td>
<td>EoL F-18 aircraft stabiliser</td>
<td>RCF-Ltd</td>
<td>MIT-LLC, Janney et al. (with Boeing)</td>
<td>UP</td>
</tr>
<tr>
<td>Aircraft–seat arm–rest [92]</td>
<td>Boeing’s testing &amp; manufact. waste</td>
<td>MIT-LLC</td>
<td>MIT-LLC (with Boeing)</td>
<td>EP</td>
</tr>
<tr>
<td>Driver’s seat of a Student Formula SAE car [62]</td>
<td>Tennis rackets</td>
<td>Nakagawa et al., Hitachi Chemical.</td>
<td>Nakagawa et al., Hitachi Chem. (with Toyohashi U. of Tech.)</td>
<td>UP</td>
</tr>
<tr>
<td>Rear structure of WorldFirst F3 green car [91]</td>
<td>Outdated woven pre-preg</td>
<td>RCF-Ltd</td>
<td>Meredith et al. U. Warwick</td>
<td>EP</td>
</tr>
</tbody>
</table>

(*) Key for rCFRP matrix: EP: epoxy resin; UP: unsaturated polyester; un.: unknown.

(e.g. for out-dated prepreg rolls) [23]. Conversely, recyclers must ensure that materials and components supplied will not undergo reversed engineering.

- Market identification and product pricing: this requires that (i) characteristics and properties of different rCFRPs are known, (ii) their processing times and costs are assessed, and (iii) the value for the recycled label is established [23].

- Life–cycle analysis: the environmental, economic and technical advantages of rCFRPs over other materials and disposal methods can be estimated only through cradle–to–grave analyses of the whole CFRP life–cycle.

- Market establishment: ultimately, the major current challenge for the success of CFRP recycling is the establishment of a market for the recyclates; this is recognised by leading researchers [12, 43], CF recyclers [23] and CF users [92]. Creating a market requires all the previous issues to be overcome, so rCFs are accepted as an environment–friendly and cost–effective material.
2.4.3 Development of structural applications for rCFRPs

One of the most promising applications for rCFRPs consists of non-critical structural components [12,43,92]. Although there are currently non-structural applications for rCFs — e.g. industrial paints [5], construction materials [5,12], electromagnetic shielding [5,87], high performance ceramic brake discs [5,96], fuel cells [87] — structural applications would fully exploit the mechanical performance of the fibres, thus increasing the final value of recycled products.

The aeronautics industry is particularly interested in incorporating rCFRPs in the interiors of aircraft [18,92], as long as the materials are traceable and their properties consistent (which may easily achieved when the feedstock is manufacturing waste). Certification of recycled materials might not be viable in the short term, and it is recognised that rCFRPs should be allowed to mature in non-aeronautics applications first [92]; nevertheless, the involvement of Boeing and Airbus in CFRP recycling and their effort in identifying suitable applications for the recyclates (specifically in aircraft interiors) suggests that rCFRPs might be incorporated back into non-critical aeronautics applications in a foreseeable future.

There is also scope to manufacture automotive components with rCFRPs, not only for technical or economic reasons, but also to boost green credentials. As legislation tightened regarding recyclability and sustainability [16], the automotive industry grew interest for natural composites [97], which are nowadays widely used in mass production despite some associated problems (e.g. consistency of feedstock); rCFRPs could follow as an environmental-friendly material with improved mechanical performance.

Currently, structural demonstrators manufactured with rCFRPs are aimed at aircraft or automotive industries (Figure 2.10, Table 2.8); other markets have also been identified, such as construction industry, sports and household goods, and wind turbines [12,83]. Table 2.9 provides a comprehensive overview of potential applications for several types of rCFRPs; this is complemented by specific applications currently manufactured with virgin materials, to allow for a direct comparison regarding manufacturing methods and mechanical properties.

2.4.4 Multiscale analysis of the mechanical response of rCFRPs

General studies on the mechanical behaviour of rCFRPs [35,37,58,62,76,94] are valuable to validate the recycling processes and to identify major weaknesses in the recyclates. They also reveal how complex and unique the architecture of rCFRPs can be, and how essential it is to investigate their mechanical response in-depth [43,109].
Table 2.9: Potential structural applications for rCFRPs [83].

<table>
<thead>
<tr>
<th>Type of rCFRP (⋆)</th>
<th>Possible processes</th>
<th>Foreseen markets for rCFRP (see Table 2.2)</th>
<th>Examples of current solutions with virgin materials (†)</th>
<th>ET (GPa)</th>
<th>XT (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(*i) Low-reinforced TS</td>
<td>Pyrolysis</td>
<td>Automotive semi-structural parts</td>
<td>Car dashboard [98]</td>
<td>5.3</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Fluid bed</td>
<td>Automotive semi-structural parts</td>
<td>Car underbody shielding [99]</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Chemical moulding</td>
<td>Automotive semi-structural parts</td>
<td>Plywood replacement [100]</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>C. mould. non-woven mats</td>
<td>Equipment housing</td>
<td>Swimming pool</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>BMC compression</td>
<td>Automotive non-critical structures</td>
<td>Car rear wing [106]</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>C. mould.</td>
<td>Automotive non-critical structures</td>
<td>Car decklid [107]</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Lay-up of aligned pre-pregs</td>
<td>Aircraft interiors</td>
<td>Aircraft seat structure [57]</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aircraft interiors</td>
<td>Aircraft overhead bin [57]</td>
<td>0.24</td>
<td>0.2</td>
</tr>
<tr>
<td>(ii) Medium-reinforced TS</td>
<td>Pyrolysis</td>
<td>Automotive non-critical structures</td>
<td>Car rear wheel [106]</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Fluid bed</td>
<td>Automotive non-critical structures</td>
<td>Wind turbine non-critical layers [108]</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Chemical moulding</td>
<td>Aircraft non-critical structures</td>
<td>Wind turbine non-critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>C. mould. non-woven mats</td>
<td>Wind-turbine structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>BMC moulding</td>
<td>Wind-turbine structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>C. mould.</td>
<td>Wind-turbine structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Lay-up of aligned pre-pregs</td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
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<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Automotive structures</td>
<td>Wind turbine critical layers</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Key for Type of rCFRP: TP: thermoplastic matrix; TS: thermosetting matrix.


Aluminium is ≈ 2 × denser than rCFRPs under comparison.

Flexural property. Calculated from specific properties, assuming same density as rCFRPs under comparison.

(*i) Metals are known to have higher specific properties than rCFRPs. Due to the different density of the two classes, the comparison is not straightforward. The specific properties of rCFRPs are calculated assuming the same density as the corresponding metallic parts.
Chapter 2

Understanding the relations between microstructure, mechanical properties and damage mechanisms of rCFRPs provides informed guidance for reclaimers and manufacturers towards recyclates with optimal structural performance. Moreover, this understanding supports design methods for rCFRPs, which are essential for the establishment of a structural applications market. Given the urgency in closing the loop on the CFRP life-cycle, analysing the mechanical response of rCFRPs at the micro and macromechanical levels has become critical for the continued use of composites.

2.5 Conclusions

A comprehensive overview on the state of the art and market outlook for CFRP recycling operations was presented; recycling and re-manufacturing processes were reviewed, and the commercialisation challenges and potential markets for the recyclates were identified.

A critical comparison between recycling processes proved each of them to have specific advantages and drawbacks, suggesting complementarity rather than competition. Most of recycling processes yield rCFs with high retention of mechanical properties, and a few commercial-scale plants already exist (Tables 2.2 and 2.3).

Re-manufacturing composites with rCFs was found to be challenging, especially regarding achieving high mechanical properties; research is therefore still on-going. Nevertheless, the mechanical performance of some rCFRPs overcomes that of some conventional structural materials, and a few structural demonstrators for the automotive and aircraft industries have been manufactured (Tables 2.4 to 2.6 and 2.8).

It has been shown that establishing applications for the recyclates is the key to finally close the loop in the CFRP life-cycle. The technical feasibility of re-introducing the recyclates in the non-critical structural market has been demonstrated, and specific potential applications have been suggested (Table 2.9). Nevertheless, there are still several non-technical issues which need to be overcome; in that sense, collaborative organisations focusing on the whole chain of CFRP recycling are essential [1].

Researchwise, more detailed, multiscale and systematic studies on the mechanical performance of rCFs and rCFRPs are needed, so as to increase the acceptance of recyclates as structural materials by engineers and designers. It is also essential to perform life-cycle analyses of the several recycling and re-manufacturing methods, to assess cost effectiveness and environmental impact of using rCFs.
Chapter 3

The effect of recycling on the mechanical response of carbon fibres and composites

3.1 Introduction

The last decade has seen a dramatic development of technologies for recycling Carbon–Fibre Reinforced–Polymers (CFRPs), but the full potential for re-using the recyclates in structural applications is yet to be realised. This chapter investigates the effect of a commercial recycling process on CFRP, by comparing recycled and virgin materials at both the fibre and composite levels.

Several methods to remove the resin and recover virgin–like fibres from composite waste have been developed [12][110]. Amongst all, pyrolysis (thermal degradation in a controlled atmosphere) is currently the only process with a commercial implementation, run by ELG Carbon Fibre Ltd. (formerly Recycled Carbon Fibre Ltd., ELG-RCF) [6].

Pyrolysis conditions (temperature, atmosphere and processing time) have a strong influence on the quality of reclaimed carbon fibres [47]. Poorly–tuned processes result on fibre strength degradation (fibre stiffness is usually unaffected) or presence of residual matrix. Nonetheless, fibres recycled at small–scale processes usually recover more than 80% of the original stiffness and more than 90% of the original strength [46,47,75], suggesting that recycled carbon fibres can be re-used in structural applications [110].

This has driven efforts to re-impregnate recycled fibres with pristine resin, generally producing composites with discontinuous and complex architectures [22,37,58,76] (see Chapter 4). While these are very suitable to the typical unsized and unstructured form
of reclaimed fibres, they inhibit a meaningful comparison between recycled and virgin composites, as the latter normally have a different fibre architecture.

Some recycling processes, e.g. ELG-RCF’s conveyor–belt pyrolysis [6], can nevertheless preserve the virgin reinforcement architecture. This has been applied by Meredith et al. [91,111] to recover structured fabrics from out–of–date woven prepreg rolls (which represent approximately 10% of the CFRP waste currently generated). The recycled weave was then prepreged and used to manufacture components of a racing car.

Despite all research on small–scale recycling processes [46, 47, 75] and discontinuous recycled composites [22, 37, 58, 76], little is known about the performance of fibres reclaimed in commercial operations and the effect of recycling on woven composites. Recent work indicates that scaled up processes may induce additional fibre damage [112], although its impact at composite level has not been investigated. Only one recycled woven composite is so far characterised in the literature [111]; results suggest that fibre properties are not directly translated into composite performance.

This chapter aims therefore at two complementary goals:

1. To assess the performance of carbon fibres reclaimed at an industrial plant by different pyrolysis cycles;

2. To understand the effect of fibre reclamation on composite performance, by comparing virgin and recycled composites with identical architectures.

The materials analysed in this study are identified in Section 3.2, and the experimental procedures described in Section 3.3. Results are presented in Section 3.4 and discussed in Section 3.5, so the main conclusions are summarised in Section 3.6.

### 3.2 Materials, recycling and manufacturing

#### 3.2.1 Virgin material

The virgin (v) material (precursor to all recyclates) under investigation is a carbon–epoxy 2–D woven composite, supplied as prepreg for out–of–the–autoclave curing [113]. Material specifications are shown in Tables 3.1 (composite level) and 3.2 (fibre level).

Eight–ply laminates were laid–up and cured according to the manufacturer’s instructions [113] for posterior analysis of the virgin composite. For single–filament analysis, a tow of virgin unsized fibres was used.
The effect of recycling on the mechanical response of carbon fibres and composites

Table 3.1: Nominal specifications of the virgin composite prepreg [113].

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Reference</th>
<th>Fibre type</th>
<th>Resin type</th>
<th>Weave geometry</th>
<th>Fibre volume fraction, $V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexcel</td>
<td>M56/37%/280H5/AS4–3K</td>
<td>AS4</td>
<td>M56</td>
<td>5 harness satin</td>
<td>52.7%</td>
</tr>
</tbody>
</table>

3.2.2 Fibre reclamation

Four small rolls of out--of--date virgin material were reclaimed by Recycled Carbon Fibre Ltd. (now ELG Carbon Fibre Ltd. [6]), using different pyrolysis cycles. This removed the (uncured) epoxy resin and recovered four different recycled fabrics (Table 3.3); owing to ELG-RCF’s conveyer–belt process, the original weave architecture was preserved. All recycled (r) fibres (A, B, C and D) were analysed at the filament level.

3.2.3 Composite re-manufacturing

Two recycled fibre mats (r-B and r-D) were selected for re-manufacturing through resin film infusion (Table 3.3 and Figure 3.1), aiming to mimic the eight–ply virgin laminates. The same type of epoxy resin (HexPly M56 [113]) was used.

Each recycled composite ply was composed by one layer of recycled fibre mat and one layer of pristine resin film, matching the original resin content of the virgin prepreg.

Figure 3.1: Fibre reclamation and composite (re-) manufacturing.
(see area densities in Table 3.4). All recycled composite plies were individually vacuum–debulked to assist fibre–resin consolidation.

Laminate lay–up was performed as for the virgin material, ensuring a through–the–thickness homogenous distribution of the resin and laminate symmetry. Three recycled woven composites were manufactured, as specified in Table 3.3: materials r-B and r-D1 were cured as indicated by the resin manufacturer [113] (no external pressure applied), while r-D2 was cured under autoclave pressure to improve ply consolidation.

3.3 Experimental analysis

3.3.1 Single–fibre analysis

3.3.1.1 Fibre inspection

The morphologies of all fibre types (virgin and recycled) were investigated through Scanning Electron Microscopy (SEM) of tows (taken from the centre of the reclaimed mats). Fibre diameters ($\phi_f$) were measured (at 4,000× magnification) in 25 filaments.

The area density ($\rho_f A$) of each recycled weave was measured using a 120 mm×100 mm sample (taken from the centre of the reclaimed mat). Similar samples were manually sheared until the tows locked-up (a dry orthogonal weave offers virtually no resistance to shear until parallel rotated tows become in contact), to assess the drapability and proneness to distortion of the recycled fabrics.

3.3.1.2 Single fibre tensile tests

The tensile strength of all fibre types ($X_f^t$, stochastic variable) were determined through Single–Fibre Tensile Tests (SFTTs). These were performed according to the BS ISO 11566 Standard [115], using in–house made grips and following the specifications shown in Table 3.5. Individual realisations of fibre strength ($\sigma_f^t$) were calculated using the average diameter of the corresponding fibre type.

As the strength of brittle fibres exhibits non–negligible scatter and length dependency [116], its characterisation requires estimating the strength distribution parameters for a chosen reference length. For each fibre type, the experimentally measured values of strength at two gauge lengths were fitted into a single Weibull distribution (thus assuming strength is governed by the weakest–link theory), defined as:

$$F_X(\sigma_f^t) = 1 - \exp \left[ -\frac{l}{l^*} \left( \frac{\sigma_f^t}{\sigma_0^t} \right)^m \right],$$

(3.1)
The effect of recycling on the mechanical response of carbon fibres and composites

where $m$ is the shape parameter (length independent), and $\hat{\sigma}_f^0$ is the scale parameter for the reference length $\hat{l}$. For all fibre types, it was considered $\hat{l} = 15$ mm (mean nominal gauge length), and $m$ and $\hat{\sigma}_f^0$ were estimated through the maximum likelihood method (details are given in Appendix A).

3.3.2 Composite analysis

3.3.2.1 Microscopy and composition

The through–the–thickness section of each laminate (v, r-B, r-D1 and r-D2) was analysed under an optical microscope.

The average thickness of each laminate ($\bar{t}$) was measured from the corresponding standard characterisation specimens (see Section 3.3.2.2). Volume fractions of fibres ($V^f$), matrix ($V^m$) and voids ($V^v$) were estimated using the measured composite thickness, measured fibre area densities ($\rho_f^A$), and nominal composite densities (shown in Table 3.4), according to the following expressions:

$$V^f = \min\left\{\frac{\rho_f^A}{\hat{\rho}_f^A}, 1 - V^m\right\}, \quad V^m = \min\left\{\frac{\max\{\rho_f^A - \hat{\rho}_f^A, 0\} + \hat{\rho}_m^A}{\hat{\rho}_m^A}, 1 - V^f\right\}, \quad V^v = 1 - (V^f + V^m).$$

(3.2)

These are derived considering that (i) during recycling, significant amounts of residual resin are associated with negligible fibre loss (and vice–versa), and (ii) during cure, significant matrix bleeding may occur only after full impregnation.

3.3.2.2 Mechanical testing

The in–plane mechanical properties of the four composites were measured according to the specifications in Table 3.6 (whereby T, C and S respectively represent tension, compression and shear). For tension and compression, the same number of specimens were tested in the warp and weft directions (respectively represented by 1 and 2). All specimens were end–tabbed and equipped with strain gauges; both faces of compression specimens were instrumented to monitor bending.

The data reduction method for the $\pm 45^\circ$ shear tests was adapted from the original standard to account for large deformations (see full derivation in Appendix B). From the testing data (longitudinal deformation $\varepsilon_L$, transverse deformation $\varepsilon_T$ and load $P$), true shear deformations ($\gamma_{12}$) and shear stresses ($\tau_{12}$) along fibre direction were calculated as:
Table 3.2: Nominal specifications of the virgin carbon fibres [114].

<table>
<thead>
<tr>
<th>Fibre description</th>
<th>Nominal fibre properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Fibre type</td>
</tr>
<tr>
<td>Hexcel AS4</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Table 3.3: Identification of materials used.

<table>
<thead>
<tr>
<th>Fibre reference</th>
<th>Reclamation process(*)</th>
<th>Composite reference</th>
<th>Manufacturing process</th>
<th>Curing pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>v virgin</td>
<td>v</td>
<td>Prepreg curing</td>
<td>0 bar</td>
<td></td>
</tr>
<tr>
<td>r-A ELG-RCF, cycle A</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>r-B ELG-RCF, cycle B</td>
<td>r-B</td>
<td>Resin film infusion</td>
<td>0 bar</td>
<td></td>
</tr>
<tr>
<td>r-C ELG-RCF, cycle C</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>r-D ELG-RCF, cycle D</td>
<td>{ r-D1, r-D2 }</td>
<td>Resin film infusion</td>
<td>0 bar/7 bar</td>
<td></td>
</tr>
</tbody>
</table>

(*) Pyrolysis temperature is reduced from cycles A to D (all other process details are proprietary).

Table 3.4: Nominal densities of the virgin composite prepreg and its constituents [113].

<table>
<thead>
<tr>
<th>Nominal property</th>
<th>Prepreg ply</th>
<th>Fibre (in prepreg)</th>
<th>Resin (in film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume density, $\hat{\rho}_V$ (g/cm$^3$)</td>
<td>1.50</td>
<td>1.79</td>
<td>1.17</td>
</tr>
<tr>
<td>Area density, $\hat{\rho}_A$ (g/m$^2$)</td>
<td>444</td>
<td>280</td>
<td>164</td>
</tr>
</tbody>
</table>

Table 3.5: Specifications for single–fibre tensile tests.

<table>
<thead>
<tr>
<th>Load cell</th>
<th>Type of glue</th>
<th>Fibre gauge length (mm)</th>
<th>Displacement rate (mm/min)</th>
<th>Number of tests (per fibre type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 N</td>
<td>3M Scotch–Weld</td>
<td>10</td>
<td>0.1</td>
<td>$\geq 25$</td>
</tr>
<tr>
<td></td>
<td>9323 B/A epoxy</td>
<td>20</td>
<td>0.2</td>
<td>$\geq 25$</td>
</tr>
</tbody>
</table>

Table 3.6: Specifications for the standard mechanical characterisation (gauge section dimensions).

<table>
<thead>
<tr>
<th>Test case</th>
<th>Stacking sequence</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Disp. rate (mm/min)</th>
<th>Valid tests (per direction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>[0$_4$], or [90$_4$]</td>
<td>138</td>
<td>25</td>
<td>2.0</td>
<td>v, r-A, r-D1, r-D2</td>
</tr>
<tr>
<td>C</td>
<td>[0$_4$], or [90$_4$]</td>
<td>7</td>
<td>19</td>
<td>1.0</td>
<td>v, r-A, r-D1, r-D2</td>
</tr>
<tr>
<td>S</td>
<td>[±45]$_2$</td>
<td>138</td>
<td>25</td>
<td>2.0</td>
<td>v, r-A, r-D1, r-D2</td>
</tr>
</tbody>
</table>

36
The effect of recycling on the mechanical response of carbon fibres and composites

\[
\gamma_{12} = 2 \cdot \tan\left(\frac{\varepsilon_L + 1}{\varepsilon_T + 1}\right) - \frac{\pi}{2} \quad \text{and} \quad \tau_{12} = \frac{1}{2} \cdot \frac{P}{t_0 \cdot w_0 \cdot (1 + \varepsilon_T)} \cdot \cos(\gamma_{12}), \quad (3.3)
\]

where \(t_0\) and \(w_0\) are the initial specimen’s thickness and width. When the operational strain gauge range was exceeded (\(|\varepsilon| \gtrsim 4\%\)), \(\gamma_{12}\) was extrapolated linearly in time.

### 3.3.2.3 Fractography

Tensile and shear failure mechanisms were investigated in post–mortem fracture surfaces. Compressive failure was analysed in reduced compact compression specimens, by optical microscopy of several post–mortem cross sections (Figure 3.2) [22,120].

### 3.4 Results

#### 3.4.1 Single–fibre analysis

##### 3.4.1.1 Fibre morphology

The throughput of different recycling processes is analysed in Figure 3.3. When compared to the virgin fabric, the most aggressive process (A) yielded a lighter weave with significantly thinner fibres. On the contrary, fibres reclaimed by process D (the least aggressive one) showed no statistically significant variation of diameter, and a small increase of area density (which indicates the present of residual resin). Processes B and C produced intermediate results.

Figure 3.4 shows that, as the reclamation process becomes more aggressive (from D to A), the weaves become more drapable but also more susceptible to distortion.

![Specimen geometry](image1)

![Test setup](image2)

![Cross sections analysed](image3)

**Figure 3.2:** Reduced compact compression specimens for study of compressive damage.
Chapter 3

Figure 3.3: Fibre yield after pyrolysis (virgin–fibre properties indicated for reference).

Figure 3.4: Recycled fabrics sheared manually up to the lock-up point.

The morphology of virgin and reclaimed fibres is analysed in Figure 3.5. Process A (Figure 3.5(b)) induced extensive and severe pitting on the fibres, as well as an irregular surface. Fibres r-B (Figure 3.5(c)) show surface damage and a burnt aspect, but only occasional and mild pitting. Process C (Figure 3.5(d)) left minimal quantities of residual resin on an otherwise smooth fibre surface, with occasional mild pitting. The least aggressive cycle (D, Figure 3.5(e)) produced tows with alternate regions of
The effect of recycling on the mechanical response of carbon fibres and composites

(i) virgin–like fibres and (ii) fibres covered by a thin layer of residual resin with imprints of transverse filaments.

3.4.1.2 Mechanical properties

Figure 3.6(a) shows the average and standard deviations of fibre strengths measured by SFTTs. A clear size effect is present in all fibre types, which validates the use of a simple model neglecting end–effects for the comparative purpose of this analysis [116]. Reclaimed fibre types A, B and C showed a substantial strength degradation relatively to the virgin precursor, slightly more severe at the larger gauge length. In contrast, process D recovered fibres with nearly full strength retention.

Weibull plots with experimental and fitted single fibre strengths for all fibre types are presented in Figures 3.6(b–3.6(f) (same scale used for comparison). To include measurements at both gauge lengths, each strength realisation $\sigma_i$ at length $l_i$ is shown normalised to $\hat{l} = 15$ mm as:

$$\hat{\sigma}_i = \left(\frac{l_i}{\hat{l}}\right)^{1/m} \cdot \sigma_i.$$  (3.4)

Weibull parameters (including $m$ used in Equation 3.4) of fitted distributions are shown in Table 3.7 as well as the corresponding expected value ($\mu_X$) and Coefficient of Variation (CoV). The quality of fitting between the maximum likelihood Weibull distribution and experimental data is very good for all fibre types (Figures 3.6(b–3.6(f)).

The variability of fibre strength increased substantially after reclamation (Table 3.7). While this effect was magnified for the most aggressive processes, it was still considerable when no significant strength degradation was observed (process D).

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>$m$</th>
<th>$\sigma_0$ (GPa)</th>
<th>$\mu_X$ (GPa)</th>
<th>CoV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>9.34</td>
<td>4.954</td>
<td>4.699</td>
<td>12.8</td>
</tr>
<tr>
<td>r-A</td>
<td>1.99</td>
<td>0.839</td>
<td>0.744</td>
<td>52.5</td>
</tr>
<tr>
<td>r-B</td>
<td>2.91</td>
<td>1.130</td>
<td>1.007</td>
<td>37.4</td>
</tr>
<tr>
<td>r-C</td>
<td>2.87</td>
<td>1.462</td>
<td>1.303</td>
<td>37.8</td>
</tr>
<tr>
<td>r-D</td>
<td>4.77</td>
<td>4.988</td>
<td>4.567</td>
<td>23.9</td>
</tr>
</tbody>
</table>
Figure 3.5: Scanning-electron micrographs of virgin and recycled carbon fibres.
The effect of recycling on the mechanical response of carbon fibres and composites

(a) Fibre strength statistics (average strength retention indicated; error bars represent one standard deviation).

(b) Weibull plot for fibres v.

(c) Weibull plot for fibres r-A.

(d) Weibull plot for fibres r-B.

(e) Weibull plot for fibres r-C.

(f) Weibull plot for fibres r-D.

Figure 3.6: Tensile strengths of the virgin and recycled fibres. The Weibull plots show strength distributions normalised for $l = 15$ mm (95% confidence intervals for percentiles are presented as well).
3.4.2 Composite analysis

3.4.2.1 Morphology

For each composite manufactured, Figure 3.7 shows the average thickness and composition (in terms of fibre, resin and void content), while Figure 3.8 analyses the morphology of a representative cross section.

Recyclate B presented a slightly lower fibre content than that of the virgin material, although it was considerably thinner (Figure 3.7) due to fibre loss during reclamation (Figure 3.3). Virtually no voids were found, even where fibres were very tightly packed (Figure 3.8(b)).

Following the standard out-of-the-autoclave re-manufacturing cycle with weave D (material r-D1) resulted in a very high void content and poor compactation both at ply and tow levels (Figures 3.7 and 3.8(c)). Applying typical autoclave pressure levels (7 bar, as indicated for Hexcel HexPly AS4–8552 [121]) in material r-D2 greatly reduced void content, although the laminate was still thicker and had a lower fibre fraction than the virgin precursor (Figures 3.7 and 3.8(d)).

3.4.2.2 Mechanical properties

The elastic properties (unidirectional moduli $E$, in-plane shear modulus $G_{12}$, Poisson’s ratio $\nu_{12}$) and strengths ($X$ for unidirectional, $S_{12}$ for in-plane shear) of the virgin and recycled composites are presented in Tables 3.8 and 3.9. Figure 3.9 shows the average (represented by an overbar) retention of stiffness and strength for each recycled

![Figure 3.7: Thickness and constituent volume fraction of virgin and recycled composites.](image)
The effect of recycling on the mechanical response of carbon fibres and composites

Figure 3.8: Micrographs of through–the–thickness cross sections of virgin and recycled composites. (Brightness and contrast of zoom–ins were adjusted to enhance voids.)

composite relatively to the virgin precursor; confidence intervals for the ratios are based on Fieller’s theorem [122] (see Appendix C for details).

The mechanical performance of recycled composites (Figure 3.9) depended on three factors: (i) fibre reclamation process, (ii) laminate re-manufacturing process, and (iii) loading case. The stiffness of composite r-B was very close to that of the virgin material in all loading cases; in contrast, materials r-D1 and r-D2 were significantly softer (especially the former). Regarding strength, the recyclates underperformed the virgin precursor in all cases but composite r-B under compression; material r-D2 (cured at 7 bar) was consistently stronger than material r-D1 (cured at 0 bar). Warp and weft
Table 3.8: Elastic properties of virgin and recycled composites (considering true specimen thicknesses).

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{T1}$ (GPa)</th>
<th>$E_{T2}$ (GPa)</th>
<th>$E_{C1}$ (GPa)</th>
<th>$E_{C2}$ (GPa)</th>
<th>$G_{12}$ (GPa)</th>
<th>$\nu_{12}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>69.3 ± 1.7</td>
<td>67.5 ± 1.2</td>
<td>62.4 ± 1.8</td>
<td>62.2 ± 2.3</td>
<td>4.6 ± 0.1</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>r-B</td>
<td>65.9 ± 1.8</td>
<td>63.9 ± 1.5</td>
<td>59.6 ± 2.1</td>
<td>61.2 ± 3.0</td>
<td>5.2 ± 0.3</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>r-D1</td>
<td>47.3 ± 1.2</td>
<td>43.1 ± 1.3</td>
<td>43.8 ± 3.1</td>
<td>46.5 ± 4.5</td>
<td>2.7 ± 0.1</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td>r-D2</td>
<td>55.9 ± 1.4</td>
<td>56.2 ± 0.6</td>
<td>53.7 ± 1.9</td>
<td>53.4 ± 2.0</td>
<td>3.7 ± 0.1</td>
<td>0.02 ± 0.01</td>
</tr>
</tbody>
</table>

performances were similar, although tensile strength retention was slightly higher in the former.

A typical stress–strain curve for each material and loading case is reproduced in Figure 3.10. The response of all composites under tension was linear up to catastrophic failure (Figure 3.10(a)). Under compression, a progressive decrease of stiffness with increasing strains was observed in all cases; failure was catastrophic as well (Figure 3.10(b)). Composites v, r-D1 and r-D2 were markedly non-linear under ±45° shear, with progressive failure; on the contrary, composite r-B sustained a nearly-linear behaviour up to higher stresses, but failed catastrophically (Figure 3.10(c)).

3.4.2.3 Damage morphology

Figure 3.11 shows representative fracture surfaces of the composites tested under different loads; no significant difference was found between warp and weft directions.

Under tension, the virgin composite (Figure 3.11(a)) failed by fracture of all load-aligned tows within a narrow area, with considerable pull-out but very little delamination and defibrillation. The fracture surfaces of recyclate B were extremely smooth, with virtually no pull-out, delamination or defibrillation (Figure 3.11(d)). The opposite was observed in composite r-D1 (Figure 3.11(g)), where large delaminations (frequently along the entire gauge length) joined individual ply failures with extensive splitting of both longitudinal and transverse tows. Material r-D2 (Figure 3.11(j)) presented a frac-
The effect of recycling on the mechanical response of carbon fibres and composites

Figure 3.9: Ratio between mean properties of recycled and virgin composites, considering true specimen thicknesses. Error bars represent 95% confidence intervals.

ture surface more similar to that of the virgin composite, although with significantly more defibrillation of tows and delamination.

Under compression, the virgin composite (Figure 3.11(b)) failed by fibre kinking in load–aligned tows, splitting of transverse tows, and delamination; these features formed a narrow damage band inclined through the thickness. Composite r-B presented a remarkably similar damage morphology to the virgin counterpart (Figure 3.11(e)). In contrast, composite r-D1 (Figure 3.11(h)) failed mainly by coalescence of voids into extensive delaminations; tow splitting and kinking occurred only occasionally and later in the process. Recyclate D2 (Figure 3.11(k)) presented damage features similar to those of the virgin material, but spread over a larger area under the influence of manufacturing voids.
3.5 Discussion

3.5.1 Defects in reclaimed fibres

Following the fibre analysis presented in Section 3.4.1, Table 3.10 summarises the typical defects that can be expected after pyrolysis, depending on the intensity of the cycle.

Selecting the adequate processing conditions is a trade–off between (i) complete matrix removal and (ii) retention of fibre properties. Previous research [47, 75] has shown that laboratory / pilot scale reclamation processes can fulfil both conditions simultaneously. However, this may not be feasible at commercial scales as well.

Fibre types r-A, r-B and r-C underwent too aggressive cycles, with significant fibre degradation and strength reduction (Figures 3.3–3.6). Fibre stiffness was not affected by reclamation, as shown by the full retention of modulus in composite r-B (Figure 3.9(a)).

On the contrary, fibre type r-D showed no signs of degradation, but it is estimated that 7.6% of the original resin content was still present (Figures 3.3 and 3.6). This was
The effect of recycling on the mechanical response of carbon fibres and composites

Figure 3.11: Damage morphology in virgin and recycled composites. For each case, load direction and tow orientation are represented respectively by white arrows and a grid.
Table 3.10: Qualitative assessment of typical defects in fibres reclaimed by different pyrolysis cycles.

<table>
<thead>
<tr>
<th>Fibre defect</th>
<th>Pyrolysis reclamation cycle</th>
<th>Too aggressive (e.g. A, B, C)</th>
<th>Ideal cycle</th>
<th>Too gentle (e.g. D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter reduction (Figure 3.3(a))</td>
<td>••</td>
<td>◦ ◦</td>
<td>◦</td>
<td>○</td>
</tr>
<tr>
<td>Fibre loss (Figure 3.3(b))</td>
<td>••</td>
<td>◦ ◦</td>
<td>◦</td>
<td>○</td>
</tr>
<tr>
<td>Pitting (Figure 3.5)</td>
<td>••</td>
<td>◦ ◦</td>
<td>◦</td>
<td>○</td>
</tr>
<tr>
<td>Surface damage (Figure 3.5)</td>
<td>••</td>
<td>◦ ◦</td>
<td>◦</td>
<td>○</td>
</tr>
<tr>
<td>Residual matrix (Figure 3.5)</td>
<td>◦ ◦</td>
<td>○ ◦</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Stiffness reduction (Figure 3.12(a))</td>
<td>◦ ◦</td>
<td>○ ◦</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Strength reduction (Figure 3.6(a))</td>
<td>••</td>
<td>○ ◦</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Increase of strength CoV (Table 3.7)</td>
<td>••</td>
<td>◦ ◦</td>
<td>◦</td>
<td>○</td>
</tr>
</tbody>
</table>

Key: ○ - none / negligible; • - minor; •• - major.

sufficient to make the weave very stiff (Figure 3.4(d)); nevertheless, SEM observations show many clean fibres (Figure 3.5(e)), and individual fibres could be easily separated.

### 3.5.2 Through–the–thickness heterogeneity in reclaimed fibre mats

Figure 3.5(e) suggests that reclamation was heterogeneous in the through–the–thickness direction of the fabric. During pyrolysis of a woven prepreg, the surface of each tow is either directly exposed to the heat and gas flow, or shielded by the presence of a perpendicular tow. This resulted, for material r-D, into alternating regions of very clean fibres and residual matrix, separated by the tow crimp line.

The weave used in this work (5 harness satin) has a warp-dominated face and a weft-dominated one. The through–the–thickness heterogeneity shown in Figure 3.5(e) could thus result into different fibre properties along the warp and weft directions, for all recyclates. This is a possible justification for the slightly different tensile strength retentions at the composite level in the two material directions (Figure 3.9(d)).

### 3.5.3 Fibre strength retention after reclamation

Fibre strength was severely degraded by processes A, B and C, with pyrolysis temperatures ranging between 500 to 700°C. This is consistent with previous reports of fibre oxidation under the presence of oxygen for temperatures above 600°C [47].

The strength distributions of recycled fibres show a good fitting with Weibull’s theory (Figure 3.6–f) and the presence of size effects. This, combined with the larger
strength variability of recycled fibres, resulted in a reduction of strength retention with increasing gauge length (Figure 3.6(a)).

Figures 3.6(b) and 3.6(f) suggest that a part of the population of r-D fibres is stronger than the corresponding virgin population. This unexpected behaviour can be due to either (i) the presence of a layer of residual matrix on some recycled fibres (as seen in Figure 3.5(e)), or (ii) an artifact from testing (e.g. different stress concentrations at fibre ends, statistical variance). The possibility of having inadvertently tested two fibres together can be discarded, as it is not corroborated by the experimental data.

3.5.4 Influence of the fibre reclamation process on the composite performance

Figure 3.12 shows the relation between (i) the retention of average fibre strength (averaged between both gauge lengths) and (ii) the retention of average composite properties (averaged between warp and weft directions for tension and compression) after recycling. Given the different fibre contents of the four laminates tested (Figure 3.7), the real effect of reclamation is better captured considering all properties normalised to $\hat{V}_f = 52.7\%$. Table 3.11 summarises the influence of fibre reclamation defects on the mechanical response of recycled composites, as discussed below.

Composite stiffness (Figures 3.12(a)–c) was only slightly affected by the reclamation process (although obviously affected by fibre content after re-manufacturing). This confirms that fibre stiffness was fully recovered, even when strength was severely degraded. Nevertheless, the weave is more prone to distortion after more aggressive cycles (Figure 3.4), hence the small reduction of tensile and compressive stiffnesses and apparent increase of $\pm 45^\circ$ shear stiffness associated with severe fibre degradation (Table 3.11).

Regarding strength, the effect of weave distortion is not likely to overcome the effect of naturally existing crimp regions, which appears to be characterised by similar crimp

| Table 3.11: Influence of recycled–fibre defects on composite performance (for normalised fibre content). |
|---|---|---|---|
| Reclamation defect | Composite defect | Influence on properties |
| Fibre degradation (r-B) | Fibre strength reduction | o | •• | o | •• / o |
| Mild weave distortion | • | o | o | o |
| Residual matrix (r-D) | Weak interface / interlayer | o | o | •• | •• / o |
| Difficult compactation / voids | o | •• | •• | •• |
| Key: o – none / negligible; • – minor; •• – major. |
angles in both virgin and recycled laminates (Figure 3.8). However, the effect of fibre strength on composite strength is very pronounced and complex (Figures 3.12(d)–f).

### 3.5.4.1 Tensile failure

Tensile failure in woven composites is dominated by fibre fracture in load–aligned tows [123]. This is illustrated in Figure 3.12(d), where tensile strength at the composite level correlates well with fibre strength. Comparing the normalised (\(\hat{V}^f\)) strength retentions of materials r-D1 and r-D2 suggests the higher void content and poorer impregnation in the former also contribute to strength degradation, by triggering delaminations and smearing failure (Figures 3.11(g) and 3.11(j)).

The presence of the matrix and the stochastic nature of fibre strength are important as well. For very degraded fibres (e.g. r-B), the weakest ones in the composite will fail at very low stresses; however, the resin will withhold the damage in a confined region, thus shielding the stronger fibres from stress concentrations (Figure 3.12(d)).
For barely degraded fibres (e.g. r-D), variability of strength is nevertheless higher than in the virgin precursors (Table 3.7). The weakest fibres will thus fail prematurely, but at stress levels sufficiently high to promote matrix splitting, large stress concentrations and, consequently, structural failure (Figure 3.12(d)).

### 3.5.4.2 Compressive failure

Although compressive failure mechanisms in woven composites constitute still an active field of research, some authors claim that kink–band initiation — and, consequently, compressive strength — is dictated by the architecture and strengths of the resin and interface, but not by the strength of the fibres themselves [124–127]. This is strongly supported by the results obtained here.

On the one hand, virgin and r-B composites show virtually identical compressive strengths (Figure 3.9(e)) and damage morphologies (Figures 3.11(b),(e)). This proves that compressive failure was insensitive to a 78% fibre strength degradation; it also suggests the fibre–matrix interface in the recyclate to be as strong as that in the virgin material.

On the other hand, composites r-D1 and r-D2 showed residual resin (Figure 3.3(b)) and a poor impregnation (Figures 3.8(c)–(d)), both susceptible to result in a weak fibre–matrix interface (or in a weak interlayer of partially pyrolysed matrix between fibres and pristine resin). This caused a significant reduction of compressive strength, further affected by the presence of voids and delaminations (Figures 3.12(e) and 3.11(h),(k)).

It is envisaged in Table 3.11 and Figure 3.12(e) that very aggressive reclamation cycles will severely degrade fibre strength but completely pyrolyse the matrix, hence potentially resulting in a total recovery of compressive strength at the composite level. Too gentle cycles will preserve fibre strength, but leave residual resin; therefore, the fibre–matrix interface (or interlayer) will have degraded properties and, consequently, the composite compressive strength should decrease.

### 3.5.4.3 Shear failure

Under ±45° shear, two independent failure modes were observed (Figure 3.11); both are considered in Table 3.11 and Figure 3.12(f) as detailed below:

- Severely degraded fibres will lead to premature tensile failure of the tows, as seen in material r-B (Figure 3.11(f)). This composite withstood nevertheless the linear behaviour up to slightly higher stresses than the virgin one (Figure 3.10(c)); this
could suggest an improved fibre–matrix interface, although it may also be simply related to the higher shear modulus measured (Figure 3.12(c)).

- Composites with stronger fibres will enter the non–linear region, after which resin and fibre–matrix interface dominate the response. Clean fibres should yield composites with good fibre–matrix adhesion and, consequently, large shear strength. A too gentle pyrolysis cycle (e.g. D) will originate residual resin, thus reducing the adhesion and the composite shear strength (Figure 3.12(f)).

### 3.5.5 Analysis of the re-manufacturing process

The dissimilar morphologies observed in the different recycled composites (Figure 3.8) show that the specific fibre reclamation cycle affects composite re-manufacturing and the quality of re-impregnation. This effect, mainly related to the presence of residual matrix in reclaimed fibres, is summarised in Table 3.12 and discussed below.

On the one hand, in the absence of residual matrix, recycled weave r-B was successfully re-impregnated by out–of–the–autoclave resin infusion. The composite presented virtually no voids and a high fibre content (Figures 3.7 and 3.8(b)), suggesting similar resin flow, ply nesting and compactation as in the virgin precursor.

It was previously concluded (Sections 3.5.4.2 and 3.5.4.3) that cycle B did not degrade the fibre–matrix interfacial strength. This agrees with previous results obtained for single–fibre and short–fibre composites [22,76] (see also Chapter 4) and proves that, from a structural point of view, re-sizing is not necessary after full pyrolysis of the resin.

On the other hand, a too gentle pyrolysis cycle yields residual matrix; this limits resin flow, compactation and fibre wetting during re-impregnation. With no external pressure applied, composite r-D1 presented a low fibre volume fraction and high void content (Figure 3.7), with consequent loss of performance (Figures 3.12).

| Table 3.12: Relation between fibre reclamation cycle and manufacturing defects. |
|---------------------------------|--------|--------|--------|--------|
| Process                        | Intensity of reclamation cycle | Additional manufacturing pressure | Too aggressive | Too gentle | Ideal |
| Presence of residual matrix    | o      | •      | •      | o/•     |
| Void content                   | o      | ••     | •      | o/•     |
| Degradation of interface / interlayer | o     | ••     | •      | o/•     |

Key: o – none / negligible; • – minor; •• – major.
Applying the typical autoclave curing cycle (7 bar external pressure) eased most problems in recyclate r-D2. However, fibre content was still lower than in the virgin material due to insufficient compaction (Figure 3.7), and voids were still present (albeit at a much smaller scale, Figure 3.8(d)). Further improvements should be obtainable by increasing the pressure during cure, and/or re-prepreging the weave beforehand.

As mentioned in Sections 3.5.4.2 and 3.5.4.3, the marked decrease in compressive and shear strengths in materials r-D1 and r-D2 indicates an apparently weaker fibre–matrix interface (or interlayer) when residual resin is present. This may nevertheless be the result of incomplete fibre wetting, as shown in Figures 3.8(c) and 3.8(d).

### 3.5.6 Quality control and optimisation of recycling processes

One of the key aspects for the success of CFRP recycling for high–performance applications is guaranteeing the quality of the recycled fibres; this is usually assessed by their strength retention.

However, measuring fibre strength directly has the disadvantages associated with SFTTs; for recycled fibres, statistical significance can be further compromised because the effects of reclamation are not uniform in the through–the–thickness direction (see Section 3.5.2). Nevertheless, the good agreement observed between the tensile strength retention of single fibres and that of composites (Figure 3.12(d)) shows that testing 50 individual filaments was sufficient to characterise the entire population.

This agreement also suggests that filament–level properties can be assessed by re–impregnating reclaimed mats with resin films and testing the composites. This requires preserving the original reinforcement architecture and controlling potential remanufacturing defects, but its significance in an industrial reclamation line (with diverse feedstock) would be far superior to any reasonable SFTT programme.

Figure 3.13 presents the relation between fibre strength retention and other measured parameters. All plots lack data for moderately strong fibres (40–90%), hence the potential of these parameters as fine quality indicators cannot be fully evaluated (this may nevertheless be beyond the needs of commercially viable operations, as discussion in Section 3.5.7). Measuring the area density of recycled weaves detects both severe fibre degradation (associated with low areal densities) and residual matrix; it is also the only method to determine the loss of carbon fibre during reclamation.

Figure 3.12 shows that composite performance is extremely dependent on the loading case, and not necessarily effected by filament strength. This is also the case for discontinuous–architecture composites, where fibre strength is not dominant and residual matrix can actually improve performance (see also Chapter 4). There is a
strong case to consider different optimisation targets — and, therefore, different quality control strategies — for reclamation processes, based on the application foreseen for the recycled fibres.

### 3.5.7 Outlook on commercial CFRP recycling for structural applications

Many fibre reclamation processes have been developed in the last decade and implemented at laboratory or pilot scales. Most methods, including ELG-RCF’s pyrolysis, successfully recovered clean fibres with the same properties as the virgin precursors.

The results of this work show that commercial–scale recycling is much more challenging. While there is still scope to explore pyrolysis cycles in between processes C and D, there is no guarantee that commercially viable reclamation processes can be tuned finely enough so as to remove all original matrix without inducing any fibre damage, due to the following challenges:

**Throughput and processing time.** Continuous processes can have running times under 30 min [6], while typical laboratory batch processes report hours for recycling a few grams of composite [17]. To guarantee the same level of matrix removal, the former implies using more aggressive cycles, so risking fibre degradation.

**Implementation as a continuous process.** In a batch process, the atmosphere and temperature can be precisely tuned. Semi-open conveyor–belt processes [6] require the cycle to be controlled relatively to position rather than time. Guaranteeing ideal and uniform conditions is therefore much more difficult.
**Unknown and mixed feedstock.** The scrap material used in this work was a specific type of uncured prepreg. Commercial recycling must deal with mixed feedstock and unknown specifications. Aiming for optimal reclamation conditions requires identifying and sorting the feedstock in great detail, which may not be always technically feasible or economically viable.

If one of the two goals of recycling — matrix removal and retention of fibre properties — is to be sacrificed, it is useful to consider the application foreseen for the recycled fibres (as suggested in Figure 3.12), as the response at the composite level is optimised differently depending on the loading case. It must be nevertheless highlighted that aggressive cycles yield a considerable loss of fibre mass (Figure 3.13(b)) and, therefore, of profit.

Finally, leaving manufacturing considerations aside, the recycled composites here analysed exhibited an outstanding retention of mechanical properties relatively to the virgin precursor: approximately 100% for stiffness, up to 80% for tensile strength, and up to 100% of compressive strength. This performance is well above that of aluminium or glass-fibre composites.

### 3.6 Conclusions

The mechanical response of several recycled carbon fibres (reclaimed by different pyrolysis cycles at a commercial plant [6]) and woven composites was analysed and compared to that of virgin precursors.

Fibre performance was dramatically affected by the pyrolysis cycle. The most aggressive conditions yielded fibres 21% thinner, with extensive pitting and surface damage, and with 84% tensile strength reduction. The most gentle cycle recovered fibres with virtually no degradation, but left 7.6% of residual resin in the reclaimed fabric.

Two reclaimed weaves were re-impregnated by resin film infusion into recycled woven composites. In the absence of residual resin, the recyclate showed similar fibre content and fibre-matrix adhesion to the virgin precursor, showing no need for re-sizing or re-prepreging. Re-manufacturing was more challenging for the weave contaminated by residual resin, but results suggest that imposing pressure during cure is sufficient to achieve a good re-impregnation.

The mechanical performance at composite level was very complex, depending not only on the reclamation cycle but also on the re-manufacturing process and loading case. Tensile strength was dominated by fibre strength, thus favouring the most gentle pyrolysis cycle. Under compression, however, composite strength was insensitive to
severe fibre degradation, but considerably affected by the presence of residual matrix. In all cases, composite stiffness (for normalised fibre content) was nearly unaffected.

While CFRP recycling at laboratory scale can reclaim virgin–like fibres, commercially viable implementations will likely operate under non–ideal conditions. This work shows that, if recycled fibres are to be re-introduced in structural components, it is critical to identify potential applications, their loading conditions, and how the intended mechanical response is affected by potential recycling defects.
Chapter 4

Mechanical analysis and toughening mechanisms of a multiscale recycled CFRP

4.1 Introduction

Both environmental and economical reasons have driven the development of recycling routes for Carbon Fibre Reinforced Polymer (CFRP) waste [12]. In this chapter, the mechanical behaviour of a state–of–the–art recycled (r-) composite is investigated.

Generally, recycling a thermoset composite comprises two steps. Firstly, the Carbon Fibres (CFs) are reclaimed from the virgin (v-) composite, using either a thermal [6,47,55] or chemical [61,67] process to degrade the matrix; this generally outputs recycled fibres with little (under 10%) mechanical degradation [75]. The second step is the reimpregnation of these rCFs with new resin to manufacture a recycled composite; several methods are documented [35,37,58], but one of the most widely used is the papermaking of intermediate non–woven mats, followed by their compression moulding with resin films [57,58,76,86].

Wong et al. [76] manufactured a rCFRP particularly similar to the one analysed in this chapter (only the epoxy resin formulation used for reimpregnation was different). After pyrolysis, the rCFs comprised both dispersed–fibres and fibre–bundles (held together by residual virgin matrix or char); due to a fibre–disentanglement stage during the papermaking process, only a few bundles remained present in the non-woven mats. In addition, it was shown that considerable fibre–fracture occurred during compression moulding, due to the high pressures applied; this would have left most of the fibres
shorter than the critical length. Nevertheless, a good adhesion was found between the longer fibres and the epoxy matrix.

The specific mechanical properties of many rCFRPs compare favourably with those of conventional materials, such as aluminium and virgin glass–fibre composites (Fig. 2.8) [37,57,58]. Nevertheless, the architecture of rCFRPs can be unique and extremely complex (e.g. with fibre–bundles and a wide fibre length distribution [76]), so it is essential to investigate their mechanical response with a deeper detail [43]. This will provide informed guidance for recyclers towards materials with optimal structural performance; moreover, it will set the scenario for developing design methods for rCFRPs, which are essential to establish a market of structural applications for these materials.

This chapter presents an experimental investigation on the mechanical response of a rCFRP, including: (i) the analysis of its microstructure, (ii) the characterisation of mechanical properties, (iii) the measurement of fracture toughnesses, and (iv) the micromechanical analysis of failure and toughening mechanisms. This study confirms that rCFRPs are a competitive alternative to conventional structural materials. It also discusses the relations amongst (a) the recycling process, (b) the multiscale microstructure, and (c) the micromechanics of damage.

The chapter is organised as follows: Section 4.2 identifies the rCFRP studied; Section 4.3 describes the experimental procedures undertaken, being the results presented in Section 4.4. Section 4.5 discusses several aspects of the mechanical response of the recyclate, and the main conclusions are summarised in Section 4.6.

### 4.2 Material

The material under investigation is a rCFRP. The precursor was a T300–epoxy woven pre-preg (Boeing’s manufacturing scrap), from which the fibres were recovered by pyrolysis at Recycled Carbon Fibre Ltd [6].

The recycled composite was manufactured at the University of Nottingham. The recycled woven fabric was chopped (at Recycled Carbon Fibre) so as to produce fibres with an average length of 12 mm, and converted in 110 g/m² rCF non-woven mats by a wet papermaking process (at Technical Fibre Products Ltd.). The mats were subsequently compression moulded at 7 MPa with 300 g/m² ACG MTM 57 epoxy films, resulting into plates with a nominal fibre volume content of \( V_f \approx 30\% \) and a thickness of \( t \approx 2.5 \) mm. A comprehensive description of a similar manufacturing process is given elsewhere [76].
Table 4.1 characterises both the v- and the r-CFs. The diameters (φᵢ), Young’s moduli (Eᵢ) and fibre tensile strengths (Xᵢ) were measured at the University of Nottingham [76]; the fibre–epoxy interfacial shear strengths (Sᵢᶠ) were measured at Imperial College London using a Single–Fibre Pull–Out (SFPO) setup described elsewhere [128]. The increase of fibre diameter after the recycling process was confirmed to be statistically significant (p-value of 5.1% in a unilateral t-test); it can be justified by the presence of a layer of residual matrix or char on the surface of some recycled fibres.

The rCFRP plates analysed had a quasi random planar short–fibre architecture, with a preferred fibre direction induced during mat production [76]; hereafter, this direction is referred as longitudinal or direction 1, while its in-plane normal is the transverse or direction 2; direction 3 is the through–the–thickness direction. The second order orientation tensor [129,130] for this recycled composite can be estimated [57] as:

\[
\begin{pmatrix}
a_{11} \\ a_{22} \\ a_{33}
\end{pmatrix} \approx \begin{pmatrix} 0.65 \\ 0.30 \\ 0.05 \end{pmatrix}.
\]

(4.1)

4.3 Experimental procedures

4.3.1 Analysis of microstructure

The microstructure of the rCFRP was studied through Optical Microscopy (OM) of the three orthogonal plate sections (material planes 1–2, 1–3 and 2–3). The fibre and void volume–contents were measured in 8 through–the–thickness sections (total area of 16 mm²), using the UTHSCSA Image Tool [131].

4.3.2 Standard mechanical characterisation

The mechanical properties of the rCFRP for in-plane tension, compression and shear (subscripts T, C and S, respectively) were measured along the two principal material

<table>
<thead>
<tr>
<th>Type of CF</th>
<th>φᵢ (µm)</th>
<th>Eᵢ (GPa)</th>
<th>Xᵢ (GPa)</th>
<th>Sᵢᶠ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>virgin (v-)</td>
<td>7.03</td>
<td>227.80</td>
<td>4.24</td>
<td>83.3</td>
</tr>
<tr>
<td>recycled (r-)</td>
<td>7.20</td>
<td>217.79</td>
<td>4.16</td>
<td>86.9</td>
</tr>
<tr>
<td>Relative difference</td>
<td>+2.4%</td>
<td>-4.4%</td>
<td>-1.9%</td>
<td>+4.3%</td>
</tr>
</tbody>
</table>
Chapter 4

directions (superscripts 1 and 2). Table 4.2 defines the test standards, specimen nominal geometries and displacement rates; for each test case, at least 4 specimens were tested. All specimens were end–tabbed and equipped with strain gauges: for tensile specimens, only the front faces were instrumented (after confirming that bending was negligible, by using an extra gauge on the back face of the first specimen tested); for the compression and shear tests, each face of the specimens was instrumented, so results were corrected for spurious bending (in $E_C$ and $X_C$) and torsion (in $G^{12}$ and $S^{12}$).

4.3.3 Fracture toughness measurements

4.3.3.1 Tensile mode

The tensile fracture toughness $G_T$ — energy required to propagate a tensile crack over a unit area — of the rCFRP was measured using Compact Tension (CT) testing [133].

The specimens (nominal geometry in Figure 4.1(a)) were cut with a diamond wet saw. The holes were opened using a steel drill, and then finished with a diamond drill. The pre-crack ($a_0 \approx 18$ mm long and approximately 0.6 mm wide) was cut with a wire saw, and sharpened with a surgical blade by sawing action. A 1 mm scale was drawn on the specimens, ahead of the pre-crack.

Before testing, each specimen was equipped with an extensometer fixed on two slots on its left edge (nominal opening of 46 mm, Figure 4.1(a)). The load was applied through continuous displacement control of the loading pins, at 0.5 mm/min. The load $P$, cross–head displacement $d_{\text{head}}$ and extensometer opening $d_{\text{extens}}$ were recorded during the test. Four specimens for each material direction (1 and 2) were tested.

The data reduction was based on compliance calibration through linear–elastic Finite Elements (FE) models [133]:

1. For each specimen geometry, material and crack length $a \in [a_0, a_0 + \Delta a_{\text{max}}]$, the relations $a_{\text{FE}}(C_{\text{extens}})$, $C_{\text{FE}}^{\text{pins}}(a)$ and $J_{t=1}^{P=1}(a)$ (where $C$ is the unit–thickness

<table>
<thead>
<tr>
<th>Test case</th>
<th>Gauge length (mm)</th>
<th>Gauge width (mm)</th>
<th>Disp. rate (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1, T2: ASTM 3039</td>
<td>70</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>C1, C2: ICSTM</td>
<td>7</td>
<td>19</td>
<td>1.0</td>
</tr>
<tr>
<td>S12: ASTM 5379</td>
<td>12</td>
<td>12</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Table 4.2: Specifications for the standard mechanical characterisation. |
Mechanical analysis and toughening mechanisms of a multiscale recycled CFRP

Figure 4.1: Nominal geometry of the fracture toughness specimens (dimensions in mm).

Compliance and $J_{P=1}$ is the J–integral for unit load $P$ and unit specimen thickness $t$) were extracted through FE (using the elastic properties measured in Table 4.4):

2. The initial linear–elastic domain in each test (represented by the superscript 0) was used to calibrate the effective initial crack length as $a_0 = a_{FE}(C_{extens}^0)$, and the compliance of the setup as $C_{setup}^t = C_{xhead}^0 - C_{pins}^{FE}(a_0)$;

3. For the entire duration of each test, the R–curves were calculated through $a = a_{FE}(C_{pins})$ and $G = J_{i=1}^{P=1}(C_{pins}).P^2/t^2$, with $C_{pins} = C_{xhead} - C_{setup}$.

Damage onset was considered to take place at a 1% increase in the specimen compliance; after initiation, the crack propagated in a stick–slip mode. A spurious transient (during $\approx 4$ s) decrease in compliance was noticed after most crack jumps; this was likely caused by the visco-elastic response of the matrix or the dynamic response of the specimen (due to the high energy released during each jump); the results were corrected by extrapolating the linear response observed after each spurious transient period.

4.3.3.2 Compressive mode

The compressive fracture toughness for damage initiation along the longitudinal direction, $G_{CI}^{1,1}$, was measured using Compact Compression (CC) testing (Figure 4.1(b)), following similar procedures to those described for the CT tests (Section 4.3.3.1).

For each specimen, a good correlation was found between (i) the visual detection of onset of crack propagation and (ii) the onset of a kink in the load $P$ vs. displacement $d^{extens}$ curve. This latter feature (highlighted in the second derivative ($\delta^2/d^{extens}/\delta P^2$))
was therefore used to determine the load $P$ for damage initiation, and subsequently used for $G_C^{1,4}$ estimation.

### 4.3.4 Investigation of failure and toughening mechanisms

The failure and toughening mechanisms of the rCFRP were investigated through (i) post-mortem Scanning Electron Microscopy (SEM) of specimens from Sections 4.3.2 and 4.3.3, and (ii) OM of specifically designed specimens (Figure 4.2); these are referred hereafter as $\mu_T$ and $\mu_C$, respectively for tension and compression.

Stable propagation of tensile cracks was observed at the in-plane surface of $\mu_T$ specimens, while loaded; the compressive damage was observed at cross–sections of post-mortem $\mu_C$ specimens. Both directions 1 and 2 were investigated.

### 4.4 Results

#### 4.4.1 Microstructure

The volume–fractions of each phase in the rCFRP are shown in Table 4.3. The main microstructural features identified are:

- Individual fibres within the matrix, forming a *dispersed–phase* (Figure 4.3(a)); fibre–length was greatly variable;

- *Fibre–bundles*, up to 1 mm thick and 30 mm long (Figure 4.3(a)); these originated from tows in the virgin composite that, after pyrolysis, remained held together by residual virgin–matrix or pyrolytic–char [76];

- *Fractured fibre–sections* within the dispersed–fibres, in untested material (Figure 4.3(b)). This fibre fracture occurred due to the high pressures applied during compression moulding (as mentioned in Section 4.2 [76]), mainly due to fibre–fibre interaction [134];

- *Through–the–thickness fibre waviness*, noticeable in Figure 4.3(c) by the discontinuous visibility of the central bundle (implying it follows a wave in and out of the micrograph plane, a common feature in SFRPs [134]);

- *Quasi-planar fibre orientation* (compare Figure 4.3(a) and Figure 4.3(d));

- *Presence of voids*, typically up to 50 $\mu$m large (Figure 4.3(d)) and randomly dispersed within the matrix (with no preferential location, shape or alignment).
Mechanical analysis and toughening mechanisms of a multiscale recycled CFRP.

Figure 4.2: $\mu_T$ and $\mu_C$ tests for investigation of failure and toughening mechanisms.

Table 4.3: Volume content of the rCFRP phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Volume content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibres, $V^f$</td>
<td>27</td>
</tr>
<tr>
<td>Matrix, $V^m$</td>
<td>66</td>
</tr>
<tr>
<td>Voids, $V^v$</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 4.3: Microstructural features in the rCFRP.
4.4.2 Mechanical properties

The mechanical properties obtained from the standard characterisation tests are presented in Tables 4.4 to 4.6; since most properties were calculated from samples with 4 specimens only, the Coefficients of Variation (CoV) are provided as coarse indicators of the variability of the population. Typical stress vs. strain curves are shown in Figure 4.4 and typical failure modes in Figure 4.5.

### Table 4.4: Elastic properties of the rCFRP.

<table>
<thead>
<tr>
<th>Property</th>
<th>$E_T^1$ (GPa)</th>
<th>$E_T^2$ (GPa)</th>
<th>$E_C^1$ (GPa)</th>
<th>$E_C^2$ (GPa)</th>
<th>$G_{12}$ (GPa)</th>
<th>$\nu_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>28.1</td>
<td>16.0</td>
<td>25.4</td>
<td>15.7</td>
<td>7.0</td>
<td>0.42</td>
</tr>
<tr>
<td>CoV</td>
<td>5.0%</td>
<td>3.2%</td>
<td>1.8%</td>
<td>3.3%</td>
<td>4.8%</td>
<td>2.1%</td>
</tr>
</tbody>
</table>

### Table 4.5: Failure strengths of the rCFRP.

<table>
<thead>
<tr>
<th>Property</th>
<th>$X_T^1$ (MPa)</th>
<th>$X_T^2$ (MPa)</th>
<th>$X_C^1$ (MPa)</th>
<th>$X_C^2$ (MPa)</th>
<th>$S_{12}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>194.5</td>
<td>117.0</td>
<td>358.3</td>
<td>285.0</td>
<td>139.7</td>
</tr>
<tr>
<td>CoV</td>
<td>7.4%</td>
<td>11.2%</td>
<td>3.0%</td>
<td>2.3%</td>
<td>6.8%</td>
</tr>
</tbody>
</table>

### Table 4.6: Extensions at failure of the rCFRP.

<table>
<thead>
<tr>
<th>Property</th>
<th>$\varepsilon_T^1$ (%)</th>
<th>$\varepsilon_T^2$ (%)</th>
<th>$\varepsilon_C^1$ (%)</th>
<th>$\varepsilon_C^2$ (%)</th>
<th>$g_{12}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.71</td>
<td>0.76</td>
<td>1.76</td>
<td>2.71</td>
<td>2.37</td>
</tr>
<tr>
<td>CoV</td>
<td>7.2%</td>
<td>13.9%</td>
<td>3.5%</td>
<td>13.8%</td>
<td>7.36%</td>
</tr>
</tbody>
</table>

**Figure 4.4:** Typical stress vs. strain curves from the standard characterisation tests.
The rCFRP responded linearly under tension, and non-linearly under compression and shear. The longitudinal strength and stiffness were higher than the transverse ones, and the material was notably stronger and more ductile in compression than tension.

The tensile specimens failed by planar brittle cracking; the failure path was parallel to the through–the–thickness direction, but irregular and curved within the 1–2 plane (especially for the longitudinal specimens, Figure 4.5(a) vs. Figure 4.5(b)). Most specimens failed near the end–tabs; tapering the end–tabs did not increase the measured strength, suggesting it was not significantly affected by stress concentrations.

Under compression, the rCFRP failed by forming two rough failure surfaces, angled in the through–the–thickness direction (at $\beta \approx 50^\circ$ to $55^\circ$, Figure 4.5(c)). The shear specimens failed by tensile cracking, with initiation at the notch tip and planar propagation at $45^\circ$ (Figure 4.5(d)).
4.4.3 Tensile fracture toughness

The CT specimens failed in a stick-slip mode (Figure 4.6). All load \((P)\) vs. pin-displacement \((d)\) and energy release rate \((G_T)\) vs. crack growth \((\Delta a)\) curves are shown in Figure 4.7. \(G_T\) increased smoothly during each stage of stable propagation (solid lines, for which \(G_T = G_T\)), and decreased suddenly during the unstable stages (dashed lines).

Table 4.7 summarises the quantitative results from the CT tests, including: the tensile fracture toughness for initiation \((G_T^i)\), the lower and upper limits of fracture toughness within each stable stage (respectively \(G_T^{low}\) and \(G_T^{up}\)), and the variation of toughness during the stable stages \((\Delta G_T^{stbl})\).

After the tests, fibre-bundles were observed at the specimens’ fracture surfaces (Figure 4.6); these bundles were either pulled-out from the material (zoom-in I) or

![Figure 4.6: Crack propagation in a typical fracture toughness specimen (GT1#4): top: \(P(d)\) and \(G_T(\Delta a)\) data curves (stages of response highlighted); bottom: fracture surfaces — correspondence with \(G_T(\Delta a)\) (right) and magnified details (left).](image-url)
Figure 4.7: All $P(d)$ and $G_T(\Delta a)$ curves from the tensile fracture toughness tests.

Table 4.7: Summary of the tensile fracture toughness measurements (kJ/m$^2$).

<table>
<thead>
<tr>
<th>Direction</th>
<th>Property</th>
<th>$G_T^i$</th>
<th>$G_T^{\text{low}}$</th>
<th>$G_T^{\text{up}}$</th>
<th>$\Delta G_T^{\text{stbl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long. (1)</td>
<td>Average</td>
<td>2.43</td>
<td>3.42$^{(a)}$</td>
<td>5.80</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>CoV</td>
<td>3.7%</td>
<td>4.6%$^{(a)}$</td>
<td>20.0%</td>
<td>36.5%</td>
</tr>
<tr>
<td>Trans. (2)</td>
<td>Average</td>
<td>1.68</td>
<td>1.99$^{(b)}$</td>
<td>3.32</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>CoV</td>
<td>8.6%</td>
<td>15.5%$^{(b)}$</td>
<td>22.1%</td>
<td>43.0%</td>
</tr>
</tbody>
</table>

$^{(a)}$ Excludes anomalous values (spec.#3@$\Delta a = 15$ mm).

$^{(b)}$ Excludes anomalous values (spec.#1@$\Delta a = 13$ mm and spec.#3@$\Delta a = 5$ mm).
defibrillated and broken (zoom-in II). A good correlation was found between the location of larger bundles and the areas of stable propagation (see $G_T(\Delta a)$ curve and the specimen’s fracture surface in Figure 4.6).

### 4.4.4 Compressive fracture toughness

All CC specimens failed in a two-stages process: (i) firstly, a thin damage band inclined through–the–thickness propagated stably over $\Delta a \approx 1$ mm to $3$ mm; (ii) then, a tensile crack propagated suddenly from the back of the specimen (Figure 4.8(a)). A typical load $P$ vs. displacement $d_{\text{extens}}$ curve is shown in Figure 4.8(b); the onset of damage is highlighted. The results of fracture toughness for damage initiation under longitudinal compression ($G_{1,i}^C$) are summarised in Table 4.8.

![Failed CC specimen](image)

**Figure 4.8:** Typical result from the longitudinal compressive toughness tests.

**Table 4.8:** Initiation fracture toughness for longitudinal compression.

<table>
<thead>
<tr>
<th>Property</th>
<th>$G_{1,i}^C$ (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>21.89</td>
</tr>
<tr>
<td>CoV</td>
<td>16.5%</td>
</tr>
</tbody>
</table>
4.4.5 Failure and toughening mechanisms

4.4.5.1 Tensile mode

Figure 4.9 presents typical in–plane OM images of \( \mu T \) specimens, while loaded. During stable crack propagation, failure followed:

(I) The fibre–matrix interface;

(II) Previously–fractured fibre–sections (formed during compression moulding, as mentioned in Section 4.4.1), with no observed failure of previously undamaged fibre–sections. This is shown by the undamaged state of the matrix ahead of the fractured fibre–section in Figure 4.9(a) together with the occurrence of extensive fibre breakage during manufacture (Figure 4.3(b)).

A typical unstable–fracture surface of a post-mortem tensile specimen (Section 4.3.2) is shown in Figure 4.10; short pulled–out fibres with barely no residual matrix (feature I) were found together with fractured fibre–sections with zero pull–out length (feature II).

The fracture surfaces of the CT specimens show two different morphologies (Figure 4.11); by correlating these SEM observations with the \( G_T (\Delta a) \) curves (Figure 4.7), it was found that stable crack propagation produced rough fracture surfaces with longer fibre pull–out (Figure 4.11(a)), while unstable crack jumps developed smoother surfaces with shorter pull–out lengths (Figure 4.11(b)). Moreover, fibre–bundles were consistently found at the transition between the two morphologies.

The failure mode of fibre–bundles depended on their geometry: thicker bundles were completely pulled–out (Figure 4.12(a)) or defibrillated (i.e. failed by splitting and pull–out of fibres within the bundle, Figure 4.12(b)); on the contrary, thinner bundles fractured across their section (Figure 4.12(c)). Transverse bundles acted as weakening points, promoting initiation and propagation of tensile cracks (Figure 4.12(d)).

4.4.5.2 Compressive mode

Under stable compression, the material failed by localised matrix–shearing and fibre–rotation within through–the–thickness shear–bands (Figure 4.13 and 4.14); the first recognisable bands had an inclination of \( \beta \approx 20^\circ \). With continued compression, the inclination of the shear–band increased progressively, up to a final value of \( \beta \approx 54^\circ \) (Figure 4.13(a)); the deformation of the material inside the band increased as well,
Figure 4.9: Failure mechanisms under stable tensile crack propagation (specimen loaded; wider white arrows represent the macroscopic crack–direction): through (I) fibre–matrix interface and (II) previously–fractured fibres.

Figure 4.10: Fracture surface of a post-mortem standard tensile specimen: (I) pulled–out fibres and (II) fractured fibre–sections.

Figure 4.11: Typical fracture morphologies in CT specimens.
Figure 4.12: Failure mechanisms of fibre–bundles under tension (wider white arrows represent the macroscopic crack–direction).

which led to the initiation and propagation of a fracture plane within the band (Figure 4.13(b)). In subsequent compression stages, complementary shear–bands initiated, propagated and broadened in the specimen (Figure 4.13(a)): sharp edges delimiting (almost) undeformed regions from highly deformed shear–bands were observed as well (Figure 4.14(b)).

The compressive failure was also affected by the presence of fibre–bundles: Figure 4.15 shows a thick bundle, initially aligned with the loading direction, which bent within the shear–band and eventually broke at several cross–sections; this delayed shear–band propagation, diffused the damage, and favoured the formation of large splits.
4.5 Discussion

4.5.1 Role of the critical fibre length on tensile failure

Tensile failure was strain dominated ($e_1^T \approx e_2^T$, Table 4.6), which suggests that the fibres failed by pull–out rather than at their cross–section; this was confirmed by OM and SEM observations (Section 4.4.5.1).

It has been shown that the extremely high moulding pressures required to manufacture rCFRPs with high fibre contents lead to a severe fibre breakage during compression moulding, which degrades fibre length considerably [76]. From the tensile strength of
the rCF and their interfacial strength with the epoxy matrix, the critical fibre–length in the rCFRP ($l_{\text{crit}}$) comes as:

$$l_{\text{crit}} = \frac{X^f_T \cdot \phi^f}{2 \cdot S^f_{\text{IF}}} \Rightarrow l_{\text{crit}} \approx 172 \ \mu m . \quad (4.2)$$

Comparing this value with the composite’s expected fibre length distribution (measured at the University of Nottingham for a similar rCFRP [76], which differed from the one analysed in this chapter only in the formulation of the epoxy resin), fewer than 40% of the fibres in the composite are longer than the critical length. Since a good
fibre–matrix adhesion was found in the recycled composite (Table 4.1), this fibre–length degradation during manufacture explains why no fibre failure was observed during stable crack propagation, and it also contributes to justify the low tensile strengths of the recyclate (Table 4.5).

### 4.5.2 Stable vs. unstable tensile failure

Stable tensile failure of the dispersed–phase occurs preferentially by fibre pull–out (with high energy absorption) and opening of previously–fractured fibre–sections. Little fibre–failure takes place due to the tensile loading (Figure 4.10 and 4.11(a)).

On the contrary, unstable crack jumps produces fibres with smaller pull–out lengths, and a smoother fracture–surface (Figure 4.10 and 4.11(b)). This suggests that previously–undamaged fibre–sections actually fail during unstable tensile propagation, so fibre pull–out is reduced.

These differences between stable and unstable tensile failure are likely due to a rate–dependent response of the matrix (which becomes more brittle as the crack growth rate increases); together with the failure of fibre–bundles, this justifies the higher fracture toughness measured during stable propagation than during the unstable stages (Figure 4.7 and Table 4.7).

### 4.5.3 Influence of fibre–bundles on the tensile fracture toughness

From the CT testing results (Figure 4.6, 4.7 and 4.11, and Table 4.7), the following sequence of events for tensile failure of notched specimens is suggested:

i) A crack initiates from the notch and propagates stably within the dispersed phase;

ii) Fibre bundles ahead of the crack tip increase the local fracture toughness, as they are slowly pulled–out or defibrillated during crack growth;

iii) After crack propagation through a thick bundle, the energy release rate in the specimen is higher than the fracture toughness of the dispersed–phase; this causes an unstable crack jump, until the elastic energy in the specimen is released and a new fibre–bundle eventually arrests the crack;

iv) The new bundle stabilises crack propagation, and the local fracture toughness increases again as in (iii). The sequence of stable vs. unstable propagation is repeated as the crack meets and passes new bundles.
The tensile fracture toughnesses of the dispersed phase can be estimated from $G_{TT}^{\text{low}}$, as these values are consistent amongst specimens (Table 4.7); this results in $G_{TT}^{1,\text{disp}} \approx 3.42$ kJ/m² and $G_{TT}^{2,\text{disp}} \approx 1.99$ kJ/m², one order of magnitude tougher than unreinforced epoxy or transverse UD vCFRPs [133]. Moreover, depending on their geometry, location and orientation, fibre–bundles increased the local fracture toughness of the rCFRP up to 3 times, relatively to the dispersed–phase (Table 4.7); this is consistent with previous research on virgin Short–Fibre Reinforced Polymers (SFRPs) [135–137].

4.5.4 Tensile failure of fibre–bundles

Under tension, several fibre–bundles failed by clean bundle pull–out (Fig 4.12(a)) or cross–section fracture (Fig 4.12(c)); these failure modes can be modelled considering bundles as large–diameter reinforcing–units [135–137]. However, bundle failure by defibrillation was frequent as well (Fig 4.12(b)); this involves a considerable absorption of energy, which should be taken into account when modelling certain vSFRPs [138] and rCFRPs.

4.5.5 Multiscale and fractal features

The rCFRP has a multiscale microstructure, with 1 mm wide fibre–bundles and 7 µm wide filaments (Figure 4.3(a)). Similar pull–out mechanisms were observed at both scales, although individual–filaments and bundles are two orders of magnitude apart in dimension (Figure 4.16).

In addition, the fracture surface of defibrillated bundles presents itself a fractal pattern. Figure 4.17 shows a representative area of the fracture contour (highlighted in dashed red lines) within a bundle, at three different magnification levels. It can be observed that the width–to–length ratios of the pulled–out fibres and bundles are statistically constant amongst the three scales presented, suggesting self–similarity in the pull–out process and formation of fracture surfaces.

4.5.6 Compressive failure mode

Under stable compression, the rCFRP failed by localised shearing. This is one of the most typical failure modes in compression, reported for many different types of material [139–141].

The compressive failure of the rCFRP presents interesting similarities with, on the one hand, fibre kinking, and, on the other, transverse compressive failure of UD CFRPs. As in fibre kinking [142–144], (i) the fibres rotate within the shear bands
(Figure 4.14(a)); (ii) the bands initiate at low angles ($\beta \approx 20^\circ$, Figure 4.14(a)), which increase with continued compression (Figure 4.13); (iii) in some cases, the band broaden and sharp edges are defined (Figure 4.14(b)). On the other hand, most of the shear–bands evolved into sharp shear–cracks, with no visible plastic deformation, inclined at $\beta \approx 54^\circ$ (Figure 4.13(a)); this is the angle commonly reported for transverse compressive failure of UD composites [141,145].

The formation of shear bands suggests that matrix yielding plays an important role in the process; this is also the case for fibre kinking [126,142] and transverse compressive failure of UD composites [141,145]. However, were the compressive failure of the rCFRP a simple shearing mechanism, one would not expect the small band angles ($\beta \approx 20^\circ \ll 45^\circ$) observed at early stages of damage (Figure 4.14(a)). The cause of this behaviour is either (i) an interaction between fibres and matrix, or (ii) a more complex phenomenon intrinsic of epoxy failure.
4.5.7 Compressive fracture toughness

While there is some uncertainty associated with measuring the compressive fracture toughness (e.g. defining damage onset), it is suggested that the rCFRP is considerably tougher under compression than under tension (\(G_{C}^{1}\) ≈ 22 kJ/m\(^2\) vs. \(G_{T} \leq 8\) kJ/m\(^2\), Tables 4.7 and 4.8). This is justified by the higher strength and ductility of the material under compression than in tension (Tables 4.5 and 4.6). The formation of a diffuse shear–band dissipates a great amount of energy (when compared with the sharp tensile–cracking); this effect is magnified by thick bundles aligned with the compressive load, due to damage diffusion and material delamination (Figure 4.15).

4.5.8 Comparison with virgin materials

Figure 4.18 compares the tensile and compressive specific properties of the rCFRP with those of conventional structural virgin materials — an aerospace grade 2024-T4 Aluminium alloy, and a random short glass-fibre phenolic–resin composite (\(V_f = 31\%\)) typically used in aircraft interiors \(^{57}\). The rCFRP performance is close to that of Aluminium, depending on the loading case; this dependence illustrates the need for developing design methods for recyclates. In addition, the rCFRP has superior properties to those of the glass composite, meaning that it could be used in similar applications with significant mass savings.

\[\text{Figure 4.18: Mechanical properties of the recycled CFRPs vs. virgin materials.}\]
4.5.9 Improvements to the recycling processes

From the analysis performed, the following directions for improving the fibre-reclamation and rCFRP-manufacturing processes are suggested:

**Reducing fibre fracture.** Since the presence of longer fibres improves the stiffness, strength and toughness of composites [134], the rCFRP is considerably weakened in tension by the great amount of very short fibres present in the composite. The manufacturers explain this fibre breakage with the high moulding pressures needed to compress the rCF mats with epoxy, due to the filamentised nature of the recycled fibres [76]; this is even more severe in composites with higher fibre contents, which are required for high-end structural applications. Therefore, developing processes for reducing fibre-breakage in manufacture (e.g. effective fibre-alignment and/or alternative reimpregnation techniques [58, 89, 146]) is critical for the full exploitation of rCFs.

**Preserving fibre-bundles.** It was shown that fibre-bundles, typically considered as recycling defects, enhance the fracture toughness of the rCFRP considerably. Studies on virgin SFRPs [135–138] support this conclusion; they also suggest that the toughening effect is also achieved when the resin for bundle consolidation is different from the resin in the dispersed phase [137]. Moreover, bundled composites are less susceptible to fibre-fracture during manufacture than individually-dispersed fibres, meaning that higher reinforcement contents can be achieved if bundles are preserved [134, 147]. Altogether, it is suggested that the optimal recycling process should aim to preserve a controlled amount of fibre bundles, depending on the foreseen application for the recyclate.

4.6 Conclusions

The mechanical response of a state-of-the-art recycled CFRP was investigated experimentally.

This recycled composite featured fibre-bundles and fractured fibre-sections; this complex and multiscale microstructure was due to both fibre-reclamation and composite-manufacturing processes.

On the overall, the mechanical performance of this rCFRP compared favourably to those of conventional structural materials. The recyclate was nevertheless much stronger under compression than under tension, due to different failure modes under the two loading cases.
Under tension, the material failed by crack propagation following the fibre–matrix interface and the pre-fractured fibre–sections. The fibre breakage occurred during manufacturing was found to reduce over 60% of the rCFs to sub-critical lengths. The fracture toughness of the recyclate was enhanced by the presence of fibre bundles, due to complex failure mechanisms.

Under compression, the rCFRP initiated shear bands at $\beta \approx 20^\circ$; during subsequent loading, complementary shear–bands formed in the composite, and some bands eventually evolved into shear–cracks at $\beta \approx 54^\circ$. Interesting similarities between the failure of this recyclate and of UD composites were pointed out.

As a guideline for the recycling process, the importance of avoiding fibre length degradation during compression moulding was stressed; the interest on preserving fibre–bundles during pyrolysis and mat–production was highlighted as well.

The experimental analysis here presented focuses on a recycled CFRP, and can be used as the foundation for the development of design methods for this type of recyclates. In addition, it also contributes for a better understanding of the mechanical response of several materials, especially the failure mechanisms of SFRPs and the toughening mechanisms of various multiscale materials.
Chapter 5

The influence of micromechanical properties and reinforcement architecture on the mechanical response of recycled composites

5.1 Introduction

The in-depth analysis of a multiphase rCFRP presented in Chapter 4 revealed an intimate relation between recycling and the composite’s fracture toughness, due to the presence of residual fibre bundles. It is therefore timely to investigate which types of architecture result from different recycling routes, and to understand how these differences influence the mechanical performance and fracture toughness of rCFRPs.

Recycled composites have been usually characterised at the macro–scale in terms of stiffness and strength [37, 57, 58, 148]. Chapter 4 provided new insight by showing that fibre bundles — held together by residual matrix not completely removed during fibre reclamation — significantly toughened the material. However, this effect was limited, as very few bundles survived the fibre disentanglement stage purposely included in the manufacturing process [76].

The toughening effect of bundles in fibre reinforced polymers has been reported in the literature for virgin materials [136, 137, 149]. The mechanism is typically justified by an increase on the dissipation of pull–out energy as the scale of reinforcement units grows, assuming constant volume fraction and aspect ratio of the reinforcement [138, 150, 151]. Nevertheless, large fibre bundles are frequently associated with composites
with lower stiffness and strength; moreover, bundling is difficult to induce and control in virgin systems \[135\].

Consequently, the concept of enhancing the toughness of CFRPs with fibre bundles has been mostly explored by researchers only. However, the recent development of several composites with meso-scale discontinuous reinforcement \([147, 152, 154]\) has proved that these materials offer not only improved manufacturability, but also compelling properties and damage tolerance.

In recycled CFRPs, fibre bundles are naturally induced by the fibre reclamation process; pyrolysis — currently the most popular method — is particularly prone to leaving small amounts of residual matrix on the fibre surfaces (unless very aggressive cycles are used, see Chapter 3) \([43, 47, 76]\). Most re-impregnation techniques involve depositing recycled fibres from a liquid medium onto preforms, which is applicable to bundles as well; achieving a high degree of filamentisation, on the other hand, requires extra processing \([76]\).

Different recycling routes can create different meso-scale architectures in a rCFRP, but they are also likely to affect the micromechanical properties of the fibres and fibre-matrix interface \([75, 112]\). In order to understand how both micro and meso levels affect the macroscopic mechanical properties, it is thus necessary to fully characterise the materials at all three existing scales.

This chapter therefore aims at extending the work initiated in Chapter 4 by analysing experimentally the relation between (i) micromechanical properties (including fibre morphology, fibre strength and matrix interface), (ii) reinforcement architecture (which are quantitatively characterised), and (iii) mechanical properties (with emphasis on the fracture toughness) of rCFRPs. Three different state-of-the-art recyclates, obtained from distinct recycling routes (regarding waste source, fibre reclamation and composite re-manufacturing processes) are investigated.

The materials analysed in this chapter are described in Section 5.2. Experimental characterisation procedures are detailed in Section 5.3 and results are presented in Section 5.4. Section 5.5 discusses the most important findings, and Section 5.6 sums up the main conclusions.

5.2 Materials

This chapter analyses three rCFRPs, with recycling and re-manufacturing routes described in Table 5.1. All materials feature an epoxy resin reinforced with discontinuous fibres reclaimed through pyrolysis.
Material T300-rRCF has been previously analysed in Chapter 4; it is included here for comparison purposes, and for characterisation at the micromechanical level. Materials T300-rMIT and T800-rMIT were reclaimed and re-manufactured through the same route; materials T300-rRCF and T300-rMIT share the same waste source. In all cases, manufacturing included preforming and subsequent resin moulding, with fibre content targeted at $V_f = 30\%$; nevertheless, due to the combination of different waste sources and processes, the architecture of the reinforcement differed significantly in the three materials.

Standard mechanical properties of the three recyclates are shown in Figure 5.1. For material T300-rRCF, these have been measured in Chapter 4, both in-plane principal directions are shown. The properties for materials T300-rMIT and T800-rMIT (nominally isotropic in-plane) were measured by the manufacturer (The Boeing Company).

### 5.3 Experimental analysis

#### 5.3.1 Single–fibre analysis

##### 5.3.1.1 Fibre inspection

The morphologies of all fibre types (virgin and recycled) were investigated through Scanning Electron Microscopy (SEM) of tows (taken from the centre of the reclaimed mats). Fibre diameters ($\phi_f$) were measured (at 4,000× magnification) in 25 filaments.

<table>
<thead>
<tr>
<th>Table 5.1: Recycling route of materials studied.</th>
</tr>
</thead>
<tbody>
<tr>
<td>rCF/ rCFRP</td>
</tr>
<tr>
<td>Waste source(^{(\star)})</td>
</tr>
<tr>
<td>T300-rRCF</td>
</tr>
<tr>
<td>T300-rMIT</td>
</tr>
<tr>
<td>T800-rMIT</td>
</tr>
</tbody>
</table>

\(^{(\star)}\) uMW: uncured Manufacturing Waste; EoL: End–of–Life component.  
\(^{(\dagger)}\) TFP: papermaking technique; MIT-RCF: 3-DEP process.  
\(^{(\ddagger)}\) U.Nottingham: compression moulded material; Boeing: RTM material.
5.3.1.2 Single fibre tensile tests

The tensile strength of all fibre types were determined through Single–Fibre Tensile Tests (SFTTs) performed at two gauge lengths, following the procedure described in Chapter 3 and the specifications shown in Table 5.2. Individual realisations of fibre strength ($\sigma_f$) were calculated using the average diameter of the corresponding fibre type.

The Weibull parameters for the strength distribution of each fibre type and at each gauge length were estimated through the MLM (Appendix A). In addition, the size–effect Weibull modulus was also calculated from the scale parameters $\sigma_{f,0,1}$ and $\sigma_{f,0,2}$, estimated at the respective gauge lengths $l_1$ and $l_2$:

$$\frac{\sigma_{f,0,1}}{\sigma_{f,0,2}} = \left( \frac{l_2}{l_1} \right)^{1/m} \quad \Rightarrow \quad m = \frac{\ln \left( \frac{l_2}{l_1} \right)}{\ln \left( \frac{\sigma_{f,0,1}}{\sigma_{f,0,2}} \right)}.$$  \hspace{1cm} (5.1)

<table>
<thead>
<tr>
<th>Load cell</th>
<th>Type of glue</th>
<th>Fibre gauge length (mm)</th>
<th>Displacement rate (mm/min)</th>
<th>Number of tests (per fibre type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 N</td>
<td>3M Scotch–Weld</td>
<td>10</td>
<td>0.1</td>
<td>$\geq 20$</td>
</tr>
<tr>
<td></td>
<td>9323 B/A epoxy</td>
<td>20</td>
<td>0.2</td>
<td>$\geq 20$</td>
</tr>
</tbody>
</table>

Figure 5.1: Standard mechanical properties of the three rCFRPs under investigation (see Chapter 4 for T300-rRCF; properties were provided by Boeing for T300-rMIT and T800-rMIT).
The influence of micromechanical properties and reinforcement architecture

This definition has the advantage of segregating the spurious effect of test variability within a gauge length $\text{[159]}$, although it can be affected by end–effects $\text{[116]}$.

5.3.1.3 Single–fibre pull–out tests

The properties of the fibre–matrix interface were estimated through Single–Fibre Pull–Out (SFPO) tests, using a setup described elsewhere $\text{[128]}$ and the specification defined in Table 5.3. For each type of composite, individual fibres were partially embedded in a matrix block and cured according to the resin manufacturer’s instructions; subsequently, the free end of each embedded fibre was pulled–out under displacement control, and the load–displacement curve $P(u)$ was recorded. The apparent interfacial shear strength ($S_{IF}$) and fibre–matrix frictional stress ($\tau_0^\mu$) were calculated using the average diameter of the corresponding fibre type as $\text{[160]}$:

$$S_{IF} = \frac{P_{\text{max}}}{\pi \cdot \phi_f \cdot l_{po}}$$

and

$$\tau_0^\mu = -\frac{dP}{du}(l_{po}) \cdot \frac{1}{\pi \cdot \phi_f}, \quad \text{with} \quad l_{po} = \{ u : P(u) = 0 \}. \quad (5.2)$$

The RTM6 matrix exhibited significant shrinkage during cure, which made the embedding process at suitable lengths difficult; for that reason, very few samples produced successful results for the T300-rMIT and T800-rMIT materials.

5.3.2 Composite analysis

5.3.2.1 Characterisation of microstructure

The volume content of fibres ($V_f$), resin ($V_m$) and voids ($V_v$) of materials T300-rMIT and T800-rMIT were estimated using the same procedure as previously described for T300-rRCF (optical microscopy of through–the–thickness sections, Chapter 4).

The architecture of materials T300-rMIT and T800-rMIT was characterised by measuring the bundle length and width distributions ($F_L(l)$ and $F_W(w)$ respectively) in the corresponding dry preforms manufactured by MIT-RCF. This required (i) cutting

<table>
<thead>
<tr>
<th>Load cell</th>
<th>Embedding matrix diameter</th>
<th>Displacement rate</th>
<th>Fibre type</th>
<th>Embedded fibre length (µm)</th>
<th>Number of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 N</td>
<td>3.5 mm</td>
<td>0.06 mm/min</td>
<td>T300-v</td>
<td>22 – 86</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T300-rRCF</td>
<td>16 – 73</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T300-rMIT</td>
<td>44 – 108</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T800-rMIT</td>
<td>76</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5.3: Specifications for single–fibre pull–out tests.
a square layer (length $\ell$) from the preform, (ii) picking $N_w$ individual bundles for image analysis, and (iii) calculating the theoretical median ranks of each realisation (as described in Appendix A). For bundle length distributions, only those ($N_l$) bundles not crossing the edges of the $\ell \times \ell$ sample were included; as this creates a bias towards shorter bundles, the rank of each observation $i$ was corrected as suggested by Fu et al. [161]:

$$i' = \sum_{j=1}^{i} \left( \frac{8 \cdot \ell \cdot l_j^0}{\pi \cdot \ell^2} - 4 \cdot \ell \cdot l_j^0 + (l_j^0)^2 + 1 \right).$$  \hspace{1cm} (5.3)

This process considered all bundles in the sample approximately wider than 0.1 mm; thinner bundles represented only a small weight fraction of the dry preforms and were not evaluated. The specifications for the measurements are shown in Table 5.4.

### 5.3.2.2 Compact tension tests

The tensile fracture toughness $G$ of materials T300-rMIT and T800-rMIT was measured through CT tests [133], following a similar FE–calibration procedure as summarised in Chapter 4 for the T300-rRCF composite. Tests were initially conducted with specimens as shown in Figure 5.2(a).

Material T800-rMIT, however, could not fully develop a process zone in type–A specimens, and the crack followed a reasonably straight path in one test only. A larger specimen (type B, Figure 5.2(b)) was then attempted, but proved unreliable due to frequent out–of–plane buckling. Finally, a multi–loading–point setup (originally proposed for mixed–mode toughness translaminar [162], but here applied to pure mode–I) was used with satisfactory results; in this case, cross–head displacements were corrected by tracking the loading pins with an image recording system (instead of an extensometer).

The tensile toughening mechanisms were investigated in post–mortem fracture surfaces of valid CT tests.

**Table 5.4:** Specifications for architecture characterisation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Layer sample size $\ell \times \ell$ (mm$^2$)</th>
<th>$N_w$</th>
<th>$N_l$</th>
<th>weight considered</th>
<th>weight total</th>
</tr>
</thead>
<tbody>
<tr>
<td>T300-rMIT</td>
<td>10 $\times$ 10</td>
<td>1596</td>
<td>1038</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>T800-rMIT</td>
<td>2407</td>
<td>1809</td>
<td></td>
<td>73%</td>
<td></td>
</tr>
</tbody>
</table>
The influence of micromechanical properties and reinforcement architecture

Figure 5.2: Geometry of CT specimens for materials T300-rMIT and T800-rMIT (for T300-rRCF, see Chapter 4).

5.4 Results

5.4.1 Single–fibre analysis

5.4.1.1 Fibre morphology

The diameters of all fibre types analysed are presented in Figure 5.3. There is no statistically significant difference between the diameters of virgin and recycled T300 fibres (contrarily to results obtained by Wong et al. for T300-rRCF [76]). However, the T800-rMIT fibres are significantly larger than the virgin precursors ($p$–value of 0.0002%), suggesting the presence of a residual matrix layer on the surface of the former.

Figure 5.3: Fibre diameters of virgin and recycled fibres. Average percent reduction (relatively to the virgin fibre) are indicated; error bars represent one standard deviation.
Figure 5.4 presents SEM images of T300 fibres. Virgin filaments are clean and smooth, apart from the striations characteristic of this fibre type. The surface of recycled fibres presented a low amount of residual matrix, but were otherwise clean and showed no evidence of fibre damage.

The morphology of virgin and recycled T800 fibres is presented in Figure 5.5. The alternate presence of clean fibres and residual matrix in the T800-rMIT recyclate is highlighted.

### 5.4.1.2 Single–fibre tensile strength

Average fibre strengths and corresponding standard deviations are shown in Figure 5.6. The strength of T300 fibres was not significantly affected by the recycling process. On the contrary, the average strength of T800-rMIT was statistically lower ($p$-value of 0.1%) than that of the virgin type; the difference is nevertheless small, and is actually
The influence of micromechanical properties and reinforcement architecture

Figure 5.5: Scanning electron micrographs of virgin and recycled T800 fibres.

Magnified by the larger diameter of the former (although it still verifies for the (non-normalised) failure load).

Figures 5.7 and 5.8 present experimental and fitted single-fibre strength distributions in Weibull plots. The quality of the fitting is good for all fibre types and at both 10 mm and 20 mm gauge lengths.

Figure 5.6: Strength statistics for virgin and recycled fibres. Average strength retentions (relatively to the virgin fibre) are indicated; error bars represent one standard deviation.

89
However, Table 5.5 shows that the Weibull moduli calculated from distributions at each gauge length are not necessarily identical to each other; moreover, they tend to be significantly different from the modulus calculated assuming a Weibull–type size effect (Equation 5.1). Strength variability in T300 fibres increased only slightly after recycling, while it was actually reduced for the T800 type. In addition, and although size effects are evident in all fibre types, strength retention after recycling was higher for the longer gauge length (Figure 5.6 and Table 5.5).

5.4.1.3 Fibre–matrix interfacial properties

The interfacial properties measured through SFPO tests are presented in Figure 5.9. Further analysis revealed that the correlation between $S_{IF}$ and $l_{po}$ was very poor, and that the load–displacement curve during the friction stage was characteristically linear; this supports the use of an average interfacial shear strength and of constant frictional stresses as assumed in Equation 5.2.
The influence of micromechanical properties and reinforcement architecture

Figure 5.8: Strength distributions of virgin and recycled T800 fibres.

Table 5.5: Weibull fitting to SFTT strengths.

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>$l = 10$ mm (⋆)</th>
<th>$l = 20$ mm (⋆)</th>
<th>Size effect (†)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$ (−)</td>
<td>$\sigma_0^f$ (GPa)</td>
<td>$m$ (−)</td>
</tr>
<tr>
<td>T300-v</td>
<td>6.69</td>
<td>3.651</td>
<td>6.52</td>
</tr>
<tr>
<td>T300-rRCF</td>
<td>5.99</td>
<td>3.649</td>
<td>4.92</td>
</tr>
<tr>
<td>T300-rMIT</td>
<td>6.04</td>
<td>3.326</td>
<td>5.43</td>
</tr>
<tr>
<td>T800-v</td>
<td>4.58</td>
<td>5.387</td>
<td>5.87</td>
</tr>
<tr>
<td>T800-rMIT</td>
<td>7.28</td>
<td>4.255</td>
<td>8.59</td>
</tr>
</tbody>
</table>

(⋆) Maximum likelihood fitting for individual distributions.
(†) Size-effect Weibull modulus (predicted by Equation 5.1).
Figure 5.9(a) suggests that the interfacial adhesion in the T300-rRCF material is at least as good as when virgin fibres are used. The frictional stresses measured in both materials have considerable scatter, but are statistically similar and consistent with literature values \[163, 164\].

Due to the low number of successful tests, results for T300-rMIT and T800-rMIT systems in Figure 5.9 are indicative only; nevertheless, they suggest a good interfacial adhesion in both materials. The higher interfacial frictional stresses measured could be caused by higher residual stresses, a rougher fibre–matrix surface, or simply by statistical variance.

5.4.2 Composite analysis

5.4.2.1 Constituents and reinforcement architecture

Figure 5.10 shows the dry preforms of materials T300-rMIT and T800-rMIT, showing bundles on a mat of dispersed fibres; the multiscale character of the reinforcement is obvious in both cases. Material T300-rMIT clearly has a finer architecture; it is also evident that most bundles in material T800-rMIT originate from non-split tows of a woven fabric.

Through–the–thickness optical micrographs of the three materials analysed further highlight the different architectures: material T300-rRCF (Figure 5.11(a)) has most fibres finely dispersed within the matrix and only a few bundles; material T300-rMIT (Figure 5.11(b)) presents a continuous range of bundle sizes; material T800-rMIT (Fig-

![Graph](image)

(a) Apparent interfacial shear strength.  
(b) Pull–out frictional stress.

**Figure 5.9:** Fibre–matrix interfacial properties obtained from SFPO tests. Error bars represent standard deviations (not available for T300-rMIT and T800-rMIT composites).
The influence of micromechanical properties and reinforcement architecture

Figure 5.10: Dry preforms of the T300-rMIT and T800-rMIT materials.

Figure 5.11(c) shows very large and compact bundles, and fewer dispersed fibres. Figure 5.12 suggests that fibre content is slightly higher in the materials manufactured at Boeing than at the University of Nottingham, and that T800-rMIT has the highest void content.

The differences between the architectures in the three materials are quantified in Figure 5.13; only the dispersed phase is considered for T300-rRCF. For each material, bundle lengths and widths are well represented by Weibull distributions; parameters fitted through the least squares method are shown in Table 5.6. Assuming elliptical bundle cross-sections, it is estimated that bundles in the T300-rMIT are thicker than those in T800-rMIT; no correlation was found between bundle length and width in either material.

Figure 5.11: Micrographs of through-the-thickness cross sections of the three recycled composites under analysis.
Figure 5.12: Constituent volume fraction of the recycled composites tested.

Figure 5.13: Characterisation of the architecture of the three rCFRPs. Distributions for the T300-rRCF material were estimated from Wong et al. [76].

Table 5.6: Architecture characterisation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Length distribution</th>
<th>Width distribution</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$l_m$ (mm)</td>
<td>$m_l$ (-)</td>
<td>$l_0$ (mm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\bar{w}$ (mm)</td>
<td>$m_w$ (mm)</td>
</tr>
<tr>
<td>T300-rRCF</td>
<td>0.199</td>
<td>0.94</td>
<td>0.194</td>
</tr>
<tr>
<td>T300-rMIT</td>
<td>35.2</td>
<td>5.02</td>
<td>38.3</td>
</tr>
<tr>
<td>T800-rMIT</td>
<td>17.7</td>
<td>2.70</td>
<td>19.9</td>
</tr>
</tbody>
</table>

(\(^{(*)}\)) Expected value of Weibull distribution.
(\(^{(1)}\)) Average of raw data.
(\(^{(2)}\)) Data from Wong et al. [76].
(\(^{(3)}\)) Estimated from the mass of bundles measured, assuming fibre density $\rho_f = 1.78 \text{ g/cm}^3$ and content $V_f = 60\%$ in dry bundles.
5.4.2.2 Fracture toughness

Figure 5.14 presents the R-curves measured for the three materials; only specimens which exhibited reasonably straight crack propagation are included. No significant difference was found between orthotropic directions (1 and 2) in materials T300-rMIT and T800-rMIT, which validates the assumption of in-plane isotropy. Moreover, the R-curves of material T800-rMIT are remarkably similar for all specimen geometries tested (Figure 5.2); this verifies the requirement of in-plane scale–independence for valid measurements of fracture toughness.

Material T300-rRCF presented the lowest toughness values (even along the preferential fibre direction), followed closely by material T300-rMIT. However, material T800-rMIT is remarkably tougher, especially considering that the process zone was not fully developed and steady-state propagation had not been reached at $\Delta a = 60$ mm.

The R-curves of representative specimens are mapped with fracture surfaces in Figure 5.14. Going from material T300-rRCF to T300-rMIT and T800-rMIT, it becomes evident that, as the architecture becomes coarser, failure surfaces become more irregular — with broken and pulled-out bundles — and the fracture toughness increases significantly.

5.5 Discussion

5.5.1 Analysis of recycling processes and reclaimed fibres

The quality of recycled fibres was thoroughly assessed, and the results were extremely positive in all domains: all fibre types were reasonably clean and showed no signs of damage (Figures 5.4 and 5.5), retained most tensile strength of their virgin precursors (Figure 5.6), and presented good adhesion to epoxy matrices (Figure 5.9). This final point shows that re-sizing is not necessary from a micromechanical point of view, as suggested in Chapter 3.

Results show that both pyrolysis processes employed by RCF and MIT are capable of recovering recycled fibres with similar quality to virgin precursors. Nevertheless, reclaiming EoL waste is clearly more challenging than recycling uncured manufacturing waste, as the former case yielded fibres with more residue and lower strength retention. The uneven distribution of residual matrix on the surface of T800-rMIT fibres (also seen in Chapter 3, Figure 3.5) suggests that recycling thicker panels or 3D shapes will likely be problematic.
Figure 5.14: Results from the CT tests.
The influence of micromechanical properties and reinforcement architecture

Figure 5.15: Representative mapping of fracture surfaces with R-curves obtained through CT tests (all images are at the same scale).
Finally, it must be noted that all recyclates analysed in this chapter were recovered through pilot–plant operations, but scaling–up towards an industrial process represents a significant challenge [112]. This is perfectly illustrated by the impeccable performance of the T300-rRCF fibres, as opposed to the much more modest results reported in Chapter 3 — corresponding to the same recycling process but implemented at a continuous scale.

5.5.2 Strength distribution of recycled fibres and size effects

All recycled fibres exhibited higher strength retention at the 20 mm gauge length than at 10 mm (Figure 5.6); this is in contrast with some literature [75] and in Chapter 3 although it has been observed in other recyclates [112]. Size effects measured for virgin fibres ($m = 4.19$ for T300-v and $m = 4.63$ for T800-v) are consistent with literature results [165–167], thus suggesting a biased sampling of recycled fibres towards stronger filaments; all reclaimed fibres went through heavy processing during preforming, and it is possible this fractured the longer filaments at the weakest points (thus excluded from the tests).

In addition, the different Weibull moduli obtained directly from fibre strength distributions and from size–effects (Table 5.2) question the applicability of Weibull–based weakest–link theory to model the strength of individual filaments. Some researchers claim that fibres have non–Weibull strength distributions [168, 169], while others suggest that testing induces spurious effects [116, 159]. Recycled fibres can indeed have more than one population of defects, but they can also be affected differently by the sampling process and testing procedures.

While Table 5.2 and Figures 5.7–5.8 are inconclusive regarding the actual shape of single–fibre strength distributions and the nature of size effects, the averages shown in Figure 5.6 do provide a solid ground for comparing the virgin and recycled fibres.

5.5.3 Effect of architecture on stiffness and strength

All three rCFRPs present similar stiffness (Figure 5.1(a)). However, taking into account that (i) material T300-rRCF is anisotropic, (ii) T800 fibres are stiffer than T300, and (iii) MTM57 resin is stiffer than RTM-6, the architecture of T300-rMIT material (with fine bundles) comes as the most favourable for the overall modulus of the recyclates, due to the large aspect ratio of reinforcing units (Table 5.6).

The large variability in modulus of the T800-rMIT material is likely caused by its heterogeneous and coarse architecture. Similar conclusions have been reported for state–of–the–art prepreg–based discontinuous composites [154, 170].
Figure 5.1(b) shows that large bundles are detrimental to the strength of rCFRPs (although the different matrices used in the filamentised and bundled cases could also have influenced the results). Failure typically initiates at large inhomogeneities due to an energetic size effect [171]: even if the aspect ratio is kept constant, debonding is favoured by large reinforcing units. Moreover, material T800-rMIT has the highest void content (Figure 5.12), probably due to the presence of residual matrix (which, as seen in Chapter 3, obstructs impregnation).

Under compression (Figure 5.1(c)), materials T300-rMIT and T800-rMIT are considerably weaker than T300-rRCF. The previous considerations regarding the influence of reinforcement size on tensile strength apply to compression as well; however, in this case, the effect of a different resin (and fibre–matrix interface) is likely stronger.

Most literature on virgin SFRPs shows that filamentised materials exhibit superior mechanical properties [135, 147]; this was verified here for strength. However, it has also been reported that filamentised materials require higher moulding pressures [147], which is likely to increase fibre failure during manufacturing — thus degrading the aspect ratio of reinforcing units and, consequently, the stiffness of the composites.

Even though research on virgin discontinuous fibre composites is insightful for the recycled counterparts, results from the two fields are not completely interchangeable due to a complex relation between presence of bundles, residual matrix and fibre strength in the latter. Studies focusing specifically on rCFRPs are thus necessary to improve the understanding of their mechanical response.

5.5.4 Effect of architecture on toughening mechanisms

The characterisation of architectures (Figure 5.13) and CT results (Figure 5.14) evidence a clear correlation between the scale of reinforcing units and the fracture toughness of the composite. Similar observations on virgin SFRPs have been reported in the literature [136, 137, 149].

Size effects on pull–out of reinforcing units have been consistently identified by most authors as the main toughening mechanism in composites with coarse architectures [135, 138, 150, 151]. The fracture surfaces of the recyclates show pulled–out bundles in locally tougher regions (Figure 5.15(a)) and overall tougher rCFRPs (Figure 5.15(c)), illustrating the importance of the mentioned size effect.

Moreover, recent observations of size effects in the toughness of UD composites [172] suggest that thicker bundles are also intrinsically tougher than thinner ones (and than single fibres). This correlates well with the presence of broken bundles in the surfaces.
Chapter 5

shown in Figure 5.15 and is strongly supported by the fractal defibrillation patterns identified in bundles (Figure 4.9 in Chapter 4).

Altogether, the fracture toughness of rCFRPs is largely affected by the reinforcement architecture; a coarser microstructure leads to tougher composites, due to size effects on the energy dissipated during both pull-out and bundle failure. While materials T300-rRCF and T300-rMIT — with a finer microstructure — are more brittle than most metals ($G < 10 \text{ kJ/m}^2$), the bundled T800-rMIT materials (with $G \approx 40 \text{ kJ/m}^2$) is significantly tougher than a structural aluminium alloy (with $G \approx 20 \text{ kJ/m}^2$).

5.5.5 Optimisation of recycling routes

This study highlights a strong relation between the architecture of a rCFRP and its mechanical performance. On the one hand, the presence of fibre bundles weakens the recylcates (Figure 5.1(b)); however, recycled materials are unlikely to be used in strength-critical structures, thus making this drawback inconsequential for most realistic cases. For stiffness and toughness driven applications, on the other hand, accepting fibre bundles in rCFRPs would present the following advantages:

- **Significantly tougher composites.** Comparing the dispersed phase in material T300-rRCF (with $G_1 \approx 3 \text{ kJ/m}^2$) with material T800-rMIT (with $G \approx 40 \text{ kJ/m}^2$), it is concluded that a coarser reinforcement architecture can boost the fracture toughness of a rCFRP by more than one order of magnitude.

- **Composites with larger fibre content.** Filamentised preforms have a high loft (freestanding thickness), thus requiring very high moulding pressures to achieve reasonable reinforcement contents, at the expense of fibre fracture. Consequently, bundled architectures can also feature larger reinforcement aspect ratios, which improves the overall rCFRP stiffness (compare materials T300-rRCF and T300-rMIT in Figure 5.1(a)).

- **Higher fibre-strength retention.** Bundles are a natural consequence of residual resin, which results from soft reclamation cycles that inflict little fibre damage. This is particularly important for industrial processes, which will most likely operate in non-ideal conditions (as discussed in Chapter 3);

- **Lower recycling costs.** Residual resin is favoured by shorter and lower-temperature reclamation cycles, which require less energy. Moreover, manufacturing highly filamentised composites requires additional intermediate steps (e.g. disentanglement stage for material T300-rRCF).
5.6 Conclusions

The mechanical response of three rCFRPs was studied experimentally. The analysis highlighted the relations between recycling routes, micromechanical properties, meso-level architectures and the macroscopic response of the recyclates.

The materials investigated comprised different virgin fibre types (T300 and T800), waste sources (uncured manufacturing scrap and EoL components) and reclamation processes (pilot-scale pyrolysis by RCFLtd and MIT). The quality of the fibres recycled from manufacturing waste was comparable to that of the virgin precursors, and was only slightly degraded for the EoL component case.

All composites analysed were composed of an epoxy resin reinforced by discontinuous rCFs, but featured very distinct architectures — from nearly fully dispersed short fibres to long and wide bundles; these differences resulted not only from the fibre-reclamation stage, but also from re-manufacturing. This study shows that, while the reinforcement architecture has limited influence on the overall stiffness and strength of rCFRPs, it dramatically affects the fracture toughness.

Preserving fibre bundles during reclamation and re-manufacturing processes toughened the recyclates by more than one order of magnitude. Fracture toughnesses in excess of $\mathcal{G} = 40$ kJ/m$^2$ were measured for one rCFRP, which is significantly above the typical value exhibited by some traditional structural materials (e.g. aluminium).

These results open a window of opportunity for rCFRPs in toughness or damage-tolerance driven applications (which include any structure with sharp geometric discontinuities). However, before these materials can be used confidently in (non-safety-critical) structures, it is necessary to further understand and be able to predict the relations between micromechanical properties, reinforcement architecture and the overall toughness of the recyclates.

This requires developing models specific for the fracture toughness of rCFRPs; these must necessarily include the two main toughening mechanism identified — pull-out and fracture of fibres and bundles —, as well as the associated size effects. Such models can then be used by recyclers to guide further optimisation of their processes, and by engineers aiming to design structures with rCFRPs.
Chapter 6

Hierarchical scaling law for the strength of composite fibre bundles

6.1 Introduction

Size effects on the strength of composite materials are widely reported in the literature, but a universally accepted modelling strategy is still to be developed \[159\]; this represents a significant challenge for the design of large structures. This chapter presents a model for size effects on the longitudinal tensile strength of UniDirectional (UD) Fibre–Reinforced Polymers (FRPs), based on the stochastic variability of fibre strength and the definition of hierarchical fibre–matrix bundles.

Several theories have been proposed to model the relation between size and strength of structures. The stochastic approach, based on the Weakest Link Theory (WLT) and formalised by Weibull \[173\], has been extensively applied to FRPs \[159, 174\]. Deterministic size effects have also been studied by Bažant et al. (on the energy dissipated by failure of quasi-brittle materials \[171\]), Carpinteri et al. (on the fractal self-similar failure of heterogeneous materials \[175\]), and Wisnom et al. (on the change of failure mode in scaled laminated composites \[176\]). All authors agree nevertheless that stochastic size effects are key for the strength of FRPs.

The WLT states that a chain withstands an external load only if all its elements survive the resulting stresses. Let \( X_{U,r} \) be the stochastic strength of the elements (with reference length \( l_r \), all statistically identical and independent) under an uniform (subscript \( U \)) stress \( \sigma \); the survival probability for each element is \( S_{U,r}(\sigma) = \Pr(X_{U,r} > \sigma) \).
Therefore, the survival probability of a chain (length \( l_n = n \cdot l_r \)) with \( n \) elements is:

\[
S_{U,n}(\sigma) = \left[ S_{U,r}(\sigma) \right]^n \quad \Rightarrow \quad \ln \left[ S_{U,n}(\sigma) \right] = n \cdot \ln \left[ S_{U,r}(\sigma) \right] = \frac{l_n}{l_r} \cdot \ln \left[ S_{U,r}(\sigma) \right]. \tag{6.1}
\]

Weibull \[173\] proposed a distribution for the strength of brittle materials, so that survival and failure probabilities of a chain under uniform stresses \( \sigma \) are:

\[
S_{U,n}(\sigma) = \exp \left[ -\frac{l_n}{l_r} \left( \frac{\sigma}{\sigma_0} \right)^m \right] \quad \text{and} \quad F_{U,n}(\sigma) = 1 - \exp \left[ -\frac{l_n}{l_r} \left( \frac{\sigma}{\sigma_0} \right)^m \right], \tag{6.2}
\]

where \( m \) and \( \sigma_0 \) are respectively the shape (size independent) and scale (measured at \( l_r \)) parameters of the distribution.

Equation 6.2 has been widely used to model the length effect on the strength of technical fibres, e.g. glass or carbon \[159\, 177\, 178\]. While alternative strength distributions have been proposed \[168\, 169\], Stoner et al. \[116\] showed that a good agreement between Weibull’s theory and experimental measurements can be achieved by taking the spurious effect of fibre gripping and testing variability into account.

At the FRP level, the parallel fibre arrangement and presence of matrix result in a quasi-brittle failure. \[169\] and \[179\] tested micro–bundles (with 4 and 7 fibres respectively) and found that bundle strengths deviated significantly from Weibull distributions; moreover, some bundles (depending on the resin) had higher mean strength than the single–fibres, but considerably lower variability. At the macroscopic scale, \[165\] and \[180\] observed several clusters of fibre breaks before final coupon failure. \[159\] also noted that both the magnitude of size effects and the variability of strength decrease for larger specimens. All these observations are incompatible with the WLT applied directly to the single–fibre level \[159\, 171\].

The asymptotic behaviour of tensile strength of FRPs has been successfully modelled in the literature (see reviews from Baˇ zant, Wisnom and Curtin \[159\, 171\, 177\]). However, the recent developments in composites with thin plies \[181\] and with discontinuous reinforcement — with individual fibres and bundles of various sizes \[22\, 147\] (see also Chapters \[4\] and \[5\]) — requires developing and validating full scaling models. It has been suggested \[159\] that Fibre Bundle Models (FBMs, firstly developed by Daniels \[182\] and recently reviewed by Pradhan \[178\]) have the potential to capture most of the physics involved in longitudinal tensile failure of FRPs and the associated size effects.

Several FBMs have been proposed to predict the longitudinal tensile strength and size effects in composites. The key challenge is to calculate the strength distribution of a bundle of parallel fibres with a given characteristic length, to then use the WLT (Equation 6.1) to scale the result for a chain of bundles \[183\, 185\]. Different
Hierarchical scaling law for the strength of composite fibre bundles

fibre arrangements, matrix responses, load sharing schemes and magnitudes of stress concentrations have been assumed (see review from [177]).

The complexity of most FBMs increases exponentially with the number of fibres considered, hence exact solutions are attainable for small bundles only; consequently, much work focused on asymptotic analyses [186–188] and Monte-Carlo simulations [189–192]. Most authors use a characteristic length independent of load and number of fibre breaks, although this is known not to be correct [193,194].

Laffan et al. [172] and Pimenta et al. [22] (see also Chapter 4) reported self–similar or quasi-fractal fracture surfaces in thin (under 0.5 mm) UD laminas and fibre bundles; this provides experimental evidence that the length–scale of the failure process increases with the number of fibres involved. Moreover, such observations suggest a hierarchical failure process, hence supporting the use of hierarchical models — e.g. Newman and Gabrielov’s model for dry bundles [195]. Here, considering that a bundle of level \([i+1]\) is composed by two sub-bundles of level \([i]\), strength distributions were calculated recursively as:

\[
F^{[i+1]}(\sigma) = F^{[i]}(\sigma) \cdot [2 \cdot F^{[i]}(2 \cdot \sigma) - F^{[i]}(\sigma)],
\]

where \(F^{[i]}(\sigma)\) is the failure probability of a level–\([i]\) bundle under an applied stress \(\sigma\). The recursive nature of this scaling law also allowed its efficient implementation, so that large–scale bundles could be computed. However — being a model for dry bundles — it does not consider the effect of an embedding matrix, and does not include any characteristic length (which is paramount for quasi-brittle materials [171]); the model is also inconsistent with the WLT for length scaling.

Altogether, a comprehensive explanation of the micromechanics and statistics of tensile failure in composites is yet to be provided, as are validated quantitative predictions over a complete range of scales. Still, FBMs surface as one of the most promising approaches to overcome this knowledge gap.

This chapter presents the development, implementation and validation of a FBM for predicting size effects on the longitudinal tensile strength of composite bundles. Following Newman and Gabrielov’s work [195], bundles are hierarchically organised; however, the role of the matrix (or fibre–matrix interface) is now considered through a simplified shear–lag model, in which the characteristic length scales hierarchically as well.

This chapter is organised as follows: Section 6.2 presents the analytical model for predicting strength distributions of FRP bundles of different dimensions. Section 6.3 explores modelling results (including experimental validation), subsequently discussed in Section 6.4. Finally, Section 6.5 draws the main conclusions.
6.2 Model development

6.2.1 Fibre bundle geometry and shear–lag boundary

This model is based on hierarchical fibre–matrix bundles (Figure 6.1(a)). These are generated by pairing individual fibres (level–[0]) into level–[1] bundles, and then sequentially grouping two level–[i] bundles into one level–[i + 1] bundle [195]. The number of fibres \( n^{[i]} \) in a level–[i] bundle is therefore:

\[
n^{[i]} = 2^i \iff i = \log_2 n^{[i]}.
\] (6.4)

The fibres (superscript \( f \), diameter \( \phi^f \), circumference \( C^f \) and area \( A^f \)) are embedded in the matrix (with volume fraction \( V^f \)) in a square architecture (Figure 6.1(b)).

During hierarchical failure of a large composite bundle (Figure 6.2(a)), shear–lag stresses will be transferred between the (unbroken) surrounding material and a broken level–[i] bundle through the shear–lag boundary, with perimeter \( C^{[i]} \). Considering preferential interfacial debonding (Figure 6.2(b)),

\[
C^{[i]} = 3 \cdot C^f + 4 \cdot \left( \sqrt{n^{[i]}} - 1 \right) \cdot s_Q + \left( \sqrt{n^{[i]}} - 2 \right) \cdot \frac{C^f}{2}, \quad \text{with} \quad s_Q = \left( \frac{\sqrt{\pi}}{2 \cdot \sqrt{V^f}} - 1 \right) \cdot \phi^f.
\] (6.5)

This expression is strictly valid only for even values of \( i \), but used for any bundle size so that \( C^{[i]} \) is a smooth function of \( n^{[i]} \).

Other geometries for bundles and their boundaries (e.g. hexagonal fibre arrangement with fractal boundary, preferential matrix failure, free–edge effects) are considered in Appendix D. These variations are shown to have a minor influence on calculated bundle strength distributions (as suggested by [196]).

\[\begin{array}{c}
\text{(a) Bundle hierarchy.} \\
\text{(b) Fibre arrangement.}
\end{array}\]

Figure 6.1: Hierarchical bundles in square fibre arrangement.
Hierarchical scaling law for the strength of composite fibre bundles

6.2.2 Stress field around a fibre break and definition of the control region

Consider a level–[1] bundle of reference length $l_r$, composed by two level–[0] fibres ($A$ and $B$) in a soft matrix ($i = 1$ in Figure 6.1(a)). The bundle is loaded in tension by a progressively increasing remote stress $\sigma^\infty$, so that each fibre undergoes a uniform stress state $\sigma^A(x) = \sigma^B(x) = \sigma^\infty$. Note that longitudinal stresses are expressed as fibre stresses, i.e. normalised by the area of fibres in the cross section.

Assume that fibre $A$ fails at the location $x = 0$ under a given $\sigma^\infty$ (Figure 6.3(a)). Shear–lag models have been shown to accurately reproduce the resulting stress fields, as validated by more complex Finite Element analyses [197, 198]. The in-situ response of the matrix / interface to this event is complex, as for instance epoxy is usually brittle in bulk, but actually ductile and much stronger in-situ [198–200]. This, together with the lack of agreement in the literature on whether fibre failure should be modelled through energy or stress based approaches [201, 202], supports the use of a perfectly–plastic shear–lag approach, for the sake of simplicity [197, 203].

According to perfectly–plastic shear–lag, the failed fibre $A$ recovers the remote stress $\sigma^\infty$ within the level–[0] effective recovery length (subscript $\epsilon$), defined as [204]:

$$l_{\epsilon}^{[0]}(\sigma^\infty) = 2 \cdot \frac{A^f}{C^{[0]} \cdot \tau_{SL}} \cdot \sigma^\infty.$$  
(6.6)

Here, $\tau_{SL}$ is the matrix / interface yield stress, and $C^{[0]}$ is the perimeter of the level–[0] shear–lag boundary (Equation 6.5 implies $C^{[0]} = C^f$).

Conversely, fibre $B$ undergoes linear stress concentrations within the length $l_{\epsilon}^{[0]}$ (Figure 6.3(a)). In this model, equilibrium of the 2 fibres yields a stress concentration factor $k = 2$. However, the true value of $k$ near a cluster of fibre breaks is still an open
(a) Stress fields after first fibre failure.

(b) Definition of critical distance between fibre breaks: the bundle fails only if fibre $B$ breaks at a distance smaller than $l_c/2$ from the break in fibre $A$.

(c) Definition of the control region and fibre segments.

Figure 6.3: Stress fields and length scales in a level-[1] fibre bundle.
issue, and depends on local fibre arrangement, size of broken cluster, matrix response and dynamic effects [192,198,205,208]. Therefore, $k$ will be treated as free parameter.

Bundle failure requires that both fibres $A$ and $B$ break in nearby locations, so as to promote complete yielding of the matrix / interface between breaks (Figure 6.3(b)). Therefore, once fibre $A$ fails, the level–[1] control region (subscript $c$) — within which a break in fibre $B$ leads to bundle failure — has a length defined by:

$$l^{[1]}_c(\sigma^\infty) = 2 \cdot l^{[0]}_e(\sigma^\infty) = 4 \cdot \frac{A^f}{C^{[0]} \cdot \tau_{SL}} \cdot \sigma^\infty.$$ (6.7)

This region, centred at the first fibre break, is partitioned into 4 fibre segments ($A_1$, $A_2$, $B_1$ and $B_2$) of equal length $l^{[0]}_e$ (Figure 6.3(c)). The probability of failure of the level–[1] bundle within the control length will be determined in Section 6.2.3.

This definition of $l^{[1]}_c$ differs from other characteristic lengths in the literature. Firstly, $l^{[1]}_c \propto \sigma^\infty$ (as opposed to fixing $l^{[1]}_c$ at a characteristic stress [183,190,209,210]). Secondly, $l^{[1]}_c = 2 \cdot l^{[0]}_e$; while [187,188] proposed $l^{[1]}_c \leq l^{[0]}_e$ for global load sharing, Equation 6.7 defines the shortest statistically independent partition of a level–[1] bundle. Finally, the control length of a larger level–[i + 1] bundle will be scaled hierarchically in Section 6.2.4.

### 6.2.3 Statistical analysis of level–[1] bundle failure

The strength distribution of the level–[1] bundle analysed in Figure 6.3 will be determined under the following assumptions:

A(i) At each remote stress $\sigma^\infty$, the bundle is represented by a chain of independent control regions of length $l^{[1]}_c$ (Equation 6.7). This shifts the first fibre break to the centre, thus neglecting bundle–end effects.

A(ii) Within a control region, each fibre may break only once (equivalent to the WLT); this guarantees that the stress fields presented in Figure 6.3 are always valid.

Statistically, a level–[1] bundle survives the remote stress $\sigma^\infty$ in the control length if (i) all its 4 fibre segments survive the uniform stress $\sigma^\infty$, or (ii) the weakest fibre fails under $\sigma^\infty$ and the strongest fibre survives the resulting stress field — comprising one segment under the uniform stress $\sigma^\infty$, and another segment under linear stress concentrations (factor $k$). The survival probability of the level–[1] bundle under uniform (subscript $U$) stresses $\sigma^\infty$ within the control length is then:

$$S^{[1]}_{U,c}(\sigma^\infty) = S^{[0]}_{U,e}(\sigma^\infty)^4 + 2 \cdot \left[ 1 - S^{[0]}_{U,e}(\sigma^\infty)^2 \right] \cdot S^{[0]}_{U,e}(\sigma^\infty) \cdot S^{[0]}_{K,e}(\sigma^\infty), \quad \text{where:} \quad (6.8)$$
Chapter 6

- $S_{0,e}^{[0]}(\sigma^{\infty})$ is the survival probability of a single–fibre segment loaded by a uniform stress $\sigma^{\infty}$ within the length $l_e^{[0]}$. Assuming that fibre strength follows a Weibull distribution with survival probability $S_{0,e}^{[0]}$ at the reference length $l_r$ (with parameters $m$ and $\sigma^f_0$ as shown below), then WLT scaling (Equation 6.2) implies:

\[
S_{0,e}^{[0]} = \exp \left[ - \left( \frac{\sigma^{\infty}}{\sigma^f_0} \right)^m \right] \quad \text{and} \quad S_{0,e}^{[0]} = \exp \left[ - \frac{l_e^{[0]}}{l_r} \cdot \left( \frac{\sigma^{\infty}}{\sigma^f_0} \right)^m \right]. \tag{6.9}
\]

- $S_{K,e}^{[0]}(\sigma^{\infty})$ is the survival probability of a single–fibre segment loaded under linear stress concentrations (variable remote stress $\sigma^{\infty}$ and constant factor $k$) within the length $l_e^{[0]}$. Generalising the WLT to non-uniform chain stresses (Appendix E),

\[
S_{K,e}^{[0]} = \exp \left[ - C_k \cdot \frac{l_e^{[0]}}{l_r} \left( \frac{\sigma^{\infty}}{\sigma^f_0} \right)^m \right] \quad \text{where} \quad C_k = \frac{k^{m+1} - 1}{(m+1) \cdot (k-1)}. \tag{6.10}
\]

While the level–[1] scaling law in Equation 6.8 was derived from a purely statistical argument, Appendix F shows it actually corresponds to the following physical sequences of events leading to bundle failure:

- $E_1$: failure of the weakest fibre and immediate (unstable) failure (with no increment of $\sigma^{\infty}$) of segment $B_1$ due to stress concentrations;
- $E_2$: failure of the weakest fibre and later (after incrementing $\sigma^{\infty}$) failure of the stress concentrations segment $B_1$;
- $E_3$: failure of the weakest fibre and later failure of the far–segment $B_2$ (stable failure due to independent fibre flaws). This includes bundle failure by growth and coalescence of matrix damage between two previously formed breaks.

6.2.4 Hierarchical law for bundle failure

Equation 6.8 relates the strength distribution of a single fibre to that of a level–[1] bundle. Assuming a self–similar hierarchical failure process as reported in the literature \cite{22, 172} (see also Chapter 4), this can be extrapolated to any bundle level and used recursively throughout bundle hierarchy. Consequently, the survival probability of a level–[i + 1] bundle under uniform stresses is (omitting $\sigma^{\infty}$ for readability):

\[
S_{0,c}^{[i+1]} = \left( S_{0,e}^{[i]} \right)^4 + 2 \cdot \left[ 1 - \left( S_{0,e}^{[i]} \right)^2 \right] \cdot S_{0,e}^{[i]} \cdot S_{K,e}^{[i]}. \tag{6.11}
\]

Level–[i] survival probabilities on the right–hand side are defined at the respective effective recovery length $l_e^{[i]}(\sigma^{\infty})$, while $S_{0,c}^{[i+1]}$ is defined at the level–[i + 1] control length.
Contrarily to most fibre bundle models in the literature \cite{183, 185, 190, 209, 210}, these characteristic lengths are also scaled hierarchically from their original definition. Using the shear–lag perimeters defined in Equation \ref{eq:6.5}

\[
 l_{e}^{[i]}(\sigma^{\infty}) = \frac{k_{i} \cdot A_{i}}{2 \cdot C_{i} \cdot \tau_{SL}} \cdot \sigma^{\infty}, \quad \eta_{e}^{[i]}(\sigma^{\infty}) = 2 \cdot l_{e}^{[i]}(\sigma^{\infty}). \quad (6.12)
\]

Equation \ref{eq:6.11} can be written in both the following logarithmic forms:

\[
 \ln \left( S_{u,c}^{[i+1]} \right) = 4 \cdot \ln \left( S_{u,e}^{[i]} \right) + \ln \left( 1 + 2 \cdot \frac{S_{k,e}^{[i]}}{S_{u,e}^{[i]}} - 2 \cdot \frac{S_{k,e}^{[i]}}{S_{u,e}^{[i]}} \right) = \ln \left( S_{u,e}^{[i]} \right) + \ln \left( S_{k,e}^{[i]} \right) + \ln \left( 2 + \frac{S_{k,e}^{[i]}}{S_{u,e}^{[i]}} - 2 \cdot \left( \frac{S_{u,e}^{[i]}}{S_{k,e}^{[i]}} \right)^{2} \right). \quad (6.13)
\]

Scaling to the reference length (using the WLT in Equation \ref{eq:6.1} and \( l_{e}^{[i+1]} \) in Equation \ref{eq:6.12}),

\[
 \ln \left( S_{u,r}^{[i+1]} \right) = 2 \cdot \ln \left( S_{u,r}^{[i]} \right) + \frac{l_{r}}{2 \cdot l_{e}^{[i]}} \ln \left( 1 + 2 \cdot \left( \frac{S_{k,r}^{[i]}}{S_{u,r}^{[i]}} \right)^{3} - 2 \cdot \left( \frac{S_{k,r}^{[i]}}{S_{u,r}^{[i]}} \right)^{3} \right) = \ln \left( S_{u,r}^{[i]} \right) + \ln \left( S_{k,r}^{[i]} \right) + \frac{l_{r}}{2 \cdot l_{e}^{[i]}} \ln \left( 2 + \left( \frac{S_{k,r}^{[i]}}{S_{u,r}^{[i]}} \right)^{3} - 2 \cdot \left( \frac{S_{u,r}^{[i]}}{S_{k,r}^{[i]}} \right)^{3} \right). \quad (6.14)
\]

The expressions above are analytically equivalent but prone to different numerical errors (due to exponential arguments); consequently, both forms will be used (Section \ref{sec:6.2.6}).

The level–\([i] \) survival probability under linear stress concentrations \( S_{k,r}^{[i]}(\sigma^{\infty}) \) can be calculated from \( S_{u,r}^{[i]}(\sigma^{\infty}) \). Bundle strengths do not follow Weibull distributions when \( i > 0 \), hence the generic relation derived in Appendix \ref{app:2} must be employed:

\[
 \ln \left[ S_{k,r}^{[i]}(\sigma^{\infty}) \right] = \begin{cases} 
 k \cdot \ln \left[ S_{L,r}^{[i]}(k \cdot \sigma^{\infty}) \right] - \ln \left[ S_{L,r}^{[i]}(\sigma^{\infty}) \right] & \text{if} \quad k > 1 \\
 \ln \left[ S_{u,r}^{[i]}(\sigma^{\infty}) \right] & \text{if} \quad k = 1 
 \end{cases}
\]

where

\[
 \ln \left[ S_{L,r}^{[i]}(\sigma) \right] = \frac{1}{\sigma} \int_{\sigma_{L}=0}^{\sigma} \ln \left[ S_{L,r}^{[i]}(\sigma_{L}) \right] d\sigma_{L}. \quad (6.15)
\]

### 6.2.5 Asymptotic behaviour

If fibre strength follows a Weibull distribution (Equation \ref{eq:6.9}), then each tail of any bundle strength distributions tends asymptotically to a Weibull as well (Appendix \ref{app:3}):
• The Right Tail Asymptote (RTA, $\sigma^\infty \to \infty$) of a bundle survival probability is:

$$S_{\sigma_{\text{RTA}}}^\infty = \exp \left[ -\left( \frac{\sigma^\infty}{\sigma_{\text{RTA}}} \right)^m \right],$$

with:

$$\sigma_{\text{RTA}}^{|i|} = \begin{cases} 
2^{-i/m} \cdot \sigma_f^0 & \text{if } C_K \geq 3 \\
\left( \frac{1 + C_K}{2} \right)^{-i/m} \cdot \sigma_f^0 & \text{if } C_K < 3.
\end{cases}$$

(6.16)

This preserves the single-fibre shape parameter $m$. As most technical fibres (e.g. carbon and glass) have $C_K \geq 3$ ($m \gg 2$), the RTA of a bundle strength distribution corresponds to the WLT applied to the fibre level. This has been observed in other FBMs as well [184].

• The Left Tail Asymptote (LTA, $\sigma^\infty \to 0$) of a bundle survival probability is defined recursively as:

$$S_{\sigma_{\text{LTA}}}^{|i+1|} = \exp \left[ -4 \cdot C_{K,LTA} \cdot \frac{n^{|i|} \cdot A^f \cdot \sigma_{\text{LTA}}^{|i|}}{C^{|i|} \cdot \tau_{BL} \cdot \tau_r} \cdot \left( \frac{\sigma^\infty}{\sigma_{\text{LTA}}^{|i|}} \right)^{2 \cdot m^{|i+1|}} \right].$$

(6.17)

Level-[$i$] parameters are defined in Equation [G.8]. It should be noticed that the shape parameter of LTAs more than doubles with each hierarchical level; therefore, one can expect lower variability for the strength of larger bundles. Such behaviour is typical of FBMs [184], although $m_{\text{LTA}}$ here increases in a more pronounced way (due to $l^{|i+1|} \propto \sigma^\infty$).

In addition to providing further insight on bundle strength distributions and size effects, the RTA behaviour is key for the implementation of this model (Section 6.2.6). Equations [6.14] and [6.15] show that defining $S_{\sigma_{\text{LTA}}}^{|i+1|} (\sigma^\infty)$ requires calculating $S_{\sigma_{\text{LTA}}}^{|i|} (k \cdot \sigma^\infty)$, and thus (following a recursive procedure down to the single-fibre level) calculating $S_{\sigma_{\text{LTA}}}^{|0|} (k^{i+1} \cdot \sigma^\infty)$. This becomes intractable as bundle level increases. Fortunately, the Weibull-like behaviour of RTAs (Equation [6.16]) allows replacing the general relation between $S_{\sigma_{\text{LTA}}}^{|i|} (\sigma^\infty)$ and $S_{\sigma_{\text{RTA}}}^{|i|} (\sigma^\infty)$ (Equation [6.15]) with its closed-form result for Weibull distributions (Equation [E.8]), when $\sigma^\infty \to \infty$:

$$\lim_{\sigma^\infty \to \infty} \ln \left[ S_{\sigma_{\text{RTA}}}^{|i|} (\sigma^\infty) \right] = C_K \cdot \ln \left[ S_{\sigma_{\text{LTA}}}^{|i|} (\sigma^\infty) \right], \quad \forall \ i \geq 0.$$  

(6.18)

This eliminates the need to compute $S_{\sigma_{\text{RTA}}}^{|i|} (k \cdot \sigma^\infty)$ for large values of $\sigma^\infty$. 

112
### I. Definition of input variables

#### I.1: Numerical variables
\[ \Delta \sigma, \sigma^{\max} \]

#### I.2: Single fibre strength
\[ l_r, \sigma^0_r, m \]

#### I.3: Composite bundle
\[ \tau_{SL}, V^l, \phi^f, k, i^{\max} \]

### II. Preliminary calculations

#### II.1: Define strength vector
\[ \nu_\sigma = \left( \frac{\sigma^{\max}}{\Delta \sigma} \right) + 1 \]
\[ \sigma = \left\{ (j-1) \cdot \Delta \sigma \right\}_{j=1}^{n_\sigma} \]
\[ n_\sigma = \left( \frac{n_\sigma - 1}{k} \right) + 1 \]

#### II.2: Define geometric parameters
\[ A^f = \pi \cdot (\phi^f)^2 \frac{2}{4} \]
\[ C^f = \pi \cdot \phi^f \]
\[ n_{SL} = \left( \frac{\pi}{2 \cdot \sqrt{\pi}} - 1 \right) \cdot \phi^f \]

#### II.3: Calculate single-fibre log-survival vectors
\[ \ln S_{iUR}^{(0)} = -\left( \frac{\sigma}{\sigma^0_r} \right) \]
\[ C^*_k = \frac{k^{i+1} - 1}{(k-1) \cdot (m+1)} \]
\[ \ln S_{iLR}^{(0)} = -C^* \left( \frac{\sigma}{\sigma^0_r} \right)^m \]

### III. Strength scaling model

#### III.0: Set bundle level counter
\[ i = 0 \]
\[ i = i + 1 \]

#### III.1: Define geometry and normalised effective length vector:
\[ n^{[i+1]} = 2^{i+1} \]
\[ C^{[i+1]} = 3 \cdot C^f + 4 \cdot \left( \frac{\sqrt{m^{[i+1]}} - 1}{n[0]} + \sqrt{m^{[i+1]}} - 2 \right) \cdot C^f/2 \]
\[ \ln n^{[i+1]} = 2 \cdot \frac{n^{[i+1]} \cdot A^f}{C^{[i+1]} \cdot \tau_{SL} \cdot l_r} \cdot \sigma \]

#### III.2: Calculate uniform-stresses bundle survival vector
\[ \ln S_{iUR}^{(j)} = 2 \ln S_{iUR}^{(j-1)} + \frac{1}{2 \cdot t_{iUR}} \ln \left[ 1 + 2 \cdot \exp \left( \frac{\ln S_{iUR}^{(j-1)} - 3 \cdot \ln S_{iLR}^{(j-1)}}{t_{iUR}} \right) \right] - 2 \cdot \exp \left( \frac{\ln S_{iUR}^{(j-1)} - \ln S_{iLR}^{(j-1)}}{t_{iUR}} \right) \]
\[ \ln S_{iLR}^{(j)} = \ln S_{iUR}^{(j)} + \ln S_{iLR}^{(j)} \frac{1}{2 \cdot t_{iLR}} \ln \left[ 2 + \exp \left( \frac{\ln S_{iUR}^{(j)} - 3 \cdot \ln S_{iLR}^{(j)}}{t_{iLR}} \right) \right] - 2 \cdot \exp \left( \frac{2 \cdot \ln S_{iUR}^{(j)} - \ln S_{iLR}^{(j)}}{t_{iLR}} \right) \]

#### III.3: Calculate bundle survival vectors under linear stress states
\[ \ln S_{iUR}^{(j)} = \frac{1}{m} \int_{0}^{\sigma} \ln S_{iUR}^{(j)} \Delta \sigma \]
\[ \ln S_{iLR}^{(j)}(j) = \frac{k}{k} \cdot \ln S_{iUR}^{(j)}(k-j) - \ln S_{iLR}^{(j)}(j) \]
if \[ j < n_\sigma \]
\[ \ln S_{iLR}^{(j)}(j) = C^*_k \cdot \ln S_{iUR}^{(j)}(j) \]
if \[ j > n_\sigma \]

### IV. Post-processing

#### IV.0: Set bundle level counter
\[ i = 0 \]
\[ i = i + 1 \]

#### IV.1: Calculate bundle strength distributions
\[ F_{iUR}^{(j)} = 1 - \exp \left[ \ln S_{iUR}^{(j)} \right] \]

#### IV.2: Calculate bundle strength statistics
\[ X_{iUR}^{(j)} = \sigma(n_\sigma) - \int F_{iUR}^{(j)} \cdot \Delta \sigma \]
\[ \text{CoV}_{iUR}^{(j)} = \frac{\sqrt{\sigma(n_\sigma)^2 - \left( X_{iUR}^{(j)} \right)^2} - 2 \cdot \int \sigma \cdot F_{iUR}^{(j)} \cdot \Delta \sigma}{X_{iUR}^{(j)}} \]
if \[ j < 2^{i+1} \]

---

**Figure 6.4:** Numerical implementation.
6.2.6 Numerical implementation

An overview of the numerical implementation of the present model is shown in Figure 6.4; using array programming (e.g. MATLAB) greatly simplifies the implementation and reduces running time, hence the following remarks are of relevance:

- In the numerical implementation, the remote stress $\sigma^\infty$ becomes a discrete vector $\sigma$, with $n_\sigma$ evenly spaced stress values from $\sigma^\infty = 0$ to $\sigma^\infty \geq \sigma^{\max}$ (step size $\Delta \sigma$);
- Accordingly, most variables are expressed in vectorial form (indicated in upright bold in Figure 6.4); all arithmetic operators represent pointwise calculations. Survival distributions are stored in logarithmic form, $\ln S = \{ \ln [S(\sigma^\infty)] \}$;
- Integration symbols represent numerical integration; these can be efficiently evaluated using MATLAB’s in-built `trapz` and `cumtrapz` functions;
- Module IV calculates bundle strength distributions $F_{U,i}^l(\sigma) = \Pr(X_{U,i}^l \leq \sigma)$, where $X_{U,i}^l$ is the stochastic strength of a level-$i$ bundle of length $l_r$ under uniform stresses. Mean values ($X_{m}^l$) and Coefficients of Variation ($\text{CoV}_{m}^l$) depend directly on the cumulative distribution function, as a result of integration by parts.

6.3 Results

6.3.1 Analysis of model predictions

Figure 6.5 summarises the results of the model for nominal input parameters (Table 6.1). Predicted bundle strength distributions (Figure 6.5(a)) show size effects, with larger bundles (e.g. $i = 15$) being weaker but less variable than their constituent fibres ($i = 0$).

In Figure 6.5(b), the model predicts an initial strengthening throughout bundle hierarchy and steep reduction in variability (validated experimentally in Figure 6.12); these aspects differ from Newman and Gabrielov’s model [195].

Table 6.1: Nominal model inputs for parametric studies (nominal outputs will be highlighted as $\ast$ in the parametric study, Figures 6.6–6.10).

<table>
<thead>
<tr>
<th>Numerical</th>
<th>Mechanical properties</th>
<th>Geometry</th>
<th>Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma^{\max}$ (GPa)</td>
<td>$\Delta \sigma$ (MPa)</td>
<td>$X_{m}^l$ (GPa)</td>
<td>$\text{CoV}_m^l$ (%)</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>4.5</td>
<td>25</td>
</tr>
</tbody>
</table>
Hierarchical scaling law for the strength of composite fibre bundles

(a) Predicted bundle strength distributions (for several levels $i$).

(b) Bundle strength size effect: present model vs. [195].

(c) Weibull plot for predicted bundle strength distributions (several levels $i$).

(d) Asymptotic behaviour in Weibull plots (region from plot (c) highlighted).

**Figure 6.5:** Overview of model results.

The Weibull plot in Figure 6.5(c) shows a concave–down curvature for all $i > 0$; this curvature initially increases for small bundles, but is progressively reduced for larger bundles within a $0.01 – 99.99\%$ probability range. Figure 6.5(d) highlights the asymptotic behaviour of bundle strength distributions (Equations 6.17 for LTAs and 6.16 for RTAs); as bundle level increases, these asymptotes are valid for progressively more reduced tails. Such behaviour is common to other FBMs [184].

6.3.2 Convergence study

The numerical implementation of the model (Section 6.2.6) is validated in Figure 6.6 by studying the convergence of the CoV of strength distributions (sensitive to both mean value and tails) when $\Delta \sigma \to 0$ and $\sigma_{\text{max}} \to \infty$. The effect of using RTAs (Equation 6.18)
in the formulation is noticeable in Figure 6.6(b), the asymptotic relation is activated for $\sigma^\infty > \sigma^{\text{max}}/k$, thus resulting in very large errors when $\sigma^{\text{max}}$ is too small for the asymptote to be applicable. Nevertheless, a fully converged set of strength distributions (from the single fibre to a standard coupon–size FRP) is computed in less than a second.

Figure 6.6: Numerical convergence of the CoV of strength distributions (for several levels $i$). Errors are relative to nominal inputs (Table 6.1), and run times were obtained with an Intel(R) Core(TM)2 Quad CPU @ 2.50 GHz, for $i^{\text{max}} = 20$ ($n[i] \approx 10^6$).

Figure 6.7: Effect of mean single–fibre strength on bundle strength statistics (for several levels $i$).
Hierarchical scaling law for the strength of composite fibre bundles

6.3.3 Parametric study on fibre and matrix properties

The relation between single–fibre and bundle strength statistics is shown in Figures 6.7 and 6.8. Mean bundle strengths increase as fibres become stronger (Figure 6.7), with a directly proportional relation for constant fibre–to–matrix strength ratios. Figure 6.8 shows that, for a deterministic fibre strength, the model predicts no size effects; for a small CoV of single–fibre strength on bundle strength statistics (for several levels $i$).

Figure 6.8: Effect of the CoV of single–fibre strength on bundle strength statistics (for several levels $i$).

(a) Mean bundle strength.

(b) Bundle strength CoV.

Figure 6.9: Bundle strength size effect for several shear–lag strengths ($\tau_{SL}$), and comparison with Newman and Gabrielov’s model [195] and WLT.

(a) Mean bundle strength.

(b) Bundle strength CoV.
Figure 6.9 shows that increasing the strength of the matrix / interface strengthens the bundles and reduces strength variability. For very low $\tau_{\text{SL}}$ values, bundle strength decreases monotonically with bundle level; as the shear–lag strength becomes negligible ($\tau_{\text{SL}} \to 0$), the model converges to the WLT (Equation 6.2).

6.3.4 Asymptotic limits

Varying the stress concentrations factor $k$ (Figure 6.10) shows the model is bounded by the WLT for $k \to \infty$. For $k = 1$, a Strongest Link Theory (SLT) applies (a level–$[i+1]$ bundle fails within $l_{[i]}^{[i+1]}$ only if no level–$[i]$ bundle survives).

Figure 6.11 compares bundle strengths obtained by either (i) running the full model for all bundle levels $i$, or (ii) running the model up to level $i^{\text{WLT}}$ followed by the WLT for levels $i > i^{\text{WLT}}$ (Equation 6.1 with $n = 2^{i-i^{\text{WLT}}}$). Although the WLT applied directly to single–fibre ($i^{\text{WLT}} = 0$) is extremely inaccurate, both approaches converge if applied from a certain bundle level onwards (in this case, for $i^{\text{WLT}} \gtrsim 5$).

6.3.5 Validation against experimental results

6.3.5.1 Micro–composites

Figure 6.12 validates the model against the experiments from [169] and [179] on micro–composites, combining different carbon fibres, epoxy matrices and bundle geometries.

![Graph](a) Mean bundle strength. (b) Bundle strength CoV.

**Figure 6.10:** Bundle strength size effect for different values of the stress concentrations factor $k$, highlighting the asymptotic limits to the WLT ($k \to \infty$) and to the SLT ($k = 1$).
Hierarchical scaling law for the strength of composite fibre bundles

Figure 6.11: Bundle strength size effect considering a WLT approximation for large bundles.

Note that, for \( r^{\text{WLT}} > 0 \), size effects on the mean strength are not linear in the log-log plot.

Table 6.2: Description of composites for model validation.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Fibre ref. ( \textit{(*)} )</th>
<th>( n[i] )</th>
<th>Matrix ref. ( \textit{(†)} )</th>
<th>( \tau_{\text{SL}} ) (MPa)</th>
<th>( V^* )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(^4)S</td>
<td>A</td>
<td>4</td>
<td>S</td>
<td>46.6(^{\text{§}})</td>
<td>70%</td>
<td>169</td>
</tr>
<tr>
<td>A(^4)F</td>
<td>A</td>
<td>4</td>
<td>F</td>
<td>10.3(^{\text{§}})</td>
<td>70%</td>
<td>169</td>
</tr>
<tr>
<td>I(^7)S</td>
<td>I</td>
<td>7</td>
<td>S</td>
<td>46.6(^{\text{§}})</td>
<td>56%</td>
<td>179</td>
</tr>
<tr>
<td>I(^7)F</td>
<td>I</td>
<td>7</td>
<td>F</td>
<td>10.3(^{\text{§}})</td>
<td>56%</td>
<td>179</td>
</tr>
</tbody>
</table>

\( T^T \) | T | \( 10^4 \text{--} 10^6 \) | T | 52.4 | 60% | 165 |

\( \text{(*)} \) See Table 6.3 for detailed description.

\( \text{†} \) Epoxy resins. Standard (S): DER 331, Dow Plastics; Flexible (F): DER 331 + DER 732 (50:50), Dow Plastics; Toughened (T): 3631, Toray Composites.

\( \text{§} \) Drucker–Prager’s criterion, using tensile and compressive strengths \(^{211}\).

Table 6.3: Carbon–fibre data for model validation.

<table>
<thead>
<tr>
<th>Fibre ref.</th>
<th>Fibre type ( \textit{(*)} )</th>
<th>( \phi_f ) (μm)</th>
<th>( l_r ) (mm)</th>
<th>( m ) ( \textit{(†)} )</th>
<th>( \sigma_0^f ) ( \textit{(†)} ) (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>AS4</td>
<td>6.85</td>
<td>10</td>
<td>4.8</td>
<td>4.493</td>
<td>169</td>
</tr>
<tr>
<td>I</td>
<td>IM6</td>
<td>5.63</td>
<td>10</td>
<td>5.4</td>
<td>5.283</td>
<td>179</td>
</tr>
<tr>
<td>T</td>
<td>T800</td>
<td>5.00</td>
<td>50</td>
<td>3.8</td>
<td>3.570</td>
<td>165</td>
</tr>
</tbody>
</table>

\( \text{(*)} \) AS4 and IM6 fibres provided by Hercules / Hexcel; T800 fibres provided by Toray.

\( \text{†} \) From the respective Reference, originally calculated through the maximum likelihood method.
Materials and input properties are shown in Tables 6.2 and 6.3; single–fibre distributions were fitted as in Figure 6.12. Free–edge effects (configuration QB, Appendix D) and a stress concentration factor $k = 2$ were considered; strength distributions were obtained directly at $i = 2$ for the 4–fibres bundles, and by spline interpolation for the 7–fibres bundles. Each plot presents strength distributions for a fibre type and corresponding bundles (with two different resins); predictions from [195] model are shown for comparison.

### 6.3.5.2 Macro-composites

[165] analysed size effects on the strength of a Toray T800H/3631 (carbon–epoxy) system (Tables 6.2 and 6.3) by testing single fibres of several lengths, as well as 10 mm long bundles with $10^4 – 10^6$ fibres. Figure 6.13 shows the experimentally measured bundle strengths, together with the strength probability map predicted by the model (the input data used can be found in Tables 6.2 and 6.3 and $k = 2$); two shear–lag strengths are considered: one at the nominal value (Figure 6.13(a)), and the other 50% higher (Figure 6.13(b)). Mean bundle strengths predicted by [195] model are shown for comparison.

![Figure 6.12](image-url)

\begin{align*}
\text{(a) AS4 fibre type} & \quad \sigma^\infty \text{ (GPa)} \\
& \quad (m = 6.6, \sigma_0^f = 4.3 \text{ GPa at } l_r = 10 \text{ mm}).
\end{align*}

\begin{align*}
\text{(b) IM6 fibre type} & \quad \sigma^\infty \text{ (GPa)} \\
& \quad (m = 4.6, \sigma_0^f = 5.3 \text{ GPa at } l_r = 10 \text{ mm}).
\end{align*}

**Figure 6.12:** Micro–composite strength distributions: experimental results (data points, [169, 179]), visually fitted single–fibre distribution for model input (thick lines), present model predictions for both resins types (thin lines), and Newman and Gabrielov’s model predictions [195] (dashed lines).
Hierarchical scaling law for the strength of composite fibre bundles

Figure 6.13: Macro-bundle strengths for model validation: experimental bundle strengths (data points, [165]), present model’s probability map (with mean strength highlighted), and [195] mean strength prediction (dashed line in (a)).

6.4 Discussion

6.4.1 Physically meaningful model features and experimental validation

The model captures many characteristic features of size–effects in the strength of FRPs:

a. Size effects result from fibre strength variability: Figure 6.8 shows no size effect for deterministic fibre strength. The WLT governs damage initiation, but propagation is constrained by the matrix / fibre–matrix interface, which limits stress concentrations and coalescence of fibre breaks.

b. Both the magnitude of size effects and the variability of tensile strength decrease with increasing specimen size [159], as shown by the upwards curvature of \( X_{\text{m}}^{[i]}(n^{[i]}) \) and CoV\(^{[i]}(n^{[i]}) \) in Figure 6.5(b) (for \( i \geq 3 \)).

c. The matrix / interface is most important for the micro–scale (\( i \lesssim 3 \)). For most reasonable \( \tau_{\text{SL}} \), small bundles are stronger than single–fibres (Figures 6.9(a) and 6.12(b)). The local geometry influences the strength of small bundles only (Appendix D).

d. Size effects at the macro–scale (\( n^{[i]} \gtrsim 50 \)) are governed by the WLT (Figure 6.11), which is consistent with the quasi-brittle nature of FRPs [159, 165, 180]. A critical fibre break cluster — after which failure is catastrophic — is defined by the bundle...
size at which full model and WLT start converging \( n^{[i]} \approx 50 \) for the nominal inputs in Table 6.1.

e. Within a 0.01 – 99.99\% probability range, predicted large–bundle strength distribution appear quasi-linear in a Weibull plot (Figure 6.5(c), \( i = 15 \)). This agrees with the good fitting usually verified between the Weibull–based WLT and experimental strength distributions and size effects in FRP coupons [159].

f. The model replicates accurately the effect of different fibres and resins on micro–bundle strength distributions (Figure 6.12); this offers a strong support to the shear–lag approach used. The model reproduces the concave–down curvature of bundle strength distributions, the different slopes and locations of the four data sets, and the relative orientations within each pair of data for the same fibre type (converging right tails in Figure 6.12(a), nearly parallel distributions in 6.12(b)).

g. Figure 6.13(b) shows a good agreement between predicted and measured strengths in the macro scale (cross sections up to 30 mm\(^2\), larger than a standard UD FRP tensile–strength specimen, are shown); this implied using a higher shear–lag strength, which is likely to be more representative of the true in-situ matrix behaviour [199,200].

6.4.2 Relation between the present model and others in the literature

6.4.2.1 Weakest link theory

The present formulation differs from the WLT by considering stable modes of bundle failure (sequences of events \( E_2 \) and \( E_3 \) in Section 6.2.3). Consequently, the scaling law (Equation 6.11) degenerates into the WLT (i.e. \( S_{[i]^+}(\sigma^\infty) \rightarrow S_{[i]}(\sigma^\infty)^4 \)) whenever these failure modes cannot take place:

a. Low CoV\(^f\) (Figure 6.8, \( C_K \geq 3 \)) and / or \( k \rightarrow \infty \) (Figure 6.10). Here, the weakest fibre’s neighbour cannot withstand the stress concentrations after first failure;

b. \( \tau_{SL} \rightarrow 0 \) (Figure 6.9). As the scaling law is formulated at the length \( l_{[i]^+} \propto 1/\tau_{SL} \), this case degenerates into a dry (loose) bundle with infinite length under local load sharing, governed by the WLT;

c. Large \( i \) or \( n^{[i]} \) (Figure 6.11). As strength variability decreases with increasing bundle size (Figure 6.5(b)), failure of a sufficiently large sub-bundle immediately triggers failure of its neighbour.
6.4.2.2 Newman and Gabrielov’s model

The present model shows key differences to the one originally developed by Newman and Gabrielov [195] (Equation 6.3):

a. This model considers a shear–lag boundary; this confines stress concentrations around fibre breaks, and defines a characteristic length ($l_i^c$, generally shorter than the original bundle length). Consequently, the present model predicts higher mean bundle strength and lower variability (Figure 6.5(b));

b. As the characteristic length is fundamental for size effects in quasi-brittle materials [171], the present work shows a much better correlation with experiments in FRPs (Figures 6.12 and 6.13) than the original model from Newman and Gabrielov, which was developed for dry fibre bundles;

c. Such characteristic length makes this model consistent with the WLT for length scaling. On the contrary, applying [195] model to bundles of different lengths yields strength distributions which cannot be related by the WLT.

d. For extremely weak matrices, the present model converges not to [195]’s model directly, but to its asymptotic limit for large bundles — the WLT (Figure 6.9). This is again due to using $l_{i+1}^c \propto 1/5\tau_{5L}$ as characteristic length.

e. [195] reduced the order of their scaling law by re-organising the computations. Instead, this was addressed in the present model by using an asymptotic result (Equation 6.18), which would be applicable to the former model as well.

6.4.2.3 Fibre–bundle models

The central aspects relating the present model and other fibre–bundle models in the literature are discussed below:

a. Analytical fibre–bundle models with local load sharing become prohibitively complex for bundles with more than 10 fibres [183]; this has been overcome in the literature through asymptotic simplifications [186, 188, 193] and Monte-Carlo simulations [189, 192]. The present model is made suitable to a complete range of scales (Figure 6.5) by the use of hierarchies and an efficient implementation scheme; still, the typical features of fibre bundle models are captured — namely size effects and the existence of a critical cluster of fibre breaks (Figure 6.11).

b. Several authors [191, 194] recognised that, although their models used a fixed characteristic length, this is not realistic nor accurate; [212] considered the characteristic length to be additive regarding the number of broken fibres, but included no
stress concentrations in their calculations. The present model uses a variable control length \( l^{[i+1]}_c \) (Equation 6.12) that depends on the level of the broken cluster; this is in agreement with experimental observations of self–similar fracture surfaces in FRPs [22,172] (see also Chapter 4).

c. This model uses simple definitions of load transfer and characteristic length (Equation 6.12), as well as a constant stress concentration factor \( k = 2 \) from equilibrium of forces. Other definitions can be explored, namely on the matrix response [190,201], the size of \( l_c \) [187], and magnitude of stress concentrations [205,206,208]. However, these are still unresolved topics in the literature, hence justifying the use of simplified approaches.

### 6.5 Conclusions

An analytical model for size effects on the longitudinal tensile strength of FRP bundles was developed, implemented and validated. The model is based on the stochastic analysis of the failure process in hierarchical fibre bundles, considering Weibull fibre–strength distributions. Matrix effects are represented through a simplified shear–lag model, so that the control length (in which fibre breaks interact) scales hierarchically as well.

The model predicts full strength distributions and statistics for bundles of any size. The matrix (or fibre–matrix interface) was shown to have a significant strengthening effect, which supports the present model over others not including this feature (WLT and Newman and Gabrielov’s model [195]). An efficient numerical scheme was proposed, leading to full–model running times below one second.

The model was validated both at the micro and macro scales, showing a remarkable agreement with experimentally measured bundle strengths in a large range of sizes. The quasi-brittle nature of composites is reproduced; the model also illustrates many experimentally observed trends, such as the tensile strength of FRPs appearing to follow a Weibull distribution, and large–scale size effects consistent with the WLT.

Predictive models for size effects in composite materials are paramount for scaling small–coupon experimental results to the design of large structures. In addition to such quantitative predictions, the present work provides insight on the longitudinal tensile failure process. The model’s ability to compute strength distributions for small bundles (rather than only for asymptotically large ones) makes it particularly suitable for state–of–the–art multiscale discontinuous–fibre composites. Further developments will include predicting the shape of fracture surfaces and the corresponding fracture toughness for FRPs under longitudinal tensile failure.
Chapter 7

An analytical model for the translaminar tensile toughness of fibre composites with stochastic fractal fracture surfaces

7.1 Introduction

The experimental study on toughening mechanisms in recycled composites (Chapter 4) has shown a dramatic size effect on the intrinsic toughness of fibre bundles. Similar findings have been recently reported for virgin laminated CFRPs, which poses a challenge for the design of damage tolerant composite structures [213]. This chapter presents a model for the translaminar tensile toughness of UD FRPs, based on fibre and interfacial properties and assuming the formation of stochastic fractal fracture surfaces.

The translaminar tensile toughness of a UD composite ($G$) is the energy required to fracture the material perpendicularly to the fibre direction (per unit nominal area fractured). This property governs the damage tolerance of structures with load–aligned fibres, as well as the strength of real components with geometric discontinuities.

The translaminar toughening mechanisms of virgin FRPs have been extensively investigated (as reviewed by Kim and Mai [150]), and methods to measure the corresponding fracture toughness have been developed (as recently reviewed by Laffan et al. [213]). All studies concluded that composites are orders of magnitude tougher than their constituents; this is due to the formation of intricate 3D fracture surfaces (Figures 7.1 and 7.2), featuring not only mode–I fibre and matrix fracture, but also large interfacial debonds and pulled–out fibres and bundles [133, 150, 172].
In addition to the inherent complexity arising from a multitude of toughening mechanisms, Laffan et al. [172] have recently reported size effects on the translaminar toughness of virgin FRPs. By blocking the 0° plies together in pairs in cross-ply Compact Tension (CT) specimens, the authors effectively doubled the thickness of the UD layer; the measured translaminar toughness was nearly twice of the value for the baseline configuration, reportedly due to the much larger pull-out features formed in the thicker plies (compare Figures 7.1(a) and 7.1(b)). Subsequent FE simulations of open-hole CFRP specimens [214] proved that such dependence is crucial to replicate experimental results.

In addition, the analysis of toughening mechanisms in recycled FRPs (presented in Chapter 4) suggested similar size effects on the translaminar toughness of fibre bundles. It was concluded that the fracture surface of bundles is hierarchical and statistically self-similar (with individual fibres pulled-out from the surface of small bundles, which are themselves pulled-out from larger bundles, as highlighted in Figure 7.2(a)). Further analysis of fracture surfaces obtained by Laffan et al. [172] showed these features are also characteristic of virgin UD composites (Figure 7.2(b)).

Despite these recent developments, the literature on translaminar fracture toughness of FRPs is still very limited [213]. Most authors agree that interfacial debonding (indicated by the subscript \text{deb}) and pull-out (indicated by the subscript \text{po}) are the main toughening mechanisms of UD composites [150,216–218]; the corresponding contributions (in terms of energy dissipated per fibre, $W_f$, and toughness, $G$) can be

![Figure 7.1: Size effects on the translaminar fracture toughness of UD carbon-epoxy plies (from Laffan et al. [172]).](image)
An analytical model for the translaminar tensile toughness of fibre composites

Figure 7.2: Hierarchical and quasi–fractal features on the translaminar fracture surface of UD composites.

approximated as [150]:

\[
\begin{align*}
W_{\text{deb}}^f &= \pi \cdot \phi^f \cdot G_{\text{SL}} \cdot l_{\text{deb}} \\
W_{\text{po}}^f &= \frac{\pi}{2} \cdot \phi^f \cdot \tau_{\mu} \cdot l_{\text{po}}^2
\end{align*}
\]

\[\Rightarrow G_{\text{deb}} = \frac{4 \cdot V^f \cdot G_{\text{SL}} \cdot l_{\text{deb}}}{\phi^f}; \quad G_{\text{po}} = \frac{2 \cdot V^f \cdot \tau_{\mu} \cdot l_{\text{po}}^2}{\phi^f}.\] (7.1)

In Equation 7.1, \(\phi^f\) is the fibre diameter and \(V^f\) is the fibre volume fraction, while \(l_{\text{deb}}\) and \(l_{\text{po}}\) are the lengths of debonding and pull–out respectively. The debonding component depends on the mode-II in-situ interfacial toughness \(G_{\text{SL}}\), while the pull–out counterpart assumes constant in-situ frictional stresses \(\tau_{\mu}\) [216] (Poisson’s effects could also be included [217], but this would in this case lead to an unjustified increase in complexity).

It is also recognised that fibre strength variability is the driver for pull–out [150]. However, only a few toughness models, such as those by Wells and Beaumont [219] and by Chiang [220], include fibre strength variability; in both cases, this has been achieved by finding the stress field along debonded fibres (with Weibull strength distribution), and subsequently calculating the probability of failure at a distance from the main fracture plane.

In addition to the stochastic analysis of pull–out [218, 219], Wells and Beaumont also considered the presence of debonded and pulled–out bundles on the fracture surface [221]. Their approach is the only attempt in the literature to acknowledge more
than one scale on the fracture surface of FRPs; still, it was restricted to single–fibres
and bundles with known cross–section, with no interaction between the two levels.

The self–similar features illustrated in Figure 7.2 suggest that a fractal approach
may be of interest to the translaminar toughness of FRPs. Carpinteri [175] first intro-
duced the analogy between the fracture surface of heterogeneous materials and invasive
(densifying) fractals; larger structures would therefore develop more hierarchical lev-
els and, consequently, present a higher apparent toughness. This approach has been
applied to theoretical materials [222–226], concrete [227] and particle–reinforced com-
posites [228], but not to FRPs.

In summary, there is a striking lack of analytical models to predict the translaminar
fracture toughness of FRPs and associated size effects. Such models would be useful
not only for the simulation of damage tolerant structures [214, 229–231], but also for
understanding the toughening mechanisms and guiding material development — both
for virgin and recycled composites.

Composite fibre–bundle models have been successfully used to predict the longitu-
dinal strength of UD composites (see Chapter 6 and review by Wisnom [159]). This
approach naturally includes most of the relevant features for translaminar fracture of
FRPs — fibre strength variability, micromechanics and self–similar failure; nevertheless,
its application to the toughness problem has not been attempted so far.

This chapter therefore presents an original model for the translaminar fracture
toughness of FRPs, developed by combining stochastic models for composite bundles,
fracture mechanics and fractal approaches. The model takes into account the works of
debonding and pull–out, as well as the effect of fibre bridging; quasi-fractal fracture
surfaces are assumed, with self–affine features and stochastic debonding and pull–out
lengths (Figure 7.2).

This chapter is organised as follows: Section 7.2 presents the development of an an-
alytical model for predicting the shape of fracture surfaces and associated translaminar
toughness. Section 7.3 explores the model’s results (including parametric studies and
experimental validation), which are later discussed in Section 7.4. Finally, Section 7.5
summarises the main conclusions.
7.2 Model development

7.2.1 Geometry of quasi-fractal surfaces

This model is based on the formation of hierarchical fracture surfaces with pulled–out fibres and bundles organised in quasi-fractal (statistically self-affine) patterns (Figure 7.3). The hierarchy is characterised by the coordination number \( c_G \), so that a level–[1] surface contains \( c_G \) individual fibres (level–[0]), one of which is pulled–out from the co-planar fracture of the remaining \( (c_G - 1) \) neighbours. Similarly, a level–[\( i + 1 \) ] surface is composed by \( c_G \) level–[\( i \)] components, one of them protruding from the reference fracture plane.
The number of fibres \((n[i])\) in a level–[i] fracture surface or bundle is therefore:

\[ n[i] = (cG)^i \quad \iff \quad i = \log_{cG} n[i]. \]  

(7.2)

Figure 7.3(a) illustrates a fracture surface with hexagonal fibre arrangement and co-

ordination number \(cG = 7\), while Figure 7.3(b) assumes a quadrangular configuration

with \(cG = 9\). The perimeter \(C[i]\) of a level–[i] bundle has been defined in Appendix D

considering several fibre arrangements and failure paths.

The pull–out length of each level–[i] bundle, \(L[i]_{po}\), is a stochastic variable; its Cumu-

lative Distribution Function (CDF) and complementary CDF (cCDF) are respectively:

\[ F[i]_{po}(l[i]_{po}) = \Pr(L[i]_{po} \leq l[i]_{po}) \quad \text{and} \quad S[i]_{po}(l[i]_{po}) = \Pr(L[i]_{po} > l[i]_{po}). \]  

(7.3a)

Each level–[i] pulled–out bundle debonds (splits longitudinally) from the surrounding

composite; the corresponding debonding length, \(L[i]_{deb}\) is also a stochastic variable, with:

\[ F[i]_{deb}(l[i]_{deb}) = \Pr(L[i]_{deb} \leq l[i]_{deb}) \quad \text{and} \quad S[i]_{deb}(l[i]_{deb}) = \Pr(L[i]_{deb} > l[i]_{deb}). \]  

(7.3b)

Debonding and pull–out length distributions will be defined in the next sections.

7.2.2 Formation of quasi–fractal surfaces

7.2.2.1 Hierarchical failure process

The stochastic distributions of debonding and pull–out lengths will be determined

considering the hierarchical failure process illustrated in Figure 7.3 defined by the

following assumptions:

\[ A(i) \text{ Fracture propagates down (e.g. inwards) the hierarchy of a fractal surface. This} \]

\[ \text{agrees with experimental evidence of failure being triggered at free surfaces or dis-} \]

\[ \text{continuities; for instance, in cross–ply CT specimens, failure starts at the 0°/90°} \]

\[ \text{interface and propagates inwards to the 0° plies [133172].} \]

\[ A(ii) \text{ Fracture occurs discretely at each fractal level: all level–[i] breaks occur simul-} \]

\[ \text{taneously, after failure of level [i + 1] and before failure of level [i – 1].} \]

\[ A(iii) \text{ Immediately after level–[i + 1] failure, the two fracture faces remain bridged by} \]

\[ \text{all the lower hierarchical levels ([0] to [i]), which share the remote load equally.} \]

\[ A(iv) \text{ A level–[i] pulled–out bundle is locally stronger than their neighbours; it fails} \]

\[ \text{therefore later and away from the surrounding fracture plane (at a distance} \]

\[ L[i]_{po}, \text{ after debonding bi–laterally along a length} L[i]_{deb}. \]
(a) Before failure onset.  
(b) Level–[3] failure.  
(c) Level–[2] failure.  
(d) Level–[1] failure.  
(e) Level–[0] failure.  
(f) Complete failure.

**Figure 7.4:** Hierarchical propagation of failure (top view, $c_G = 7$). Key: white circles — bridging (surviving) fibres; black circles — fibres undergoing failure; coloured circles — broken fibres.

(a) Geometry.  
(b) Stress fields.

**Figure 7.5:** Axi-symmetric model for level–$[i]$ failure.

131
7.2.2.2 Stress fields during failure

Consider now an axi-symmetric model of a level–[i] bundle (superscript A) surrounded by \(c_g - 1\) partially–broken neighbours (superscript B), under the remote longitudinal tensile stress \(\sigma^\infty\) (Figure 7.5(a)). Following assumption A(iii), all bridging fibres will be under the same stress concentration factor \(k_G^i\) at the level–[i + 1] fracture plane \((x = 0)\); this is calculated in Appendix H as:

\[
k_G^i = \frac{1}{1 - \left(1 - \frac{1}{c_g}\right)^{i+1}}, \quad \text{hence} \quad \begin{cases} k_G^0 = c_g \\ \lim_{i \to \infty} k_G^i = 1 \end{cases} .
\]

(7.4)

Consequently, the average stresses transmitted by bundles A and B at \(x = 0\) are:

\[
\sigma_A^0 = k_G^i \cdot \sigma^\infty \quad \text{and} \quad \sigma_B^0 = \frac{c_g - k_G^i}{c_g - 1} \cdot \sigma^\infty .
\]

(7.5)

Such stress mismatch triggers a longitudinal debond at the interface between A and B, growing symmetrically from the fracture plane up to a distance \(|x| = a\) (Figure 7.5(b)). Within the debonded region, stresses are transferred through a shear–lag mechanism with constant frictional stresses \(\tau_\mu\) (hence neglecting Poisson’s effects); the remote stress is recovered with a discontinuity at \(x = a\), thus assuming a very small damage process zone (compared to the debonded distance). The longitudinal stress fields are therefore:

\[
\sigma_A(x) = \begin{cases} k_G^i \cdot \sigma^\infty - \lambda_\mu^i \cdot x, & x \leq a \\ \sigma^\infty, & x > a \end{cases} , \quad \sigma_B(x) = \begin{cases} \frac{(c_g - k_G^i) \cdot \sigma^\infty - \lambda_\mu^i \cdot x}{c_g - 1}, & x \leq a \\ \sigma^\infty, & x > a \end{cases} ,
\]

(7.6)

where

\[
\lambda_\mu^i = \tau_\mu \cdot \frac{C^i}{A^i} .
\]

(7.7)

Imposing balance between the system’s energy release rate and the in-situ mode–II debonding toughness \(G_{SL}\), it is demonstrated in Appendix H that, at a given applied stress \(\sigma^\infty\), the level–[i] equilibrium debonding distance \(a^i\) is:

\[
a^i(\sigma^\infty) = \begin{cases} 0, & \sigma^\infty \leq \sqrt{\frac{\psi^i_a}{\kappa^i_a}} \\ \frac{(c_g - 1) \cdot \sigma^\infty - \sqrt{\left[(c_g - k_G^i) \cdot \sigma^\infty\right]^2 + \psi^i_a}}{\lambda_\mu^i} , & \sigma^\infty > \sqrt{\frac{\psi^i_a}{\kappa^i_a}} \end{cases} ,
\]

(7.8)

\[
\psi^i_a = \frac{2 \cdot (c_g - 1) \cdot E^i \cdot G_{SL} \cdot C^i}{c_g \cdot A^i} \quad \text{and} \quad \kappa^i_a = (k_G^i - 1) \cdot (2 \cdot c_g - k_G^i - 1),
\]

132
An analytical model for the translaminar tensile toughness of fibre composites

It must be noticed that both $G_{SL}$ and $\tau_\mu$ are in-situ properties. Methods to estimate their value based on measurable properties — respectively mode–II delamination toughness ($G_{IIc}$) and single–fibre composite interfacial friction ($\tau_\mu$) — are derived in Appendices I and II.

7.2.2.3 Sequence of events for level–[i] failure

Let $X^{[i]}_{\text{deb}}$ be the stochastic strength of a level–[i] bundle within the debonded length, so that failure occurs at the remote stress $\sigma^\infty$ within $x^{[i]} \in [-a^{[i]}(\sigma^\infty), +a^{[i]}(\sigma^\infty)]$ if and only if $\sigma^\infty = X^{[i]}_{\text{deb}}$. In order to ensure the stress fields in Figure 7.5 remain valid, two possible sequences of events leading to debonding, failure and pull–out of a level–[i] bundle are considered:

$E_1$: Debonding followed by bundle fracture. The bundle fractures at a remote stress $\sigma^\infty = X^{[i]}_{\text{deb}}$, at a stochastic location $|x| = L^{[i]}_{\text{po}}$ within the debonded length ($L^{[i]}_{\text{po}} < a^{[i]}(X^{[i]}_{\text{deb}})$). This neglects the influence of breaks formed away from the level–[i + 1] fracture plane on the stress field in the debonded region.

$E_2$: Bundle fracture followed by debonding. The bundle fractures at a remote stress $\sigma^\infty < X^{[i]}_{\text{deb}}$ outside the debonded length (at a location $|x| = L^{[i]}_{\text{po}} > a^{[i]}(\sigma^\infty)$), but the stresses are locally recovered (and the field near the level–[i + 1] fracture plane is not significantly disturbed). Failure becomes effective as the remote stress increases to $\sigma^\infty = X^{[i]}_{\text{deb}}$, and the debond reaches the location of fracture ($a^{[i]}(\sigma^\infty) = L^{[i]}_{\text{po}}$).

In both cases, the realisations of debonding and pull–out lengths (see Figure 7.6) are:

$$L^{[i]}_{\text{deb}} = 2 \cdot a^{[i]}(X^{[i]}_{\text{deb}}) \quad \text{and} \quad L^{[i]}_{\text{po}} \leq a^{[i]}(X^{[i]}_{\text{deb}}) \quad \implies \quad L^{[i]}_{\text{po}} \leq \frac{L^{[i]}_{\text{deb}}}{2}. \quad (7.9)$$

7.2.3 Determination of debonding and pull–out length distributions

7.2.3.1 Debonding length distribution

The unequivocal relation between realisations of level–[i] debonding length and level–[i] bundle strength (Equation 7.9) implies that the probability distributions of both variables coincide; consequently,

$$S^{[i]}_{\text{deb}}(l^{[i]}_{\text{deb}}) = \Pr(L^{[i]}_{\text{deb}} > l^{[i]}_{\text{deb}}) = \Pr(X^{[i]}_{\text{deb}} > \sigma^\infty), \quad \text{with} \quad l^{[i]}_{\text{deb}} = 2 \cdot a^{[i]}(\sigma^\infty). \quad (7.10)$$
Chapter 7

Each distribution \( S^{[i]}_{\text{deb}}(l^{[i]}_{\text{deb}}) \) is thus related to the bundle strength distribution for the corresponding fractal level. Therefore, consider that the size-dependent survival probability of a level-\([i]\) bundle of length \( l_{\tau} \) under uniform stresses \( \sigma^{\infty} \) is known and represented as \( S^{[i]}_{\text{deb}}(\sigma^{\infty}) \); this can be promptly obtained through the strength model developed in Chapter 6. To account for the non-uniform stress field within the debonded region (Figure 7.6(a)), it is convenient to define the strength distribution under a bilateral triangular field with peak stress \( \sigma^{\max} \) and constant slope \( \lambda^{[i]}_{\mu} \) (Figure 7.6(c)), hereby represented as \( S^{[i]}_{\lambda_{\mu}}(\sigma^{\max}) \). This can be calculated by extending the WLT to non-uniform stresses; following the derivation in Appendix E:

\[
\ln \left[ S^{[i]}_{\lambda_{\mu}}(\sigma^{\max}) \right] = \frac{2}{\lambda^{[i]}} \cdot \int_{\sigma=0}^{\sigma^{\max}} \ln \left[ S^{[i]}_{\sigma_{0}^{\text{deb}}}(\sigma) \right] d\sigma. \tag{7.11}
\]

Combining this definition with the stress field in Figure 7.6(a), the debonding length distribution is:

\[
S^{[i]}_{\text{deb}}(l^{[i]}_{\text{deb}}) = \frac{S^{[i]}_{\lambda_{\mu}}(\sigma^{[i]}_{0}(\sigma^{\infty}))}{S^{[i]}_{\lambda_{\mu}}(\sigma^{[i]}_{\lambda_{\mu}}(\sigma^{\infty}))} = \exp \left( \ln \left[ S^{[i]}_{\lambda_{\mu}}(\sigma^{[i]}_{0}(\sigma^{\infty})) \right] - \ln \left[ S^{[i]}_{\lambda_{\mu}}(\sigma^{[i]}_{\lambda_{\mu}}(\sigma^{\infty})) \right] \right), \tag{7.12}
\]

where the relevant stress points are (from Equation 7.6):

\[
\begin{cases}
\sigma^{[i]}_{0}(\sigma^{\infty}) = k^{[i]}_{0} \cdot \sigma^{\infty}
\sigma^{[i]}_{\lambda_{\mu}}(\sigma^{\infty}) = k^{[i]}_{0} \cdot \sigma^{\infty} - \lambda^{[i]}_{\mu} \cdot \sigma^{\infty} = (1 - c_{G} + k^{[i]}_{0}) \cdot \sigma^{\infty} + \sqrt{[(c_{G} - k^{[i]}_{0}) \cdot \sigma^{\infty}]^{2} + \psi^{[i]}_{\lambda_{\mu}}}. \tag{7.13}
\end{cases}
\]

Figure 7.6: Locations of failure for length distributions.
7.2.3.2 Pull–out length distribution

To define the level–[i] pull–out length distribution, consider Figure 7.6(b) where:

\[
\sigma_{po}^{[i]}(\sigma^\infty, l_{po}^{[i]}) = \frac{7.6}{k_G} \cdot \sigma^\infty - \lambda_{\mu}^{[i]} \cdot l_{po}^{[i]} .
\]  

(7.14)

Let \( S_l^{[i]}(\sigma^\infty, l_{po}^{[i]}) \) be the bundle survival probability in Region I, and \( F_l^{[i]}(\sigma^\infty, l_{po}^{[i]}) \) be the bundle failure probability in Region II. According to Figure 7.6(b), the pull–out length distribution for a given strength \( X_{deb}^{[i]} = \sigma^\infty \) is:

\[
\Pr(X_{deb}^{[i]} = \sigma^\infty \land L_{po}^{[i]} \geq l_{po}^{[i]}) = S_l^{[i]}(\sigma^\infty, l_{po}^{[i]}).d[l_{po}^{[i]}] , \quad \forall a^{[i]}(\sigma^\infty) \geq l_{po}^{[i]} .
\]  

(7.15)

Integrating Equation (7.15) for all valid debonded distances \( a^{[i]} \), the pull–out length distribution comes as:

\[
S_{po}^{[i]}(l_{po}^{[i]}) = \Pr(L_{po}^{[i]} > l_{po}^{[i]}) = \int_{a^{[i]}(\sigma^\infty)=l_{po}^{[i]}}^\infty \Pr(X_{deb}^{[i]} = \sigma^\infty \land L_{po}^{[i]} \geq l_{po}^{[i]}) .
\]  

(7.16a)

After some mathematical manipulation (see Appendix [K]), this results in:

\[
S_{po}^{[i]}(l_{po}^{[i]}) = 2 \cdot \frac{2}{\lambda_{\mu}^{[i]} \cdot l_\lambda} . \int_{\sigma^\infty = \sigma_{min}}^\infty \sigma_{deb}^{[i]}(\sigma^\infty) . \left( \frac{d\sigma_{a}^{[i]}}{d\sigma^\infty} \cdot \ln \left[ S_{U,x}(\sigma_{a}^{[i]}) - k_G^{[i]} \cdot \ln \left[ S_{U,x}(\sigma_{po}^{[i]}) \right] \right] \right) . d\sigma^\infty ,
\]

where

\[
\begin{align*}
\sigma_{a}^{[i]} &= \sigma_a(\sigma^\infty) \quad \text{ (as defined in Equation 7.13)}, \\
\sigma_{po}^{[i]} &= \sigma_{po}^{[i]}(\sigma^\infty, l_{po}^{[i]}) \quad \text{ (as defined in Equation 7.14)}, \\
\frac{d\sigma_{a}^{[i]}}{d\sigma^\infty} &= \frac{d\sigma_{a}^{[i]}}{d\sigma^\infty}(\sigma^\infty) = 1 - c_G + k_G^{[i]} + \frac{(c_G - k_G^{[i]})^2 \cdot \sigma^\infty}{\sqrt{[(c_G - k_G^{[i]}) \cdot \sigma^\infty]^2 + \psi_{a}^{[i]}}}, \\
\sigma_{min} &= \sigma_{min}^{[i]}(l_{po}^{[i]}) = \frac{\lambda_{\mu}^{[i]} \cdot l_{po}^{[i]}}{\kappa_{\alpha}^{[i]}}, \quad 
\left( c_G - 1 + \frac{c_G - k_G^{[i]}}{\sqrt{(\lambda_{\mu}^{[i]} \cdot l_{po}^{[i]})^2 + \psi_{a}^{[i]}}} \right) .
\end{align*}
\]  

(7.16b)

7.2.3.3 Extreme value length distributions for quasi–fractal surfaces

The quasi-fractal configuration of fracture surfaces (Figure 7.3 and Section 7.2.1) assumes that, for each level [i], only one out of \( c_G \) bundles debonds and pulls–out significantly, while the remaining \( (c_G - 1) \) neighbours present negligible (i.e. much smaller) features. Therefore, the best estimates of debonding and pull–out lengths for the protruded bundles in the idealised fracture surfaces are not the expected distributions (as calculated in Equations 7.12 and 7.16) represented by printscript or block letters e.g. \( L, F, S \), but their extreme value distributions (as previously defined in Equation 7.3, rep-
Chapter 7

represented by cursive or joined-up letters e.g. \( L, F, S \). Mathematically, if \( j \) corresponds to each level–\([i]\) bundle within a level–\([i+1]\) surface,

\[
L_{\text{deb}}^{[i]} = \max \{ L_{\text{deb}}^{[i],j} \} \quad \text{and} \quad L_{\text{po}}^{[i]} = \max \{ L_{\text{po}}^{[i],j} \}, \quad \forall j \in \{1, \cdots, c_G\}. \tag{7.17}
\]

Consequently, and according to the probability distributions defined in Equations 7.3, 7.12 and 7.16, the CDFs of level–\([i]\) debonding and pull–out lengths in a quasi-fractal fracture surface are:

\[
F_{\text{deb}}^{[i]}(l_{\text{deb}}) = \left[ 1 - S_{\text{deb}}^{[i]}(l_{\text{deb}}) \right]^{c_G} \quad \text{and} \quad F_{\text{po}}^{[i]}(l_{\text{po}}) = \left[ 1 - S_{\text{po}}^{[i]}(l_{\text{po}}) \right]^{c_G}. \tag{7.18}
\]

7.2.4 Fracture toughness of quasi-fractal surfaces

The fracture toughness of UD composite bundles can now be calculated as the energy dissipated in the formation of quasi-fractal fracture surfaces as shown in Figure 7.3. This considers explicitly the contributions of (i) fibre–matrix debonding and matrix fracture, and (ii) friction during fibre and bundle pull–out (neglecting Poisson’s effects); for each level–\([i]\) bundle debonded and pulled–out, the mean values for energy dissipated are \([150]\):

\[
W_{\text{deb}}^{[i]} = C^{[i]} \cdot G_{\text{SL}} \cdot L_{\text{deb},m}^{[i]} \quad \text{and} \quad W_{\text{po}}^{[i]} = \frac{1}{2} C^{[i]} \cdot \tau_{m} \cdot \left[ \left( L_{\text{po}}^{[i]} \right)^2 \right]_{m}, \tag{7.19}
\]

where \( G_{\text{SL}} \) and \( \tau_{m} \) are in-situ properties (Appendices I and J). The subscript \( m \) represents the mean value: \( \left( L_{\text{po}}^{[i]} \right)^2 \) \( m \) = \( (L_{\text{po},m}^{[i]})^2 \) \( \cdot \left[ 1 + (\text{CoV}_{L_{\text{po}}^{[i]}})^2 \right] \), being CoV the Coefficient of Variance.

The fractal arrangement of fracture surface features implies that one level–\([i]\) bundle will debond and pull–out from each level–\([i+1]\) bundle. The toughness components associated with each level are therefore:

\[
g_{\text{deb}}^{[i]} = \frac{W_{\text{deb}}^{[i]}}{c_G \cdot A^{[i]} / V_f} \quad \text{and} \quad g_{\text{po}}^{[i]} = \frac{W_{\text{po}}^{[i]}}{c_G \cdot A^{[i]} / V_f}, \quad \text{with} \quad g^{[i]} = g_{\text{deb}}^{[i]} + g_{\text{po}}^{[i]}. \tag{7.20}
\]

The (expected) total toughness \( G \) is additive both regarding all fractal levels formed (from \( i = 0 \) to \( i = i^{\max} \)) and the debonding and pull–out components,

\[
G^{[i^{\max}]} = \sum_{i=0}^{i^{\max}} g^{[i]} = G_{\text{deb}}^{[i^{\max}]} + G_{\text{po}}^{[i^{\max}]} \quad \text{with} \quad G_{\text{deb}}^{[i^{\max}]} = \sum_{i=0}^{i^{\max}} g_{\text{deb}}^{[i]} \quad \text{and} \quad G_{\text{po}}^{[i^{\max}]} = \sum_{i=0}^{i^{\max}} g_{\text{po}}^{[i]}.
\tag{7.21}
\]

The number of fractal levels formed in a fracture surface \( i^{\max} \) can be calculated depending on the filament count \( n^{[i]} \) of the surface (Equation 7.2) and its configuration.
An analytical model for the translaminar tensile toughness of fibre composites

Table 7.1: Number of fractal levels \( i_{\text{max}} \) for difference types of fracture surface.

<table>
<thead>
<tr>
<th>Type of surface</th>
<th>Filament count</th>
<th>( i_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated bundle(^{(\star)})</td>
<td>( n_{\text{max}} ) fibres in the cross-section</td>
<td>( \log_{c_{G}} n_{\text{max}} - 1 )</td>
</tr>
<tr>
<td>Embedded bundle(^{(\dagger)})</td>
<td>( n_{\text{max}} ) fibres in the cross-section</td>
<td>( \log_{c_{G}} n_{\text{max}} )</td>
</tr>
<tr>
<td>Embedded UD ply(^{(\dagger)})</td>
<td>( \sqrt{n_{\text{max}}} ) fibres across the thickness</td>
<td>( \log_{c_{G}} n_{\text{max}} )</td>
</tr>
</tbody>
</table>

\(^{(\star)}\) No debonding or pull–out can occur at level–\(i_{\text{max}}\).

\(^{(\dagger)}\) Accounts for level–\(i_{\text{max}}\) debonding and pull–out, as reported for CT specimens 133, 172.
I. Definition of input variables

I.1: Numerical
\{Δσ, n_u, ε_p\}

I.2: Fibre properties
\{l_r, σ_f^0, m, E^f\}

I.3: Interface properties
\{τ_u, G_m\} or \{τ_f^0, G_p\}

I.4: Composite properties
\{V_f, φ_f, n_{max}, c_f\}

I.5: Bundle stresses and strengths
\[S_{U\ell}^{(i)} = \left(\sigma_{U\ell}^{(i)}(σ)\right)\] where \(σ = (j-1)Δσ\) and \(i_k = \{0, \ldots, n_{max}\}\), \(n_{X}(0) = n_{max}\)

II. Preliminary calculations

II.1: Bundle geometry
\[A^f = \frac{(φ_f^2)}{4}\]
\[l^i = n_k \cdot A^f\]
\[C^f = ϕ_f\]

\[s_{mn} = \left(\frac{\sqrt{2}}{2}\right) - 1 \cdot φ_f\]

\[C^{(i)} = 3 \cdot C^f + 4 \cdot \left[\sqrt{(n_k - 1)} \cdot s_{mn} + (\sqrt{n_k - 2}) \cdot \frac{C^f}{σ}ight]\]

II.2: Strength distributions
\[lnS_{U\ell}^{(i)} = ln\left(S_{U\ell}^{(i)}\right)\]
\[lnS_{L\ell}^{(i)} = \frac{1}{σ} \int S_{U\ell}^{(i)} \cdot Δσ\]

IV. Fracture toughnesses at fractal levels

IV.1: Level 0
\[n_{X}^{\left[i\ell\right]} = 1\]

\[C_{deb}^{(i)} = C_{deb}^{(i)} + C_{deb}^{(i)}\]

IV.2: Fractal levels
\[n_{X}^{\left[i\ell\right]} = \log_{2}\left(k_{max}\right)\]

\[C_{deb}^{(i)} = (c_{f}^{i})^{2}\]

\[C_{deb}^{(i)} = \frac{2 \cdot (c_{f}^{i})^{2} \cdot C_{deb}^{(i)}}{c_{f}^{i} \cdot A^{f} / V_{f}^{2}}\]

Figure 7.7: Numerical implementation. Level superscripts \([i\ell]\) or \([i\ell]\) are omitted for all internal variables.


In the present case, bundle survival distributions \( S_{u}[iX](\sigma) \) are calculated using the previously developed strength model for hierarchical fibre bundles (although any other set of size–dependent distributions could be used); because this assumes a coordination number of 2, the correspondence between filament count, strength–levels and toughness–levels is given by:

\[
 n_{iX}^{[i]} = 2^{iX} \quad \Rightarrow \quad i_{X} = i_{G} \cdot \log_{2}(c_{G}). \tag{7.22}
\]

### 7.3 Results

#### 7.3.1 Analysis of model predictions

Figure 7.8 presents an overview on the results of the toughness model, considering the nominal inputs given in Table 7.2. All hierarchical levels \([i]\) correspond to toughness levels, thus with \( n_{i}^{[i]} = (c_{G})^{i_{G}} \).

Bundle strength distributions (obtained through the strength model presented in Chapter 6) are shown in Figure 7.8(a). Size effects are evident in Figure 7.8(b) as the toughness increases considerably with filament count. The relative contributions of debonding and pull–out components is also affected: the former dominates in thinner bundles, but the latter progressively gains importance as size increases.

Larger bundles are toughened by the presence of more levels in their fracture surface, each making a positive contribution (\( g_{[i]} \) in Figure 7.8(c)) to the overall toughness. Nevertheless, this contribution becomes progressively smaller for very large bundles (see for instance \( g_{[i]}^{\text{deb}} \) decreasing for \( i > 4 \) in Figure 7.8(c)).

Figure 7.8(d) presents the mean value of debonding and pull–out lengths for each fractal level. Their stochastic distributions are shown in Figures 7.8(e) and 7.8(f), as functions of the corresponding aspect ratios (relative to the equivalent bundle thickness.

#### Table 7.2: Nominal model inputs for parametric studies (nominal outputs will be highlighted as \( \diamond \) in the parametric study, Figures 7.9–7.14).

<table>
<thead>
<tr>
<th>Numerical</th>
<th>Fibre</th>
<th>Interface</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{\sigma} )</td>
<td>( \Delta \sigma )</td>
<td>( \tau_{po} )</td>
<td>( l_{r} )</td>
</tr>
<tr>
<td>((10^3))</td>
<td>(MPa)</td>
<td>(−)</td>
<td>(mm)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>( 10^{-8} )</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^{(i)}\) Corresponding to \( \sigma_{C}^{B} = 4.93 \) GPa and \( m = 4.54 \).  
\(^{(1)}\) Interfacial shear strength (for strength model).
(a) Bundle strength distributions ($L_r = 10$ mm).

(b) Size effect on the fracture toughness.

(c) Toughness contribution from each bundle level.

(d) Size effect on average debonding and pull–out lengths.

(e) Debonding aspect ratio distributions (for several approximate bundle levels $i$).

(f) Pull–out aspect ratio distributions (for several approximate bundle levels $i$).

Figure 7.8: Overview of model results.
An analytical model for the translaminar tensile toughness of fibre composites

\[ t[i]: \]

\[ \alpha[i]_{\text{deb}} = \frac{t[i]_{\text{deb}}}{t[i]} \quad \text{and} \quad \alpha[i]_{\text{po}} = \frac{t[i]_{\text{po}}}{t[i]}, \quad \text{with} \quad t[i] = \sqrt{\frac{A[i]}{V_f}}. \tag{7.23} \]

### 7.3.2 Convergence study

Figure 7.9 shows that calculated fracture toughnesses converge for \( \Delta \sigma \to 0 \) and \( \epsilon_{\text{po}} \to 0 \), thus validating the numerical implementation proposed in Section 7.2.5. Numerical errors are higher for the lower levels; nevertheless, due to their minor contribution for the toughness of larger bundles, this vanishes upwards in the hierarchy. Converged sets of toughnesses and debonding and pull–out length distributions are computed in less than one minute.

### 7.3.3 Parametric study

The relation between single–fibre strength statistics and expected fracture toughneses is shown in Figures 7.10 and 7.11. Stronger fibres lead to tougher composites (Figure 7.10), both in terms of debonding and pull–out contributions. The effect of fibre strength variability (Figure 7.11) is more complex: as \( \text{CoV}_X \) decreases from large values, so do the toughnesses of all hierarchical levels; however, this relation becomes non-monotonic for relatively low variability on fibre strength, and both components

![Figure 7.9](image.png)

**Figure 7.9:** Numerical convergence study (for several fractal levels \( i \)). Errors are relative to nominal inputs (Table 7.2), and run times were obtained with an Intel(R) Core(TM)2 QUAD CPU @ 2.50 GHz.
reach deterministic limits as $\text{CoV}_f^X \to 0$:

\[
\begin{align*}
G_{\text{deb}}^{[\text{max}]}(\text{CoV}_f^X = 0) &= \sum_{i=0}^{i_{\text{max}}} c_f A[i] \frac{a[i]}{G_f} \left( X_m^f / k[i] \right) \\
G_{\text{po}}^{[\text{max}]}(\text{CoV}_f^X = 0) &= 0.
\end{align*}
\]

(7.24)

Figures 7.12 and 7.13 evaluate the effect of fibre–matrix interfacial properties on the toughness of bundles. The energy dissipated by debonding becomes negligible for very brittle interfaces; however, as the interfacial toughness increases, debonding growth is

\begin{figure}
\centering
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{debonding_component}
\caption{Debonding component.}
\end{subfigure}
\hspace{0.05\textwidth}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{pull_out_component}
\caption{Pull–out component.}
\end{subfigure}
\caption{Effect of mean single–fibre strength on the expected fracture toughness (for several levels $i$).}
\end{figure}

\begin{figure}
\centering
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{debonding_coef_var}
\caption{Debonding component.}
\end{subfigure}
\hspace{0.05\textwidth}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{pull_out_coef_var}
\caption{Pull–out component.}
\end{subfigure}
\caption{Effect of the fibre–strength CoV on the expected fracture toughness (for several levels $i$).}
\end{figure}
inhibited ($G_{\text{SL}} \to \infty$ in Equation 7.8) and both toughness components progressively vanish (Figure 7.12). Similarly, very large frictional stresses reduce the energy dissipated by debonding ($\lambda_{\mu}^{(i)} \to \infty$ in Equation 7.8, Figure 7.13(a)); the effect of friction on the pull–out toughness (Figure 7.13(b)) depends on the bundle level considered.

The influence of the assumed coordination number on the resulting fracture toughness is shown in Figure 7.14. For relatively large coordination numbers ($c_G \gtrsim 6$), such effect is very small; however, as $c_G$ decreases to lower values, the fracture toughness is reduced as well.

**Figure 7.12:** Effect of interfacial toughness (in-situ, $G_{\text{SL}}$, or mode–II delamination $G_{\text{IIc}}$) on the expected fracture toughness (for several levels $i$).

**Figure 7.13:** Effect of the friction coefficient (in-situ, $\tau_\mu$, or in SFPO, $\tau_{\mu}^0$) on the expected fracture toughness (for several levels $i$).
7.3.4 Validation against experimental results

Figure 7.15 compares model predictions against literature results for the translaminar fracture toughness of unidirectional CFRP plies, obtained experimentally through compact tension tests [133, 172, 232]. The materials combine different carbon fibres, epoxy matrices and ply thicknesses, as described in Table 7.3.

Model inputs for the validation are shown in Tables 7.3 and 7.4. Single-fibre strength parameters were determined experimentally (Chapter 5); the Weibull modulus $m$ estimated using the average strengths of 10 and 20 mm long fibres.

The strength distributions for each bundle level (required inputs) were calculated through the strength model presented in Chapter 6; for each material system, the average strength measured in standard UD specimens ($\bar{X}_{\text{UD}}$ [229, 233, 234]) was used to calibrate the corresponding shear-lag strength ($\tau_{\text{SL}}$).

7.4 Discussion

7.4.1 Experimental validation

Model results presented in Section 7.3 are largely supported by experimental observations on the toughness of UD composites:

a. The trans laminar fracture toughness of a UD composite increases with the size of the cross section (Figures 7.8(b) and 7.15). This has been directly observed in CT
An analytical model for the translaminar tensile toughness of fibre composites

Table 7.3: Description of composites for model validation.

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Epoxy type</th>
<th>Reference for CT tests</th>
<th>$X_{UD}$ ($^\dagger$) (GPa)</th>
<th>$G_{IIc}$ ($^\dagger$) (kJ/m$^2$)</th>
<th>$\tau_0$ ($^\dagger$) (MPa)</th>
<th>$V^\dagger$ ($^\dagger$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T300</td>
<td>913</td>
<td>Pinho et al. [133]</td>
<td>2.006 [229]</td>
<td>1.10 [229]</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>T300</td>
<td>920</td>
<td>Laffan et al. [172]</td>
<td>1.697 [233]</td>
<td>1.40 [233]</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>

($^\dagger$) Average strength of composite UD specimens (cross section of 1.0 mm $\times$ 15 mm, 138 mm long).
($^\dagger$) Experimental result for mode–II delamination. The corresponding in-situ debonding toughnesses are $G_{II}=\alpha \cdot G_{IIc}$, with $\alpha = 0.683$ for $c_G = 7$ (hexagonal arrangement) and $\alpha = 0.667$ for $c_G = 9$ (quadrangular arrangement).
($^\dagger$) Typical SFPO test result reported in the literature for carbon–epoxy systems [163, 164]. The corresponding in-situ frictional stress at $V^\dagger = 60\%$ is $\tau_\mu = 4.0$ MPa (Appendix J).
($^\dagger$) Nominal value.

Table 7.4: Fibre properties for model validation.

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>$\phi^\dagger$ ($^\dagger$) (µm)</th>
<th>$E_f$ ($^\dagger$) (GPa)</th>
<th>$\sigma_f^0$ ($^\dagger$) (GPa)</th>
<th>$m$ ($^\dagger$) (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T300</td>
<td>155</td>
<td>7.0</td>
<td>230</td>
<td>3.904</td>
</tr>
<tr>
<td>T800</td>
<td>158</td>
<td>5.0</td>
<td>294</td>
<td>5.662</td>
</tr>
</tbody>
</table>

($^\dagger$) Nominal values.
($^\dagger$) Measured through SFTTs (Chapter 5), normalised for the reference length $l_r = 10$ mm.

Figure 7.15: Validation of the fracture toughness model (for hexagonal (QI boundary, $c_G = 7$) and quadrangular (HI boundary, $c_G = 9$) configurations) against experimental results from the literature (averages and standard deviations from Pinho et al. [133], Laffan et al. [172] and Teixeira et al. [232]).
specimens with blocked ply thickness \[172\]; it is also supported by a significant toughening effect observed in rCFRPs due to pull–out and failure of large bundles (Chapter 4).

b. The model predicts the formation of longer debonds and pull–outs as the number of fibres in the fracture surface grows (Figure 7.8(d)). This is corroborated by experimental observations in virgin UD plies (Figure 7.1 [172]) and in discontinuous rCFRPs with different degrees of bundling (Chapter 4).

c. The pull–out aspect ratios of different level–\([i]\) bundles are in the same order of magnitude for several fractal levels (Figure 7.8(f)); therefore, although the model imposes self–affinity only (i.e. anisotropic scaling), it actually predicts nearly self–similar fracture surfaces (i.e. with isotropic scaling). This is supported by experimental evidence, as shown in Figure 7.2.

d. The variability of pull–out lengths is larger than the variability of fibre strength (compare Figures 7.8(a) and 7.8(f)), as observed experimentally in CFRP specimens [218].

e. Composite toughness increases with fibre strength (Figure 7.10); a similar trend is suggested by experiments in carbon–epoxy systems with different fibres [213]. On the contrary, composites with very weak fibres should be brittle and present smooth fracture surfaces; this has been observed experimentally in recycled woven composites with extreme fibre degradation (Chapter 3, Figure 3.11).

f. Model predictions agree well with experimental fracture toughness measurements (Figure 7.15). These validate the ability of the model to cope with different fibre types (T800/M21 vs. T300/913 and T300/920), different matrices (T300/913 vs. T300/920), and different ply thickness (T300/920 at 0.125 mm vs. 0.250 mm).

### 7.4.2 Interpretation of toughening mechanisms

a. The model considers debonding and pull–out as the main toughening mechanisms (Equation 7.21); additionally, it also accounts for fibre bridging (through \(k_{G}^{[i]}\) in Equation 7.4) and for the release of elastic energy during debonding (through \(a_{d}^{[i]}(\sigma_{\infty})\) in Equation 7.8).

b. Each of the sequences of events for level–\([i]\) bundle failure (Section 7.2.2.3) are dominant for different bundle sizes:

- Figure 7.8(d) suggests that small bundles fail through sequence \(E_{2}\): large stress concentrations \((k_{G}^{[i]}\) in Equation 7.4) lead to premature translaminar fracture,
An analytical model for the translaminar tensile toughness of fibre composites

and the load–bearing capacity is lost as soon as a debonding propagates until the failure site (hence $L_{deb,n}^{[i]} \approx 2L_{po,m}^{[i]}$ for $n^{[i]} \lesssim 20$).

- On the contrary, sequence $E_1$ prevails for large–scale bundles, which firstly debond from their neighbours (favoured by a large $A^{[i]} / C^{[i]}$ ratio, Equation 7.8), and then eventually fracture within the debonding length (thus $L_{deb,n}^{[i]} \gg 2L_{po,m}^{[i]}$ for $n^{[i]} \gtrsim 100$ in Figure 7.8(d)).

c. For given interfacial properties, the debonding length is governed by bundle strength (Equation 7.8 and Figure 7.10(a)); below a given threshold (dictated by $\sigma^\infty = \psi^{[i]}_a / \kappa^{[i]}_a$ in Equation 7.8), debonding becomes negligible. This also justifies why the variability of debonding length (Figure 7.8(e)) decreases for large bundles (as does bundle strength, Figure 7.8(a)), and the similar effect of single–fibre strength variability on both $X^{[i]}_m$ (Chapter 6, Figure 6.8(a)) and $G_{deb}^{[i]}$ (Figure 7.11(a)).

d. The pull–out process is governed by the debonding length — which defines an upper bound $l_{po}^{[i]} \leq l_{deb}^{[i]} / 2$ (Equation 7.9 and Figure 7.8(d)) — and bundle strength variability. Figure 7.11(b) shows that composites with deterministic fibre strength would present no pulled–out fibres or bundles. The close link between pull–out length and strength variability is further illustrated by the identical effect that $CoV^{[i]}_X$ has on both $G_{po}^{[i]}$ (Figure 7.11(b)) and $CoV^{[i]}_X$ (Figure 6.8(b) in Chapter 6).

e. The model predicts that the translaminar fracture toughness increases monotonically with the size of the fracture surface (non-negative contributions in Equation 7.21). The contribution of each individual level is maximised for intermediate values of $i$ (note the $g_{deb}^{[i]}$ curve in Figure 7.8(c) and the concave–down toughness curves in Figure 7.15), due to competing mechanisms:

- The debonding component is directly related to the mean debonding aspect ratio $a_{deb}^{[i]}$ (Figure 7.8(c)). As bundle size increases, debonding is initially favoured by the decreasing ratio $C^{[i]} / A^{[i]}$ (Equation 7.8), but later hindered by the progressively smaller stress concentrations ($k_{G}^{[i]}$ in Equation 7.4).

- The pull–out component is mainly influenced by the squared mean pull–out length (Equation 7.19 and Figure 7.8(f)). Consequently, its contribution increases for a larger range of scales than the debonding counterpart; nevertheless, as both the debonding aspect ratio and the bundle strength variability decrease for larger bundles, $g_{po}^{[i]}$ eventually falls as well.

f. The results from the parametric study suggest that the translaminar toughness of UD composites could be greatly improved by increasing mean fibre strength (Figure 7.10) and / or fibre strength variability (Figure 7.11). The effect of interfacial properties is non-monotonic (Figures 7.12 and 7.13), thus the overall toughness is maximised by intermediate values of both $G_{SL}$ and $\tau_H$. 

147
7.4.3 Novel model features and challenging results

The model developed in this chapter offers a novel approach to estimate the translaminar fracture toughness of UD composites, and provides some challenging results open to further validation:

a. The present model is the first attempt in the literature to combine fractal geometries with physically-based toughening mechanisms in UD composites, and offers the first predictions for size effects in translaminar fracture toughness. The experimental validation (Figure 7.15) is extremely encouraging.

b. The hierarchy in fracture surfaces is characterised by the coordination number \( c_G \), which is currently a mathematical parameter. However, \( c_G \) is likely related to physical properties of the constituent materials (e.g. fibre strength variability) and/or fracture surfaces (e.g. the fractal dimension \[222\]).

c. Figure 7.8(b) suggests that the main translaminar toughening mechanism depends not only on material properties, but also on size: debonding dominates for small bundles, but pull-out becomes increasingly important as the filament count grows; at the conventional ply scale (\( t_{\text{ply}} \approx 0.125 \) mm, \( n_{[i]} \approx 2400 – 4800 \)), pull-out and debonding have similar contributions. This dependence may justify the lack of agreement in the literature on which is the main toughening mechanism in CFRPs \[150,221\].

d. The effect of interfacial properties (\( G_{\text{SL}} \) and \( \tau_\mu \)) on the overall fracture toughness (Figures 7.12 and 7.13) is complex and far from the direct proportionally suggested in Equation 7.1. Although maybe counter-intuitive, model predictions are supported by experimental evidence: comparing the T300/913 and T300/920 systems (Figure 7.15) illustrates how a tougher matrix can actually embrittle the composite; similar findings are reported the literature \[236\]. In addition, reducing matrix shrinkage — and, consequently, decreasing the frictional stress \( \tau_\mu \) — has been shown to increase the translaminar toughness of CFRPs \[150,237\].

e. The model predicts that the fracture toughness initially increases with filament count, but then reaches a plateau for very large areas (see Section 7.4.2(e)). While this agrees with the typical fractal-based scaling law \[222,225\], it cannot be experimentally validated for FRPs due to lack of data in the literature.

7.5 Conclusions

An analytical model for the translaminar fracture toughness of FRP bundles was developed, implemented and validated. The model assumes a hierarchical failure process
An analytical model for the translaminar tensile toughness of fibre composites

with formation of stochastic variations of fractal fracture surfaces; debonding and pull-out lengths of each fractal level are stochastic variables, whose distribution is calculated by combining fracture mechanics with a probabilistic analysis of failure. The overall translaminar toughness includes the contributions of debonding and pull-out for all fractal levels formed in a fracture surface, which generates a size effect.

The model requires, as inputs, the in-situ properties of the fibre–matrix interface, as well as the bundle strength distributions associated with each fractal level (which, in the present case, were calculated using the strength model developed in Chapter 6). It was found that the translaminar toughness is enhanced by stronger fibres with large variability, and by intermediate values of interfacial toughness and friction.

Model predictions were validated against experimentally measured translaminar fracture toughnesses available in the literature. The model was able to reproduce the effect of different fibre and matrix types, as well as the marked increase of toughness for thicker plies.

This work proposes the first model for predicting size effects on the translaminar fracture toughness of FRP bundles or unidirectional plies, which is essential for the accurate simulation and design of damage-tolerant composite structures [214, 229, 231]. In addition, this model is also paramount for understanding and predicting the mechanical behaviour of state-of-the-art multiscale discontinuous-fibre composites, both virgin [147, 152, 170] and recycled (Chapter 8).
Chapter 8

Predicting the fracture toughness of multiscale recycled composites

8.1 Introduction

Chapter 2 highlighted the potential of recycled composites for non-safety critical structural applications. Chapters 4 and 5 exposed the micro-structure of a typical state-of-the-art recycled composite. The matrix is reinforced by a continuous range, from short fibres to relatively large bundles, with a certain orientation distribution. The failure mechanisms observed in Chapter 4 indicated that failure and pull-out of the bundles was responsible by the magnitude of the energy dissipated during fracture. The comparison of the micro-structures analysed in Chapter 5 with the respective fracture toughnesses (Figure 5.15) further corroborated the relation between the presence of bundles and the fracture toughness.

The importance of virgin discontinuous carbon fibre polymeric matrix systems has also increased in recent years [152,153,170]. The motivation for this is excellent damage tolerance and manufacturability. For the automotive industry, which is constrained simultaneously by pressing manufacturing schedules and the need for the manufacture of complex parts not devoid of notches (such as holes), these advantages are paramount.

The use of both recycled composites and virgin discontinuous systems in structural parts motivates the study of their fracture response. While this can be done experimentally (as in Chapters 4 and 5), a theoretical understanding of the fracture response of these materials holds the potential to not only contribute to structural design with these materials, but also to design more effectively the micro-structure of these materials.
Developing a theoretical model for the fracture of a material reinforced with bundles over a continuous range of scales and with a generic orientation distribution (see Figures 4.6, 4.9 and 4.12) poses a challenge which cannot be underestimated. There are several aspects which must be overcome to address this problem:

**Modelling failure of bundles** Modelling failure of bundles is challenging particularly because of the size effects, both on the length and on the fibre count. The size-dependent strength and toughness of fibre bundles has been addressed in Chapters 6 and 7.

**Modelling pull–out of bundles** Modelling the pull–out process of a bundle at a given angle to the fracture surface is challenging as it requires representing:

– the support from the matrix on the bundle;
– the elastic deformation of the bundle;
– the contact pressure and frictional stresses between the bundle and the matrix, including the snubbing effect (increase of contact and frictional stresses due to bending);
– the pull–out process itself, including the energy dissipated;
– the possibility of the bundle breaking before or during the pull–out process.

These challenges are addressed in this chapter.

This chapter is organised in the following way. Section 8.2 presents the derivation of the model. Section 8.3 introduces the main results and these are discussed in Section 8.4. The main conclusions are drawn together in Section 8.5.

## 8.2 Model development

### 8.2.1 Methodology

The model for predicting the fracture toughness of multiscale rCFRPs considers a distribution of fibres and bundles — hereafter denominated Reinforcing Units (RUs) — embedded in a matrix, crossed by a macroscopic crack propagating in–plane over an area $A_{\text{macro}}$ (Figure 8.1).

Each RU crossed by the crack faces is characterised by the length of its shortest embedded end ($l_{po}$) and its angle with the crack normal ($\varphi$). The RU cross section is assumed to be elliptical and characterised by the width $w$ and aspect ratio $a_R = t/w$.
Predicting the fracture toughness of multiscale recycled composites

Figure 8.1: Geometry of a reinforcing unit crossed by a macroscopic crack.

(which defines the thickness \( t \), perimeter \( C \) and area \( A \)). The intrinsic fibre content in an RU is \( V^{f, RU} \), and the overall fibre volume fraction in the rCFRP is \( V^{f} \).

As the crack opens, each RU crossed by the crack faces will either fracture (subscript \( fr \)) or pull-out (subscript \( po \)). Neglecting crack directionality, debonding and pull-out will systematically initiate from the shortest embedded side \( l_{po} \leq l/2 \), where \( l \) is the RU length); consequently, both processes depend on the parameters \( w \), \( \varphi \) and \( l_{po} \). The overall composite fracture toughness \( G \) can be calculated by integrating the energy dissipated by each RU \( (W^{RU}) \) over the rCFRP architecture (represented by the domain \( \Omega \)), yielding:

\[
G = \frac{1}{A_{macro}} \int_{\Omega} W^{RU} (l_{po}, \varphi, w) \ d\Omega.
\]  

The response of reinforcing units to crack propagation will depend on their geometry. The integration domain \( \Omega \) can be therefore split into two subdomains: \( \Omega_{fr} \) comprises all supercritical bundles (which fracture before debonding), and \( \Omega_{po} \) is composed of subcritical bundles (which fully debond and initiate pull-out). Consequently,

\[
G = \frac{1}{A_{macro}} \left( \int_{\Omega_{fr}} W_{fr} (l_{po}, \varphi, w) \ d\Omega_{fr} + \int_{\Omega_{po}} W_{po} (l_{po}, \varphi, w) \ d\Omega_{po} \right),
\]

where \( W_{fr} \) and \( W_{po} \) are the energies dissipated during each of the events fracture and pull-out (after debonding). Section 8.2.2 addresses whether a RU is sub or supercritical; Section 8.2.3 defines \( W_{fr} \), and Section 8.2.4 presents the derivation of \( W_{po} \); finally, Section 8.2.5 details the integration scheme for calculating \( G \).

8.2.2 Sub and supercritical reinforcing units

The presence of sub and supercritical integration subdomains in Equation 8.1b requires defining a critical pull-out length \( (l_{po}^{crit}) \) — below which a RU will debond and initiate
Chapter 8

pull–out, and above which a RU will fracture during debonding. The strength of fibres and bundles is largely affected by their filament count and stress field (Chapter 6), hence the critical pull–out length must account for statistical size effects.

Consider a perfectly plastic interface between the RU and the matrix (with associated shear–lag strength $\tau_{\text{SL}}$), and assume a mode–II shear–lag debonding process; this generates a linear tensile stress field in the shortest embedded length, defined by the maximum stress $\sigma_{\text{deb}}$ and slope $\lambda_{\text{deb}}$:

$$\sigma_{\text{deb}} = \lambda_{\text{deb}} \cdot l_{\text{po}}, \quad \text{with} \quad \lambda_{\text{deb}} = \frac{\tau_{\text{SL}}}{C}. \quad (8.2)$$

The tensile stresses at the longest embedded end (with length $l - l_{\text{po}} \geq l_{\text{po}}$) are assumed to be symmetric of those in the shortest end; consequently, a RU undergoes a triangular stress field while debonding. According to the generalisation of the WLT presented in Appendix E the corresponding survival probability $S_{\lambda_{\text{deb}}} (\sigma_{\text{deb}})$ is defined by:

$$\ln \left[ S_{\lambda_{\text{deb}}} (\sigma_{\text{deb}}) \right] = 2 \frac{\lambda_{\text{deb}}}{l_{\text{r}}} \int_{\sigma=0}^{\sigma_{\text{deb}}} \ln \left[ S_{U,\sigma}(\sigma) \right] d\sigma. \quad (8.3)$$

In the previous equation, $S_{U,\sigma}(\sigma)$ is the survival probability of a RU of length $l_{\text{r}}$ under uniform stresses $\sigma$ (normalised by the total cross section $A$); its computation for different bundle filament counts has been addressed in Chapter 6.

The critical pull–out length can now be defined as the embedded length that yields a 50% probability of survival to the debonding process; mathematically,

$$l_{\text{crit}po} = l_{\text{po}} : \left\{ S_{\lambda_{\text{deb}}} (\lambda_{\text{deb}} \cdot l_{\text{po}}) = 50\% \right\}. \quad (8.4)$$

The overall fracture toughness (Equation 8.1b) will be calculated including all RUs with $l_{\text{po}} > l_{\text{crit}po}$ in subdomain $\Omega_{\text{fr}}$, and those with $l_{\text{po}} \leq l_{\text{crit}po}$ in subdomain $\Omega_{\text{po}}$.

8.2.3 Intrinsic fracture energy of reinforcing units

The energy dissipated during fracture of a RU ($W_{\text{fr}}$) depends on its intrinsic fracture toughness $G_{\text{fr}}$ and the fractured area $A_{\text{fr}}$,

$$W_{\text{fr}} = G_{\text{fr}} \cdot A_{\text{fr}} \quad \text{with} \quad A_{\text{fr}} = \frac{A}{\cos \varphi}. \quad (8.5)$$

Chapter 7 has shown that the intrinsic translaminar fracture toughness of UD bundles — represented as $G_{\text{fr}}^0$, with $\varphi = 0$ — increases dramatically with filament count. The intrinsic toughness of a $0^\circ$ aligned RU will therefore be governed by its thickness $t$, and $G_{\text{fr}}^0(t)$ can be calculated using the methodology proposed in Chapter 7.
In addition, $G_{fr}$ also varies with the orientation of the fracture plane $\varphi$. At $\varphi = 90^\circ$, the intrinsic toughness corresponds to mode–I delamination, and $G_{fr}(90^\circ)/G_{fr}^0 \approx 0$. Experimental data for intermediate orientations is virtually non-existent; nevertheless, recent measurements for carbon–epoxy suggest that $G_{fr}(45^\circ)/G_{fr}^0 \approx 0.6$. Considering these values, a simple, smooth empirical relation is proposed:

$$G_{fr}(\varphi) = G_{fr}^0 \cdot \cos^2 \varphi. \quad (8.6)$$

Replacing these relations in Equation 8.5, the energy dissipated during fracture of a RU is:

$$W_{fr} = W_{fr}(\varphi, t) = A \cdot G_{fr}^0(t) \cdot \cos \varphi. \quad (8.7)$$

### 8.2.4 Pull–out process of reinforcing units

#### 8.2.4.1 Dissipation mechanisms during pull–out

To calculate the energy dissipated during pull–out for determining $W_{po}$, consider a RU with shortest embedded length $l_{po} \leq l/2$ being pulled-out at an angle $\varphi$ from an elastic foundation with stiffness $k_{el}$ (Figure 8.2). The pulled-out length $s_{po}$ is progressively increased, until the RU is either completely pulled-out ($s_{po}^{\text{max}} = l_{po}$) or fails during the process ($s_{po}^{\text{max}} < l_{po}$). Three toughening mechanisms are considered:

- Frictional dissipation due to residual interfacial stresses ($W_{\Delta T}$);
- Frictional dissipation due the snubbing effect [238,239] ($W_{\mu,el}$);
- Fracture energy of the RU ($W_{fr}$), included if it fails during the pull-out process.

Figure 8.2: Pull-out model for reinforcing units.
The total pull-out work of a RU is thus given by:

\[ W_{po} = W_{\Delta T} + W_{\mu,el} + f_{po} \cdot W_{fr} \]

where

\[ f_{po} = \begin{cases} 0 & \text{for complete pull-out } (s_{po}^{max} = l_{po}) \\ 1 & \text{for premature RU failure } (s_{po}^{max} < l_{po}). \end{cases} \] (8.8)

### 8.2.4.2 Frictional dissipation due to residual stresses

After curing, cooling down the rCFRP from the polymer’s glass transition temperature to room temperature develops residual compressive stresses at the fibre–matrix interface. Neglecting Poisson’s effects, this generates constant frictional stresses \( \tau_{\mu} \) during pull–out (which can be estimated from SFPO tests, as shown in Appendix J). For a fibre with circular cross section and circumference \( C_f \), the energy dissipated due to residual thermal stresses is:

\[ W_{\Delta T} = \int_{s_{po}=0}^{s_{po}^{max}} C_f \cdot \tau_{\mu} \cdot (l_{po} - s_{po}) \, ds_{po} = C_f \cdot \tau_{\mu} \cdot s_{po}^{max} \cdot \left( l_{po} - \frac{s_{po}^{max}}{2} \right). \] (8.9a)

For bundles with elliptical cross section, there is no closed–form solution for residual thermal stresses. Nevertheless, detailed Finite Elements analyses \( ^{[240]} \) suggested that Equation 8.9a is a valid approximation provided that an equivalent circumference \( C_{\Delta T} \) is used:

\[ W_{\Delta T}(l_{po}, \varphi, w) = C_{\Delta T} \cdot \tau_{\mu} \cdot s_{po}^{max} \cdot \left( l_{po} - \frac{s_{po}^{max}}{2} \right), \quad \text{with} \quad C_{\Delta T} \approx \pi \cdot t. \] (8.9b)

### 8.2.4.3 Frictional dissipation due to the snubbing effect

An inclined RU relatively to the crack faces will dissipate additional energy due to the snubbing effect — i.e., the increase of contact pressure and friction between the RU and the matrix at the crack faces. To take this into account, consider Figure 8.2, showing a RU bending in an anti-symmetric shape as it pulls–out at an angle \( \varphi \) from the matrix. Assuming small deflections,

\[ l_{sup} = l_{po} - s_{po}, \quad l_{uns} = \frac{s_{po}}{2}, \quad \text{and} \quad \delta = l_{uns} \cdot \tan \varphi, \] (8.10)

where \( \delta \) is the deflection at the anti-symmetry plane, and the subscript \( uns \) indicates the already pulled–out (unsupported) region. The subscript \( sup \) represents the em-
bedded region, within which the RU is supported by the surrounding material; this is mathematically represented by an elastic foundation with stiffness \( k_{el} \approx E_m \).

The deflection \( v(x) \) of an RU (with longitudinal stiffness \( E_{RU} \) and second moment of area \( I_{RU} \)) is thus governed by the following differential equations (where \( v^{(n)}(x) = \frac{d^n v(x)}{dx^n} \)):

\[
v(x) : \begin{cases}
v^{(4)}_{\text{sup}}(x) = -\frac{k_{el}}{E_{RU}} \cdot v_{\text{sup}}(x), & \text{for } 0 \leq x \leq l_{\text{sup}} \\
v^{(4)}_{\text{uns}}(x) = 0, & \text{for } l_{\text{sup}} < x \leq l_{\text{sup}} + l_{\text{uns}} ,
\end{cases}
\]

under the boundary conditions

\[
v^{(2)}(0) = 0, \quad v^{(3)}(0) = 0, \quad v(l_{\text{sup}} + l_{\text{uns}}) = -\delta \quad \text{and} \quad v^{(2)}(l_{\text{sup}} + l_{\text{uns}}) = 0 .
\]

The previous equation assumes that the elastic foundation reacts with a force per unit length in the \( y \)-direction, \( q_{el}(x) \). According to the classical solution for pin–loaded plates \[241\], this generates cosinusoidal contact stresses at the half–surface of a circular RU, which integrate to a contact force per unit length \( n_{el}(x) \); mathematically,

\[
q_{el}(x) = -k_{el} v_{\text{sup}}(x) \quad \text{and} \quad n_{el}(x) = \frac{4}{\pi} q_{el}(x)
\]

In the absence of residual thermal stresses, a distributed friction force \( t_{el}(x) \) would develop during pull–out, governed by the fibre–matrix friction coefficient \( \mu \) (which can be measured through SFPO tests, see Appendix J). This would consequently generate a snubbing pull–out force \( P_{el} \), defined as:

\[
P_{el}(s_{\text{po}}) = \int_{x=0}^{l_{\text{sup}}} t_{el}(x) \, dx , \quad \text{where} \quad t_{el}(x) = \mu \cdot |n_{el}(x)| .
\]

The combination of thermal and snubbing frictional stresses is non-linear, thus simply adding both effects (Equations \[8.9\] and \[8.13\]) would overestimate the resulting friction. For the sake of simplicity and due to the oscillatory nature of \( v_{\text{sup}}(x) \) (Equation \[8.11\]), this effect can be empirically overcome by removing the modulus operation from Equation \[8.13\]; such approach naturally cancels the effect of small oscillations away from the crack faces, while preserving the snubbing effect at the exit point. Consequently,

\[
P_{el}(s_{\text{po}}) \approx \int_{x=0}^{l_{\text{sup}}} \mu \cdot n_{el}(x) \, dx = \frac{4}{\pi} \mu \cdot V_{\text{sup}}(s_{\text{po}}) , \quad \text{where} \quad V_{\text{sup}}(s_{\text{po}}) = \int_{x=0}^{l_{\text{sup}}} q_{el}(x) \, dx ,
\]
and $V_{\text{sup}}(s_{p0})$ is calculated as:

$$V_{\text{sup}}(s_{p0}) = \frac{3 \cdot k_{\text{cl}}}{4 \cdot k_{\text{sup}}} \cdot l_{\text{uns}} \cdot \tan \varphi \cdot \xi_{\text{sup}},$$

with (8.15)

$$k_{\text{sup}} = \left( \frac{k_{\text{cl}}}{4 \cdot E_{\text{RU}} \cdot I_{\text{RU}}} \right)^{1/4}, \quad \xi_{\text{sup}} = \frac{\cosh \kappa_a + \cos \kappa_a - 2}{\xi_{\text{den}}},$$

$$\kappa_a = k_{\text{sup}} \cdot l_{\text{uns}} \quad \kappa_s = 2 \cdot k_{\text{sup}} \cdot l_{\text{sup}} \quad \text{and}$$

$$\xi_{\text{den}} = \kappa_a^3 \cdot (\cosh \kappa_a + \cos \kappa_a - 2) + 3 \cdot \kappa_a^2 \cdot (\sinh \kappa_a + \sin \kappa_a)$$

$$+ 3 \cdot \kappa_a \cdot (\cosh \kappa_a - \cos \kappa_a) + 3/2 \cdot (\sinh \kappa_a - \sin \kappa_a).$$

Finally, the energy dissipated by a RU due to the snubbing effect is obtained by integrating numerically the snubbing force along the pull–out process, hence

$$W_{\mu,\text{el}}(l_{p0}, \varphi, w) = \int_{s_{p0}=0}^{s_{p0}} P_{\text{el}}(s_{p0}) \, ds_{p0}.$$  (8.16)

### 8.2.4.4 Fracture of reinforcing units during pull-out

During pull–out, an inclined RU undergoes considerable bending stresses, which can cause bundle failure and interrupt the pull–out process. The corresponding tensile stresses $\sigma_b$ are maximised near the exit point (as confirmed by detailed Finite Elements analysis [240]); following Equations 8.11 and 8.15, the maximum bending stresses at $x = l_{\text{sup}}$ are:

$$\sigma_{\text{bend}}^{\text{max}}(s_{p0}) \approx \frac{w}{2} \cdot E_{\text{RU}} \cdot \psi(2)(l_{\text{sup}}) = \frac{3}{2} \cdot w \cdot E_{\text{RU}} \cdot k_{\text{sup}}^3 \cdot l_{\text{uns}}^2 \cdot \tan \varphi \cdot \xi_{\text{sup}}.$$  (8.17)

The distribution of bending stresses along the RU is very complex, which hinders the calculation of exact strength distributions for this particular loading case. In order to evaluate whether bending stresses are sufficient to fracture the fibre or bundle during pull–out, the true strength distribution $S_{\text{bend}}(\sigma_{\text{bend}}^{\text{max}}, l_{p0})$ is approximated to that of a RU under linear stresses within a length $2 \cdot l_{p0}$. Following the extension of the WLT derived in Appendix E, this is defined by:

$$\ln \left[ S_{\text{bend}}(\sigma_{\text{bend}}^{\text{max}}(s_{p0}), l_{p0}) \right] = \frac{2 \cdot l_{p0}}{l_r} \cdot \frac{1}{\sigma_{\text{bend}}^{\text{max}}(s_{p0})} \cdot \int_{\sigma=0}^{\sigma_{\text{bend}}^{\text{max}}(s_{p0})} \ln \left[ S_{\text{U},\text{f}}(\sigma) \right] \, d\sigma,$$  (8.18)
The threshold for RU failure during pull-out is defined in a similar way as for the debonding process (Equation 8.4), thus:

\[ s_{\text{po}}^{\text{max}} = s_{\text{po}} : \{ S_{\text{bend}}(s_{\text{bend}}^{\text{max}}(s_{\text{po}}), l_{\text{po}}) = 50\% \}. \]  

(8.19)

The binary failure variable \( f_{\text{po}} \) — which controls whether the RU fracture energy \( W_{\text{fr}} \) (Equation 8.5) is included in \( W_{\text{po}} \) (Equation 8.8) — is then formally defined as:

\[ f_{\text{po}} = \begin{cases} 0 , & \text{for } s_{\text{po}}^{\text{max}} = l_{\text{po}} \text{ and } S_{\text{bend}}(s_{\text{bend}}^{\text{max}}(s_{\text{po}}), l_{\text{po}}) < 50\% , \forall s_{\text{po}}^{\text{max}} \leq l_{\text{po}} \\ 1 , & \text{for } s_{\text{po}}^{\text{max}} \leq l_{\text{po}} \text{ and } S_{\text{bend}}(s_{\text{bend}}^{\text{max}}(s_{\text{po}}^{\text{max}}), l_{\text{po}}) = 50\% \end{cases} \]  

(8.20)

### 8.2.5 Integration over the reinforcement architecture

The integration scheme for \( W_{\text{fr}}(l_{\text{po}}, \varphi, w) \) and \( W_{\text{po}}(l_{\text{po}}, \varphi, w) \), as defined in Equation 8.1b, is illustrated in Figure 8.3. This considers a specimen with width \( w_s \) and thickness \( t_s \), with a crack across its length \( \Delta a \) and oriented at an angle \( \alpha \) relatively to the normal to the main material direction (orthotropy is assumed).

Consider that the rCFRP architecture is characterised by the Probability Density Functions (PDFs) of length, width and orientation of RUs, respectively \( f_L(l) \), \( f_W(w) \) and \( f_\psi(\psi) \). The former two can be described by Weibull distributions (see Table 5.6) with parameters \( \{m_l, l_0\} \) and \( \{m_w, w_0\} \), and the latter by the second order Tucker’s tensor [129,130] (defined by the parameter \( a_{11} \) for planar architectures, see Equation 4.1):

![Figure 8.3: Geometric model for integration of individual energies over the rCFRP architecture.](image)
Chapter 8

\[
\begin{align*}
\mathcal{G} &= \frac{N^{RU}}{A_{macro}} \int_{0}^{\infty} \int_{\varphi=-\pi/2}^{\pi/2} \int_{l_{po}=0}^{\infty} W \left( l_{po}, \varphi, w \right) \cdot \\
& \quad \cdot \left[ \int_{l=2l_{po}}^{\infty} f_{L}(l) \, dl \right] \cdot f_{L_{po}} \left( l_{po} \mid \{ l, \varphi \} \right) \, dl_{po} \cdot f_{\Phi}(\varphi) \, d\varphi \cdot f_{W}(w) \, dw 
\end{align*}
\] (8.26)

which can be expressed as:

Through geometric considerations, the PDFs of variables in the integration domain of Equation 8.1b — \( f_{L_{po}}(l_{po}) \) and \( f_{\Psi}(\psi) \) — are related to the PDFs above by:

\[
\begin{align*}
\mathcal{G} &= \frac{N^{RU}}{A_{macro}} \int_{0}^{\infty} \int_{\varphi=-\pi/2}^{\pi/2} \int_{l_{po}=0}^{\infty} W \left( l_{po}, \varphi, w \right) \cdot \\
& \quad \cdot \left[ \int_{l=2l_{po}}^{\infty} f_{L}(l) \, dl \right] \cdot f_{L_{po}} \left( l_{po} \mid \{ l, \varphi \} \right) \, dl_{po} \cdot f_{\Phi}(\varphi) \, d\varphi \cdot f_{W}(w) \, dw 
\end{align*}
\] (8.26)

Assuming \( l, \psi \) and \( w \) to be independent,

\[
d\Omega = N^{RU} \cdot f_{L_{po}}(l_{po}) \cdot f_{\Psi}(\psi) \cdot f_{W}(w) \cdot dl_{po} \, dl \, d\varphi \, dw
\] (8.23)

where \( (N^{RU}) \) is the total number of RUs in the composite. This is related to the overall rCFRP fibre volume fraction \( V^{f} \) and the local RU fibre content \( V^{f, RU} \) by:

\[
V^{f} = \frac{N^{RU} \cdot \int l \cdot f_{L}(l) \, dl \cdot \int V^{f, RU} \cdot A^{RU} \cdot f(A^{RU}) \, dA^{RU}}{\Delta a \cdot t_{s} \cdot w_{s}}.
\] (8.24)

Solving the integrals in Equation 8.24 and assuming constant aspect ratio \( a_{R} \) and local fibre content \( V^{f, RU} \) for all RUs, leads to:

\[
\int l \cdot f_{L}(l) \, dl = l_{m} \quad \text{and} \quad \int V^{f, RU} \cdot A^{RU} \cdot f(A^{RU}) \, dA^{RU} = V^{f, RU} \cdot \frac{\pi}{4} \cdot a_{R} \cdot (w^{2})_{m}
\] (8.25)

where \( l_{m} \) is the mean RU length, and \( (w^{2})_{m} \) is the squared quadratic mean RU width.

Substituting Equations 8.22–8.25 in Equation 8.1b, the rCFRP fracture toughness \( \mathcal{G} \) is finally obtained as:

\[
\mathcal{G} = \frac{N^{RU}}{A_{macro}} \int_{0}^{\infty} \int_{\varphi=-\pi/2}^{\pi/2} \int_{l_{po}=0}^{\infty} W \left( l_{po}, \varphi, w \right) \cdot \\
& \quad \cdot \left[ \int_{l=2l_{po}}^{\infty} f_{L}(l) \, dl \right] \cdot f_{L_{po}} \left( l_{po} \mid \{ l, \varphi \} \right) \, dl_{po} \cdot f_{\Phi}(\varphi) \, d\varphi \cdot f_{W}(w) \, dw
\] (8.26)

which can be expressed as:
\[ G = \frac{8}{\pi} \cdot V^2 \cdot \int_{l_m}^{\infty} \int_{w=0}^{\infty} \int_{\varphi=-\pi/2}^{\pi/2} W(l_{po}, \varphi, w) \cdot \left(1 - F_L(2 \cdot l_{po})\right) \, dl_{po} \cdot \cos \varphi \cdot f_\Phi(\varphi) \, d\varphi \cdot f_W(w) \, dw. \]  

(8.27)

### 8.3 Results

#### 8.3.1 Model predictions and experimental validation

The model presented in this chapter, which includes as components the models from Chapters [5](#) and [6](#), is used to predict the fracture toughness of the three material systems (T300-rRCF, T300-rMIT and T800-rMIT) characterised in Chapters [4](#) and [5](#). For convenience, Table 8.1 maps the location of all relevant data about these materials in the mentioned chapters; these data are used as input to the model in this section.

Figure 8.4 superposes the fracture toughness value predicted by the model to the experimental R-curve measured for each material. It should be noted that the model predicts homogenised toughnesses; consequently, modelling results should be compared to experimental measurements within the steady-state domain, and averaging unstable and stable crack propagation modes.

**Table 8.1:** Mapping of all relevant data for the three material systems studied.

<table>
<thead>
<tr>
<th>Material</th>
<th>T300-rRCF</th>
<th>T300-rMIT</th>
<th>T800-rMIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre</td>
<td>T300-rRCF</td>
<td>T300-rMIT</td>
<td>T800-rMIT</td>
</tr>
<tr>
<td>Matrix</td>
<td>MTM57</td>
<td>RTM 6</td>
<td>RTM 6</td>
</tr>
<tr>
<td>Recycling route</td>
<td></td>
<td></td>
<td>Table 5.1</td>
</tr>
<tr>
<td>Volume fraction of constituents</td>
<td>Figure 5.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fibre diameter</td>
<td></td>
<td></td>
<td>Figure 5.3</td>
</tr>
<tr>
<td>RU orientation ((a_{11}), Eq. 8.21)</td>
<td>0.65</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Strength of the fibres</td>
<td></td>
<td></td>
<td>Table 5.5</td>
</tr>
<tr>
<td>Architecture of reinforcement</td>
<td>Table 5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interfacial shear strength</td>
<td></td>
<td></td>
<td>Figure 5.9</td>
</tr>
<tr>
<td>Pull-out frictional stresses</td>
<td></td>
<td></td>
<td>Figure 5.9</td>
</tr>
<tr>
<td>Measured toughness</td>
<td></td>
<td></td>
<td>Figures 5.14 and 5.15</td>
</tr>
</tbody>
</table>
8.3.2 Parametric study

The complexity of the model makes it difficult to assess directly the effect of its input parameters. In addition, some of these parameters are actually difficult to measure accurately. For this reason, a parametric study is presented here for the most relevant properties, with a focus on those that are particularly more difficult to measure accurately. The material systems from the previous section are used as baselines (i.e. providing nominal properties) for the parametric study.

8.3.2.1 Material anisotropy

The toughness predictions depend on the anisotropy of the material micro-structure, i.e. they depend on the preferential alignment of the fibres. Figure 8.5(a) shows the predicted fracture toughness for material system T300-rRCF as function of the angle $\alpha$ of the fracture plane with material direction 1 for several values of anisotropy (defined by the component of the orientation tensor $a_{11}$).

The shape of the curves in Figure 8.5(a) can be observed to be that of a cosine function. The experimental data for directions 1 and 2 ($\alpha = 0^\circ$ and $\alpha = 90^\circ$) is also included in the graph, and should be compared to the predictions with $a_{11} = 0.65$ (see Equation 4.1).

8.3.2.2 Matrix support

The matrix support is expressed through the stiffness of the elastic foundation $k_{el}$. Figure 8.5(b) shows the predicted toughness for material system T300-rRCF as function
of the angle $\alpha$ of the fracture plane with material direction 1 for elastic foundation stiffnesses between 10% and $5 \times$ the matrix Young’s modulus.

As in the previous section, the shape of the curves in Figure 8.5(b) can be observed to be that of a cosine function.

### 8.3.2.3 Single fibre strength statistics

The fracture toughness model depends on the stochastic fibre strength. The effect of two intuitive statistics, the mean and the coefficient of variation, is presented in Figure 8.6 for the material system T800-rMIT.

Figure 8.6(a) shows predicted fracture toughnesses for mean fibre strengths between 3.0 and 5.0 GPa (the experimental average is 3.988 GPa). Figure 8.6(b) shows the predicted fracture toughnesses for coefficients of variation (in single fibre strength) between 10 and 30% (the measured experimental value is 16.2%).

### 8.3.2.4 Friction

The effect of friction in the predicted fracture toughness is analysed through the effect of the single fibre friction stress $\tau_0^f$ and the friction coefficient $\mu$.

![Figure 8.5: Effect of crack direction on the fracture toughness of an orthotropic rCFRP (considering T300-rRCF; experimental data corresponds to $G_{\text{low}}^{\text{low}}$ in Table 4.7 (dispersed phase), and the error bars represents one standard deviation).](image)

- (a) Effect of material anisotropy.
- (b) Effect of matrix support.
8.3.2.5 Architecture of the reinforcement

The architecture of the reinforcement affects the predicted fracture toughness through the distributions of bundle widths, lengths, etc.

Figure 8.8(a) shows the predicted fracture toughness for the T300-rMIT material system, together with the respective experimental data. The same graph shows the model predictions that would be obtained if the model were used with the architecture corresponding to material T800-rMIT.

Similarly, Figure 8.8(b) shows the predicted fracture toughness for the T800-rMIT material system, together with the respective experimental data. The same graph shows the model predictions that would be obtained if the model were used with the architecture corresponding to material T300-rMIT.
Predicting the fracture toughness of multiscale recycled composites

Figure 8.7: Effect of friction properties on the fracture toughness of a multiscale rCFRP (considering T300-rMIT).

(a) Effect of single fibre friction stress $\tau_0^\circ$.

(b) Effect of friction coefficient $\mu$.

Figure 8.8: Effect of reinforcement architecture on the fracture toughness of multi-scale rCFRPs. Each plot shows model predictions considering the same micro-mechanical properties, but different architectures.

(a) Micromechanical properties from T300-rMIT.

(b) Micromechanical properties from T800-rMIT.

8.4 Discussion

8.4.1 Model predictions and experimental validation

Figure 8.4 shows good predictions for three different materials—with different fibre types, different matrices, different multiscale architectures of reinforcement, different fibre reclamation routes and different (re-)manufacturing routes. The consistency of
good results across these different materials suggests that the model is robust and indeed suitably captures the most relevant physics involved in the fracture process.

8.4.2 Parametric study

8.4.2.1 Material anisotropy

As $a_{11}$ increases, the degree of anisotropy also increases. The more anisotropic the material ($a_{11} \uparrow$), then the higher is the toughness for cracks propagating along the preferential fibre direction ($\alpha = 0^\circ$); similarly, as $a_{11}$ increases, the toughness for cracks propagating perpendicularly to the preferential fibre direction decreases. Albeit eventually counter-intuitive, this is due to the competition between pull–out and fibre failure: when a crack propagates perpendicularly to the preferential fibre direction, the toughness is lower because of premature fibre failure.

8.4.2.2 Matrix support

As the stiffness of the elastic foundation $k_{el}$ increases, then this increases the energy contribution due to the snubbing effect for fibres with low misalignment (which resist to failure), thus leading to an increase in the fracture toughness.

8.4.2.3 Single fibre strength statistics

Figure 8.6(a) shows that stronger fibres lead to tougher composites. This is because stronger fibres lead to tougher bundles and delay failure of the reinforcing units.

The increase in toughness with the coefficient of variation of fibre strength shown in Figure 8.6(b) is due to the bundle strength and toughness models. Experimental variability was quite low in the T800-rMIT (lower than the virgin fibres), so the results for higher CoV are likely to be more realistic.

8.4.2.4 Friction

The decrease in predicted fracture toughness with single fibre friction stress $\tau^0_{\mu}$ shown in Figure 8.7(a) is due to the effect of $\tau^0_{\mu}$ on the intrinsic bundle toughness. In fact, this effect more than counter-balances the increase in pull–out dissipation with $\tau^0_{\mu}$ due to residual stresses.

The increase in fracture toughness with $\mu$ visible in Figure 8.7(b) is due to the increase in energy dissipated through the snubbing effect.
8.4.2.5 Architecture of the reinforcement

Figure 8.8 shows that the architecture is the main responsible for the different toughnesses of the recyclates. Comparing the corresponding predictions in Figures 8.8(a) and 8.8(b), it is also possible to infer a comparatively small effect of the lower T300 fibre strength (vs. T800).

8.5 Conclusions

This chapter presented a model which includes components from Chapters 6 and 7 and was used to predict the fracture toughness of the three material systems characterised in Chapters 4 and 5, with the aim of facilitating their introduction as non-safety critical structural materials (Chapter 2).

The model was shown to accurately predict the fracture toughness for a range of very dissimilar materials. A parametric study was then used to show how the model predictions depended on input parameters that are either difficult to measure or that could be controlled by manufacturers of this materials.

The model appears to be highly suitable for the design of micro-structures for materials (recycled or virgin) with optimal fracture toughness for structural applications with requirements driven by damage tolerance.
Chapter 9

Conclusions

9.1 On recycling CFRPs for structural applications

The last decade has seen a tremendous development of CFRP recycling technologies, motivated by the ever increasing amount of waste generated. These efforts, coupled with environmental, economic and legal drivers, paved the way for the first companies dedicated to recover the valuable carbon fibres from composite waste; pyrolysis is the only process currently implemented at a commercial scale.

The literature review and experimental work (Chapters 2 to 5) show that many reclamation processes recover clean fibres with nearly full retention of mechanical properties. However, Chapter 3 highlighted that scaling up towards industrial implementations constitutes a considerable challenge; nevertheless, it is also shown that fully optimised processes (which completely remove the matrix and do not damage the fibres) may not be necessary for achieving the best performance at the composite level.

Several processes for re-manufacturing composites were considered, being impregnating rCF preforms the most developed one. The mechanical properties of all recycled composites analysed in Chapters 4 and 5 are similar to those of conventional structural materials, which confirms their applicability in (non-safety critical) structural components. It is also highlighted that residual fibre–bundles, instead of being a fibre–reclamation defect, can actually improve the fracture toughness of the recyclates by several orders of magnitude.

One of the major challenges identified for the CFRP recycling industry is the establishment of markets for the recyclates. This work aimed to assist their re-introduction in non-safety–critical structural applications, by (i) studying the mechanical response of recycled fibres and their composites, and (ii) developing predictive models for their mechanical response.
9.2 On the mechanical analysis of recycled composites

The experimental component of this work opened with a key question: if recycled composites are to be used in structural applications, how good can their mechanical performance be? Chapter 3 analysed fibres reclaimed in commercial facilities, and compared the performance of subsequently manufactured woven recycled composites to that of virgin precursors. Different pyrolysis cycles resulted into different compromises between matrix removal and fibre-strength retention, which affected the composites in a load-dependent way; nevertheless, the mechanical properties of the best performing recyclate — with residual matrix — did approach that of the virgin precursor.

Chapter 4 investigated the response of a representative state-of-the-art rCFRP, which exhibited a multiscale microstructure with discontinuous fibres and bundles of different sizes and orientations. A full mechanical characterisation disclosed properties similar to those of aluminium and glass-fibre composites, putting the load-bearing capability of the recyclates to evidence. The most important outcome of this work was the suggestion that fibre bundles considerably toughened the material.

This proposition was further confirmed in Chapter 5 which analysed and compared the fracture toughness of three rCFRPs with significantly different multiscale architectures, as quantified through bundle size distributions. Although the micromechanical properties, stiffness and strength of all recyclates were similar, their toughnesses were dramatically different, undoubtedly proving that the presence of large reinforcing units leads to a considerable increase on the fracture toughness.

These observations show that, depending on the foreseen application, fibre-reclamation and re-manufacturing processes should aim to preserve a controlled amount of fibre bundles. Moreover, they demonstrate that rCFRPs with coarse architectures are highly damage-tolerant materials which can be fully exploited in non-safety-critical structures governed by energy-absorption criteria.

9.3 On modelling the fracture toughness of multiscale recycled composites

Following the experimental evidence of the toughening effect of fibre bundles, an analytical model for the fracture toughness of multiscale rCFRPs was developed in Chapter 8. The model is based on the micromechanical properties of fibres and matrix in the material, as well as the reinforcement architecture.
Conclusions

The model considers, as energy–dissipation mechanisms, debonding, fracture and pull–out of fibres and bundles bridging two macroscopic crack faces propagating in the material. The microstructure of the composite was taken into account through the actual length, width and orientation distributions of reinforcing units in the material.

To model the effect of different orientations during pull–out, fibres and bundles were idealised as beams supported by an elastic foundation. Snubbing forces were distributed as contact stresses, using a pin–loaded hole analogy. This, together with residual interfacial stresses, generated friction during fibre and bundle pull–out.

The analytical model was applied to the three multiscale rCFRPs previously analysed, and successfully validated against experimental results. This work proves that, by considering similar energy–dissipating mechanisms operating in a wide range of scales, the fracture toughness of these materials can be accurately predicted.

To take into account size effects on the properties of reinforcing units, this formulation relied on two auxiliary models for the intrinsic strength and toughness of composite bundles of different sizes (Chapters 6 and 7). Such models, while required for calculating the toughness of a multiscale, randomly–oriented discontinuous rCFRP, are actually ideally suited for modelling the failure process in any continuous UD composite.

Moreover, the fracture toughness model developed in Chapter 8 is also applicable to virgin composites with a similar architecture; these are becoming increasingly popular in high–volume applications [147, 152, 153, 170], expanding significantly the scope of the model. This shows that the inherent complexity of recycled composites, while a formidable challenge, actually constitutes a platform for research on the mechanical behaviour of their virgin precursors as well.

9.4 On modelling size effects on the strength and toughness of composite fibre bundles

The analytical models for the strength and toughness of fibre bundles developed in Chapters 6 and 7 addressed the significant challenge of modelling size effects in UD virgin composites. Both models rely on fibre strength distributions and fibre–matrix interfacial properties, assuming a hierarchical failure process leading to the formation of self–similar fracture surfaces.

The strength model is based on fibre–bundle theory, but crucially accounts for the presence of the matrix. This leads to milder size effects for low filament counts; however, predicted size effects for larger bundles were shown to be consistent with the WLT, thus suggesting the existence of a critical fibre–break cluster size. As opposed
to other composite–bundle models in the literature, the one developed in Chapter 6 considers a characteristic length dependent on the bundle filament count. Moreover, its implementation allows for bundle strength distributions and size effects to be calculated almost instantaneously. Model predictions were validated against experimental results from the literature in a wide range of scales.

The toughness model presented in Chapter 7 has proved the original concept of combining micromechanics, stochastic fibre failure and fractal geometries to predict the translaminar fracture toughness of UD composites. It considers, as energy dissipation mechanisms, debonding and pull–out of bundles from quasi-fractal fracture surfaces; the associated lengths are stochastic variables predicted by the model, based on the respective bundle strength distributions. The model was applied to four different FRP plies tested in the literature, proving the ability of this formulation to capture the effect of different fibres, resins and thicknesses.

9.5 Novelty

The novelty of the work presented here can be categorised in two items: firstly, the experimental analysis of new types of materials (recycled composites), and secondly, the development of original analytical models for the toughness and strength of composites. The following contributions to the state of the art in the mechanical response and modelling of composites are highlighted:

- The literature review on CFRP recycling presented in Chapter 2 is the first to encompass not only fibre reclamation and composite re-manufacturing processes, but also an outlook on promising applications for the recyclates and the main challenges ahead;
- The experimental analysis of recycled fibres and woven composites presented in Chapter 3 represents the first attempt in the literature to relate fibre–reclamation process, re-manufacturing, single–fibre properties and composite performance, and highlighted complex interactions;
- Chapter 4 presents the most (to date) comprehensive analysis of the mechanical response and failure mechanisms of a rCFRP. This is also the first study to suggest a toughening effect of fibre bundles, and that the tensile failure processes in these materials has self–similar features;
- Chapter 5 established an unequivocal relationship between the architecture of a recycled composite and its fracture toughness. Showing that fibre bundles are not necessarily a defect from recycling but can actually considerably toughen the
materials represents an important contribution to the state of the art in CFRP recycling;

- The tensile strength model for FRPs (Chapter 6) introduces the novel concept of variable characteristic length. In addition, the numerical implementation proposed is able to compute size–dependent strength distributions without relying on Monte–Carlo simulations or asymptotic approximations;

- The model for the translaminar toughness of FRPs is the first model in the literature to predict not only the fracture toughness of composite bundles or UD plies, but also the associated size effect. The modelling approach itself is also innovative for combining stochastic fibre failure, fracture mechanics and fractal geometries;

- The fracture toughness model for multiscale rCFRPs is original not only for the type of architecture considered, but also for integrating self–similar dissipation mechanisms operating across a large of scales. This is the first model specifically formulated for the mechanical response of multiscale recycled composites.

9.6 Impact

The findings and conclusions of this research can be used by academics and industrials working with virgin and recycled composites. More specifically, the potential for impact includes the following areas:

- Chapter 2 gathered a comprehensive overview of the key players, processes and challenges for the CFRP recycling industry. This is particularly useful for those aiming to start working in such a multidisciplinary field;

- The direct comparison between recycled fibres & composites and their virgin precursors (Chapter 3) exposed the effect of recycling on the response of composites. This can potentially help the recycling industry to improve their processes towards materials with optimised performance, and it can also help build confidence in using recyclates in non-safety–critical structural applications;

- The experimental work with multiscale rCFRPs (Chapters 4–5), particularly the toughness analysis, creates a new viewpoint on the presence of fibre bundles in recycled composites. Showing that bundles dramatically increase the toughness and damage tolerance of the recyclates allows the recycling industry to re–define their optimisation targets, and extends the range of application of rCFRPs;
• Chapters 3 to 5 have shown that the mechanical performance of recycled composites can already compete with that of conventional structural materials, encouraging their use in non-safety–critical structures. Moreover, the experimental observations can guide further research, particularly on developing design criteria for recycled composites;

• The analytical models for size effects on the strength and toughness of composite bundles can be used not only to predict the response of multiscale discontinuous composites, but also that of virgin UD plies. The outputs of the analytical models can be directly used as inputs for simulation tools (e.g. FE models); because size effects influence the response of many composite structures [214], such models can actually help reducing the test pyramid for composite structures;

• The fracture toughness model for rCFRPs can guide the optimisation of recycling and re-manufacturing processes towards damage tolerant materials. Moreover, this model can be used to analyse complex structural components, by relating a non-uniform architecture to local mechanical properties;

• A great part of this work, while focused on multiscale recycled composites, can be transposed to virgin materials with similar architectures. Discontinuous multiscale CFRPs offer multiple advantages relatively to the conventional laminated counterparts (e.g. manufacturability of complex shapes, low production times, damage tolerance); this extends the potential impact of the reported experimental observations and models to many thriving industries, e.g. automotive.

• Altogether, this work proves that rCFRP are materials of structural calibre and that recycling is a worth–pursuing route for CFRP waste. This safeguards the sustainability of virgin CFRPs in high–volume applications (e.g. automotive industry), which supports the exploitation of all benefits associated with these light–weight materials.
Chapter 10

Further work

10.1 Recycling routes for CFRPs

CFRP recycling technologies are producing materials with compelling structural performances and reaching the commercialisation stage. Nevertheless, Chapters 2 to 5 highlighted some of the remaining challenges and opportunities:

- *Scaling-up and optimising pyrolysis*, taking into account not only the technical quality of the recyclates, but also the uncertainty on feedstock, running costs, and the actual requirements of potential applications;
- *Developing auxiliary processes for fibre reclamation* (e.g. waste sorting and quality control);
- *Continuing research on alternative fibre–reclamation processes* (e.g. fluidised bed and chemical recycling);
- *Improving fibre alignment during re-manufacturing*. This would not only increase the fibre–direction properties, but also allow for higher fibre contents;
- *Exploring the use of hybrid feedstock*, as it could improve the consistency of recycled composites (thus circumventing the need for waste sorting);
- *Controlling and preserving fibre bundles* for selected applications, exploring not only the the benefit on damage tolerance (Chapter 5), but also the relation between residual matrix and retention of fibre properties.

10.2 Mechanical analysis of recycled composites

The experimental work presented in Chapters 3 to 5 has shown that the mechanical performance of recycled composites, although very complex, makes them suitable for
non-safety-critical structures. This prospect requires continued efforts on understanding the response of these materials, particularly regarding:

- **Studying the interactions between fibre-reclamation, re-manufacturing and mechanical performance** in rCFRPs produced by new and improved processes;
- **Analysing the response of highly aligned systems** [89], and understanding how the conclusions of the current work may apply to other recyclates;
- **Investigating more complex loading cases** such as impact, multi-axial solicitations, fatigue and extreme environments;
- **Supporting the development of structural simulation tools** (e.g. FE) to be used by engineers and designers.

10.3 Mechanical analysis of discontinuous multiscale composites

While this work focused mainly on recycled composites, many conclusions of Chapters 4 and 5 can be transposed to virgin materials with similar architectures. Discontinuous multiscale CFRPs are becoming prolific in most applications requiring improved manufacturability, high volume and low-cost [152, 153, 170] (e.g. automotive industry), making it timely to:

- **Systematically analyse virgin SFRPs with different bundle size distributions** but similar micromechanical properties, as this would provide a sound understanding on the effect of coarse architectures;
- **Verify the applicability of the analytical model for the fracture toughness** of rCFRPs (Chapter 8) to similar virgin materials;
- **Extend the experimental analysis to failure initiation and strength**;
- **Quantify interactions between manufacturing processes and resulting architectures**, and develop corresponding predictive models.

10.4 Modelling the mechanical response of recycled composites

The analytical model for the fracture toughness of multiscale rCFRPs (Chapter 8) is the first model in the literature simultaneously for recycled composites and for multiscale SFRPs. While the results are positive, a few improvements and extensions would be of interest, namely to:
Further work

- **Calculate R-curves of multiscale discontinuous composites**, which could be achieved by coupling the present model with a crack-opening law. This would allow modelling the increase in toughness of material T800-rMIT with crack length (Figure 8.4);
- **Validate the pull-out model further**, both through FE (e.g. on the stiffness of the elastic foundation, matrix spalling criterion, and snubbing effect) and experiments (e.g. pull-out tests of inclined fibres and bundles).
- **Improve the strength criterion for off-axis bundles**, e.g. by coupling existing failure models with stochastic approaches;
- **Measure the fracture toughness of off-axis plies** and improve the toughness criterion for off-axis bundles. Because of the significant lack of literature in this topic, this would be extremely important for virgin UD composites as well;
- **Extend the experimental validation** to other rCFRPs with similar architectures, rCFRPs with highly aligned fibres, and virgin multiscale SFRPs.
- **Identify closed-form analytical relations** between the local fracture toughness and several microstructural parameters (e.g. preferential alignment and bundle size distributions). This would make the model more insightful and improve its efficiency;
- **Couple the micromechanical models with manufacturing simulation tools**, so as to predict the homogenised local fracture toughness of structural components with complex geometries and non-uniform architecture;
- **Extend the model concept** (integration of the effect of reinforcing units) to other mechanical properties, e.g. stiffness and strength, creating a complete modelling tool for discontinuous composites.

10.5 Characterisation of fibre strength

The fibre strength distributions presented in Chapter 5 lack a full agreement with the Weibull-based weakest link theory; similar observations are recurrently reported in the literature, with no sound explanation at present. While this does not hinder a meaningful comparison between different fibre types, it is particularly problematic for micromechanical models involving fibre failure (as developed in Chapters 6 to 8). Further work is therefore suggested on the following topics:

- **Micromechanical modelling of the SFTT** to quantify the influence of stress concentrations or system misalignments. This could be used to verify the magnitude of spurious gripping effects [116].
Performing SFTTs with systematic fibre selection, to understand the effect of variations in fibre diameter and biased selection of fibres. This could be achieved by testing different segments of a same filament and correlating results.

Investigate alternative theoretical distributions for single–fibre strength, and how they would be affected by spurious effects as mentioned above;

Developing alternative test methods (e.g. dry bundle testing) for an easier, faster and more representative characterisation of fibres. This would benefit the recycling industry in particular, as using SFTTs as quality control is unreasonable under their operational conditions.

10.6 Size effects on the strength and toughness of UD composites

The analytical models for the strength and toughness of fibre bundles developed in Chapters 6 and 7 can be further improved and exploited to different areas of size–effects in fibre–reinforced composites, such as:

- Applying the strength model to a broad range of problems (Chapter 6): (i) critical fibre–break cluster size (already predicted by the model, but requiring quantitative characterisation), (ii) simulating full stress–strain curves (by coupling the model with a compliance analysis of a partially–broken bundle), and (iii) hybrid–fibre bundles (requires generalising the input fibre strength distribution);
- Extending the strength model to different coordination numbers (e.g. \( c = 7 \) or \( 9 \)), which would bring stress concentrations down to more realistic values, and would also improve the compatibility between strength and toughness models;
- Calculating R-curves of UD composite plies, by coupling the toughness model with a crack–opening law [242];
- Simulating fracture surfaces using the toughness model; this is currently possible for integer bundle levels, and could be extended to generic configurations;
- Validating the toughness model against a comprehensive experimental programme, isolating the effects of different fibres, resins and sizes;
- Identifying closed-form analytical expressions for bundle strength distributions, debonding and pull–out length distributions, fracture toughnesses, and associated size effects. This would make models more efficient, and their outputs more readily usable in further calculations;
- Understand the effect of non-idealised geometries, e.g. with random interfibre distances [243];
- Unifying the modelling approach for shear–lag boundaries. Currently, the strength model assumes a strength–governed plastic response (realistic at small scales),
Further work

while the toughness one considers a fracture criterion and negligible damage process zones (which governs at larger scales). While this is consistent with size effects in quasi-brittle materials [171], it would nevertheless be preferable to have such transition as a model output instead of an input.
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Bibliography


Appendix A

Estimation of single–fibre strength distributions

Due to the brittle nature of carbon–fibres, characterising their strength requires taking into account the associated stochastic variability. An overview of the methods used in this thesis for (i) estimating fibre strength Weibull distribution parameters and for (ii) estimating percentile ranks of experimental observations is given below.

Assume that, for each fibre type, the strength of single fibres \( X \) follows a Weibull distribution, and has a dependency on the gauge length \( l \) in agreement with the weakest link theory; the effect of stress concentrations at fibre ends is neglected \[116\]. The single–fibre strength distribution is then characterised by a Cumulative Distribution Function (CDF) and a Probability Density Function (PDF) defined respectively as:

\[
F_X(\sigma) = 1 - \exp \left[-\frac{l}{\hat{l}} \left(\frac{\sigma}{\hat{\sigma}_0}\right)^m\right] \quad \text{and} \quad f_X(\sigma) = \frac{dF_X(\sigma)}{d\sigma} = \frac{m}{\sigma} \cdot \hat{l} \cdot \left(\frac{\sigma}{\hat{\sigma}_0}\right)^m \cdot \exp \left[-\frac{l}{\hat{l}} \left(\frac{\sigma}{\hat{\sigma}_0}\right)^m\right],
\]

where \( m \) and \( \hat{\sigma}_0 \) are respectively the shape and scale parameters, being the latter defined at the reference length \( \hat{l} \).

The log–likelihood \( \mathcal{L} \) associated with a set \( \sigma = \{\sigma_1, \sigma_2, \ldots, \sigma_i, \ldots, \sigma_N\} \) of \( N \) strength realisations (each measured at a length \( l_i \), with \( i = 1 \ldots N \)) is:

\[
\mathcal{L} = \ln \left[ \prod_{i=1}^{N} f_X(\sigma_i) \right] = N \cdot \ln(m) + \sum_{i=1}^{N} \ln(l_i) - N \cdot \ln(\hat{l}) + (m - 1) \sum_{i=1}^{N} \ln(\sigma_i) - N \cdot m \cdot \ln(\hat{\sigma}_0) - \sum_{i=1}^{N} \frac{l_i \cdot \sigma_i^m}{l \cdot \hat{\sigma}_0^m}.
\]
Appendix A

The maximum likelihood estimators of the parameters $m$ and $\hat{\sigma}_0$ define a stationary point of $L$, hence verifying:

$$
\begin{align*}
\frac{\partial L}{\partial \hat{\sigma}_0} &= -N \cdot \frac{m}{\hat{\sigma}_0} + \frac{m}{\hat{\sigma}_0} \sum_{i=1}^{N} \frac{l_i}{i} \left( \frac{\sigma_i}{\hat{\sigma}_0} \right)^m = 0, \\
\frac{\partial L}{\partial m} &= \frac{N}{m} + \sum_{i=1}^{N} \ln(\sigma_i) - N \cdot \ln(\hat{\sigma}_0) - \sum_{i=1}^{N} \frac{l_i}{i} \cdot \ln \left( \frac{\sigma_i}{\hat{\sigma}_0} \right) \left( \frac{\sigma_i}{\hat{\sigma}_0} \right)^m = 0.
\end{align*}
$$

(A.3)

Solving the first condition results in the explicit definition of $\hat{\sigma}_0$ as:

$$
\sum_{i=1}^{N} \frac{l_i}{i} \left( \frac{\sigma_i}{\hat{\sigma}_0} \right)^m = N \iff \hat{\sigma}_0 = \left( \frac{1}{N \cdot i} \sum_{i=1}^{N} l_i \cdot \sigma_i^m \right)^{1/m},
$$

(A.4)

and solving the second condition results in the implicit definition of $m$ as:

$$
\frac{N}{m} + \sum_{i=1}^{N} \ln(\sigma_i) - N \cdot \ln(\hat{\sigma}_0) - \sum_{i=1}^{N} \ln(X_i) \cdot \frac{l_i}{i} \left( \frac{\sigma_i}{\hat{\sigma}_0} \right)^m + \ln(\hat{\sigma}_0) \sum_{i=1}^{N} \frac{l_i}{i} \cdot \left( \frac{\sigma_i}{\hat{\sigma}_0} \right)^m = 0 \iff
$$

Equations [A.4] and [A.5] can be used to estimate Weibull parameters $m$ and $\hat{\sigma}_0$ from an experimental data set $\sigma$.

To plot the experimentally obtained CDF of fibre strength, it is necessary to estimate the rank percentile $F_X$ for each strength realisation $\sigma_i$. The procedure adopted here was proposed by Gilchrist [244], and is summarised below.

Let $X^{(j,N)}$ (with $j = 1, \ldots, N$) be the $j$th order statistic of the random sample of size $N$, with CDF represented as $F_X^{(j,N)}(\sigma) = \text{Prob}(X^{(j,N)} \leq \sigma)$. Because the unordered realisations are independent and identically distributed, $F_X^{(j,N)}(\sigma)$ can be related to $F_X(\sigma)$ by [244]:

$$
F_X^{(j,N)}(\sigma) = \sum_{k=j}^{N} \binom{N}{k} \left[ F_X(\sigma) \right]^k \left[ 1 - F_X(\sigma) \right]^{N-k}.
$$

(A.6)

The right-hand side of Equation [A.6] can be re-written using a binomial distribution, and thus using the Regularised Incomplete Beta Function $I$, with parameters
Estimation of single–fibre strength distributions

\( (j, N - j + 1): \)

\[
F_{X(j,N)}(\sigma) = 1 - \sum_{k=0}^{j-1} \binom{N}{k} [F_X(\sigma)]^k \cdot [1 - F_X(\sigma)]^{N-k} = I_\sigma \left( F_X(\sigma); j, N - j + 1 \right). \tag{A.7}
\]

The theoretical median rank for the \( j \)th order statistic is obtained when

\( F_{X(j,N)}(\sigma) = 0.5. \)

For each experimental realisation \( \sigma^{(j)} \) \( (j = 1, \ldots, N) \), the median rank \( F_{X}^{[0.5]}(\sigma^{(j)}) \) can therefore be estimated as (following Equation \( \text{(A.7)} \)):

\[
F_{X}^{[0.5]}(\sigma^{(j)}) = I^{-1}(0.5; j, N - j + 1). \tag{A.8}
\]

Similarly, a confidence interval \( (1 - \alpha) \) for the CDF of each ordered realisation \( \sigma^{(j)} \) can be estimated as:

\[
\left[ F_{X}^{[\alpha/2]}(\sigma^{(j)}) ; F_{X}^{[1 - \alpha/2]}(\sigma^{(j)}) \right] = \left[ I^{-1}(\alpha/2; j, N - j + 1) ; I^{-1}(1 - \alpha/2; j, N - j + 1) \right], \text{ for } j = 1, \ldots, N. \tag{A.9}
\]
Appendix B

Data reduction for $\pm 45^\circ$ shear tests considering large deformations

The ASTM standard for $\pm 45^\circ$ shear tests [119] discards all experimental data for $\gamma_{12} > 5\%$, as the assumptions of a nominal $\pm 45^\circ$ configuration and negligible extensional stresses are no longer valid. However, such procedure would hinder the comparison between the performances of recycled and virgin composites. Therefore, a data reduction method accounting for large deformations and fibre extension is proposed.

Figure B.1 represents schematically one quadrant (defined by the two in–plane symmetry axes) of an orthogonal 2–D woven composite during the $\pm 45^\circ$ shear test; the initial configuration is represented by the subscript 0, and the tensile load ($P$) is applied vertically. Let $l$ be the length of a tow crossing the origin and $\alpha$ its angle with

\[ \gamma_{12} \frac{2}{2} \\alpha_0 = \frac{\pi}{4} \]

Figure B.1: Kinematics of deformation in an orthogonal 2–D composite during a $\pm 45^\circ$ shear test.
the horizontal axis, so that the longitudinal ($\varepsilon_L$), transverse ($\varepsilon_T$), fibre ($\varepsilon_1$) and shear ($\gamma_{12}$) deformations are:

$$
\varepsilon_L = \frac{l \cdot \sin(\alpha)}{l_0 \cdot \sin(\alpha_0)} - 1, \quad \varepsilon_T = \frac{l \cdot \cos(\alpha)}{l_0 \cdot \cos(\alpha_0)} - 1, \quad \varepsilon_1 = \frac{l}{l_0} - 1 \quad \text{and} \quad \gamma_{12} = 2 \cdot (\alpha - \alpha_0). 
$$

(B.1)

Combining $\varepsilon_L$ and $\varepsilon_T$ with $\varepsilon_1$ yields:

$$
\varepsilon_L = \frac{(1 + \varepsilon_1) \cdot \sin(\alpha)}{\sin(\alpha_0)} - 1 \quad \text{and} \quad \varepsilon_T = \frac{(1 + \varepsilon_1) \cdot \cos(\alpha)}{\cos(\alpha_0)} - 1.
$$

(B.2)

Solving both equalities relatively to $\varepsilon_1$,

$$
\varepsilon_1 = \frac{(1 + \varepsilon_L) \cdot \sin(\alpha_0)}{\sin(\alpha)} - 1 = \frac{(1 + \varepsilon_T) \cdot \cos(\alpha_0)}{\cos(\alpha)} - 1,
$$

(B.3)

and, as $\alpha_0 = \pi/4$ and following the definition of $\gamma_{12}$ in Equation B.1,

$$
\tan(\alpha) = \frac{\varepsilon_L + 1}{\varepsilon_T + 1} \quad \Rightarrow \quad \gamma_{12} = 2 \cdot \tan\left(\frac{\varepsilon_L + 1}{\varepsilon_T + 1}\right) - \frac{\pi}{2}.
$$

(B.4)

In the global coordinate system, only longitudinal stresses ($\sigma_L$) are applied; being $t_0$ and $w_0$ the initial thickness and width of the specimen, and considering the variation of the latter,

$$
\sigma_L = \frac{P}{t_0 \cdot w_0 \cdot (1 + \varepsilon_T)}.
$$

(B.5)

Once $\gamma_{12}$ (or $\alpha$) is known, $\sigma_L$ can be rotated to the local material coordinate system, so shear stresses in material coordinates are defined as:

$$
\tau_{12} = \frac{\sigma_L}{2} \cdot \sin(2\alpha) \quad \text{Eq. B.1} \quad \frac{\sigma_L}{2} \cdot \sin(\gamma_{12} + \pi/2) \quad \text{Eq. B.3} \quad \frac{P}{2 \cdot t_0 \cdot w_0 \cdot (1 + \varepsilon_T) \cdot \cos(\gamma_{12})}.
$$

(B.6)
Appendix C

Estimation of confidence intervals for ratio of means

The effect of recycling on the performance of composites can be assessed by the retention of mechanical properties of the recycled composites relatively to their virgin precursor. The confidence intervals for the retention shown in Figure 3.9 were calculated from Fieller’s theorem \[122\], as described below.

Consider the experimental measurements of a mechanical property \(\chi\) (e.g. stiffness or strength). For each material (recycled and virgin composites, here identified with subscripts \(r\) and \(v\)), the measured average and variance are respectively \(\bar{\chi}\) and \(s^2\), and the sample size is \(N\). The (unknown) expected value and variance of the population are represented as \(\mu\) and \(\sigma^2\); \(\bar{\chi}\) can be assumed as normally distributed.

The retention ratio \(p\) and its estimator (\(\hat{p}\)) are defined as:

\[
p = \frac{\mu_r}{\mu_v} \quad \text{and} \quad \hat{p} = \frac{\bar{\chi}_r}{\bar{\chi}_v}. \tag{C.1}
\]

Let the auxiliary stochastic variable \(d\) be defined as:

\[
d = \bar{\chi}_r - p \cdot \bar{\chi}_v. \tag{C.2}
\]

Being a linear combination of normal variables, \(d\) follows a normal distribution as well, with expected value \(\mu_d = 0\) and unknown variance \(\sigma_d^2\). Standardising,

\[
t = \frac{d - \mu_d}{\hat{\sigma}_d} \sim T_{N_d} \quad \text{with} \quad \begin{cases} \mu_d = 0, \\ \hat{\sigma}_d^2 = \frac{s_r^2}{N_r} + p^2 \cdot \frac{s_v^2}{N_v}, \end{cases} \tag{C.3}
\]

where \(T(N_d)\) represents the t-distribution with \(N_d = N_r + N_v - 2\) degrees of freedom.
Taking the square of Equation C.3 and solving relatively to $p$,

$$
p = \frac{\bar{\chi}_r \cdot \bar{\chi}_v \pm t \cdot \sqrt{s_v^2 \cdot \bar{\chi}_r^2 - t^2 \cdot \frac{s_v^2}{N_v} \cdot \frac{s_r^2}{N_r} + \frac{s_r^2}{N_r} \cdot \bar{\chi}_r^2}}{\bar{\chi}_v^2 - t^2 \cdot \frac{s_v^2}{N_v}}.
$$

Taking the positive root and dividing both numerator and denominator by $\bar{\chi}_v^2$,

$$
p = \frac{\bar{\chi}_r}{g \cdot \bar{\chi}_v} \left( 1 + t \cdot \sqrt{\frac{s_v^2}{N_v} \cdot \frac{1}{\bar{\chi}_v^2} + g \cdot \frac{s_r^2}{N_r} \cdot \frac{1}{\bar{\chi}_r^2}} \right), \quad \text{with} \quad g = 1 - t^2 \cdot \frac{s_v^2}{N_v \cdot \bar{\chi}_v^2}.
$$

Equation C.5 represents a probability distribution for $p$. The $(1 - \alpha)$ confidence interval for the retention of mechanical performance is thus defined as:

$$
p \in \left[ \frac{\bar{\chi}_r}{g \cdot \bar{\chi}_v} \left( 1 + t_{N_d}(\alpha/2) \cdot c_p \right) ; \frac{\bar{\chi}_r}{g \cdot \bar{\chi}_v} \left( 1 + t_{N_d}(1 - \alpha/2) \cdot c_p \right) \right],
$$

with $g = 1 - t^2 \cdot \frac{s_v^2}{N_v \cdot \bar{\chi}_v^2}$ and $c_p = \sqrt{\frac{s_v^2}{N_v \cdot \bar{\chi}_v^2} + g \cdot \frac{s_r^2}{N_r \cdot \bar{\chi}_r^2}}$. (C.6)
Appendix D

Effect of bundle and shear–lag boundary geometry on strength

Table D.1 defines alternative geometries for the shear–lag boundary, taking into account different fibre arrangements, failure paths and free–edge effects.

Matching the perimeter of these different geometries with the corresponding mean bundle strength (Figure D.1) reveals that the largest shear–lag boundary at low–level bundles (QM geometry) yields the strongest bundles throughout the whole hierarchy. On the contrary, a large boundary at high–level bundles (HI geometry) yields no strengthening effect. Free–boundary effects (QB vs. QI geometries) affect small bundles only.

All these observations support that (i) the shear–lag boundary plays a critical role for the strength of small–scale bundles, while (ii) the weakest link theory dominates size effects for large–scale bundles (see Section 6.4.1 for further discussion).
Table D.1: Alternative definitions of the shear–lag boundary.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Description and perimeter $C^{[i]}$</th>
<th>Diagram</th>
</tr>
</thead>
</table>
| QM   | Square fibre arrangement, preferential matrix failure:  

\[ C_{\text{QM}}^{[i]} = 4 \cdot \sqrt{n^{[i]}} \cdot l_q \quad \text{with} \quad l_q = \frac{\sqrt{\pi} \cdot \phi^f}{2 \cdot \sqrt{V_f}} \]  

\[(D.1)\]  |
| QI   | Square fibre arrangement, preferential interfacial failure (default configuration, Equation [6.5] in Section [6.2.1]):  

\[ C_{\text{QI}}^{[i]} = 3 \cdot C^f + 4 \left[ \left( \sqrt{n^{[i]}} - 1 \right) \cdot s_q + \left( \sqrt{n^{[i]}} - 2 \right) \cdot \frac{C^f}{2} \right] \]  

\[(D.2)\]  |
| QS   | Square fibre arrangement, shortest failure path:  

\[ C_{\text{QS}}^{[i]} = C^f + 4 \cdot \left( \sqrt{n^{[i]}} - 1 \right) \cdot l_q \]  

\[(D.3)\]  |
| HI   | Hexagonal fibre arrangement, preferential interfacial failure (fractal boundary, hence initial recursive relation):  

\[ C_{\text{HI}}^{[i_H]} = 6 \cdot \left( \frac{C_{\text{HI}}^{[i_H-1]} + C^f}{2} + s_{\text{HI}} \right) \quad \text{with} \quad s_{\text{HI}} = \left( \frac{\sqrt{\pi}}{2 \sqrt{3 V_f}} - 1 \right) \cdot \phi^f \]  

\[ C_{\text{HI}}^{[i_H]} = 3^n \cdot C^f + \frac{3^n - 1}{2} \cdot \left( C^f + 6 \cdot s_{\text{HI}} \right) \]  

\[(D.4)\]  |
| QB   | Square fibre arrangement, preferential interfacial failure, considering free–edge effects in levels $i^{\text{max}} - 2$ and $i^{\text{max}} - 1$ (configuration QI should be used up to level $i^{\text{max}} - 3$):  

\[ C_{\text{QB,edge}}^{[i^{\text{max}}-1]} = \sqrt{2} \cdot n^{[i]} \left( s_q + \frac{C^f}{2} \right) \quad \text{with} \quad s_q = \left( \frac{\sqrt{\pi}}{2 \sqrt{V_f}} - 1 \right) \cdot \phi^f \]  

\[(D.5)\]  |
|      | $C_{\text{QB,corner}}^{[i]} \equiv C_{\text{HI}}^{[i]} = 3 \cdot \left( 3 \cdot \log_3 \sqrt{n^{[i]}} - 1 \right) \cdot s_{\text{HI}} + \left( 3 \cdot \log_3 \sqrt{n^{[i]}} - 1 \right) \cdot \frac{C^f}{2} \]  

\[(D.4)\]  |
|      | $C_{\text{QB,corner}}^{[i]} = \frac{C^f}{4} + 2 \cdot \left( \sqrt{n^{[i]}} - \frac{1}{2} \right) \cdot \left( s_q + \frac{C^f}{2} \right) \]  

\[(D.6)\]  |
Effect of bundle and shear–lag boundary geometry on strength

Figure D.1: Bundle strength size effect for several shear–lag geometries.
Appendix E

Generalisation of the weakest link theory to non-uniform stress fields

E.1 Piecewise generic stress field

The Weakest Link Theory (WLT) can be generalised to non-uniform stress fields (required for Chapters 6 and 7). Consider a chain composed by $n$ elements, each of length $l_r$ and under a uniform tensile stress $\sigma_j$, $j = \{1 \ldots n\}$. The chain (of length $l_n = n \cdot l_r$) is subjected to a piecewise constant but otherwise generic stress field $\Phi$, with survival probability $S_{\Phi,n}$ related to those of the uniformly loaded element ($S_{U,r}$) and the chain with same length ($S_{U,n}$):

$$S_{\Phi,n} = \prod_{j=1}^{n} S_{U,r}(\sigma_j) \implies \ln \left[ S_{\Phi,n} \right] = \sum_{j=1}^{n} \frac{l_r}{l_n} \ln \left[ S_{U,r}(\sigma_j) \right]. \quad (E.1)$$

This relation will be applied to the stress fields shown in Figure E.1.

E.2 Pure linear stresses

Consider a fibre or bundle of length $l$ under a pure linear stress field (Figure E.1(a)), defined as:

$$\sigma_L(x) = \frac{\sigma_\infty}{l} \cdot x, \quad x \in [0, l]. \quad (E.2)$$
Dividing the chain into \( n \to \infty \) links of length \( \Delta x = l/n \), the survival probability \( S_L \) of the chain under \( \sigma_L(x) \) relates to that of a uniformly loaded chain \( (S_U) \) by:

\[
\ln \left[ S_L \right] = \lim_{n \to \infty} \frac{\Delta x}{l} \sum_{j=1}^{n} \ln \left[ S_U(\sigma_L(x_j)) \right] = \frac{1}{l} \int_{x=0}^{l} \ln \left[ S_U(\sigma_L(x)) \right] \, dx .
\]  

(E.3)

Changing the integration variable from \( x \) to \( \sigma_L \) (using the field in Equation (E.2)),

\[
\ln \left[ S_L(\sigma^\infty) \right] = \frac{1}{\sigma^\infty} \int_{\sigma_L=0}^{\sigma^\infty} \ln \left[ S_U(\sigma_L) \right] \, d\sigma_L .
\]

(E.4)

### E.3 Linear stress concentrations

A similar procedure as followed in the previous case can be applied to a linear stress field, defined by the variable remote stress \( \sigma^\infty \) and fixed stress concentration factor \( k \) (Figure E.1(b)):

\[
\sigma_K(x) = \sigma^\infty + \frac{\sigma^\infty \cdot (k-1)}{l} \cdot x , \quad x \in [0, l] .
\]

(E.5)

The survival probability \( S_K \) of the chain under \( \sigma_K(x) \) then verifies:

\[
\ln \left[ S_K(\sigma^\infty) \right] = \begin{cases} 
\frac{1}{\sigma^\infty \cdot (k-1)} \int_{\sigma_L=\sigma^\infty}^{k \cdot \sigma^\infty} \ln \left[ S_U(\sigma_L) \right] \, d\sigma_L & \text{if } k > 1 \\
\ln \left[ S_U(\sigma^\infty) \right] & \text{if } k = 1 .
\end{cases}
\]

(E.6)

Combining Equations (E.4) and (E.6), \( S_K(\sigma^\infty) \) can also be defined by:

\[
\ln \left[ S_K(\sigma^\infty) \right] = \begin{cases} 
\frac{k \cdot \ln \left[ S_L(k \cdot \sigma^\infty) \right] - \ln \left[ S_L(\sigma^\infty) \right]}{k-1} & \text{if } k > 1 \\
\ln \left[ S_U(\sigma^\infty) \right] & \text{if } k = 1 .
\end{cases}
\]

(E.7)
Generalisation of the weakest link theory to non-uniform stress fields

This analysis is valid regardless of the shape of the strength distribution $S_U(\sigma^\infty)$. For the particular case of a Weibull distribution with parameters $m$ and $\sigma_0$,

$$\ln \left[ S_K(\sigma^\infty) \right] = C_K \cdot \ln \left[ S_U(\sigma^\infty) \right] \Rightarrow S_K(\sigma^\infty) = \exp \left[ -C_K \cdot \left( \frac{\sigma^\infty}{\sigma_0} \right)^m \right],$$

where $C_K = \frac{k^{m+1} - 1}{(m+1)(k-1)}$. \hfill (E.8)

E.4 Triangular stresses with constant slope

Consider now a triangular stress field with constant slope $\lambda$, with maximum stress $\sigma^\infty$ (Figure [E.1(c)]); this is similar to the pure linear field (Figure [E.1(a)]), but now extended over a (variable) length $l_\lambda$. The corresponding survival probability $S_\lambda$ of the chain can be defined as:

$$\ln \left[ S_\lambda(\sigma^\infty) \right] = \frac{l_\lambda}{l_\tau} \ln \left[ S_{L,\tau}(\sigma^\infty) \right], \quad \text{where} \quad l_\lambda = \frac{2 \cdot \sigma^\infty}{\lambda}. \hfill (E.9)$$

Following Equation [E.4], this can also be expressed through the survival probability under uniform stresses $S_U$:

$$\ln \left[ S_\lambda(\sigma^\infty) \right] = \frac{2}{\lambda \cdot l_\tau} \cdot \int_{\sigma=0}^{\sigma^\infty} \ln \left[ S_{U,\tau}(\sigma) \right] \, d\sigma. \quad \hfill (E.10)$$

E.3
Appendix F

Physically–based derivation of the hierarchical scaling law

The scaling law in Equation 6.8 can be derived from the physically reasonable sequences of events \( E_1, E_2 \) and \( E_3 \) defined in Section 6.2.3. This requires extending the concept of stochastic strength of a fibre segment to the linear stress concentrations field that occurs near a fibre break (Figure 6.3).

Consider the stress field after failure of segment \( A_1 \) in a level–1 bundle (Figure 6.3(a)). Let \( X_{B_2}^{U,e} \) be the stochastic strength of the fibre segment \( B_2 \) under uniform stresses (indicated by the subscript \( U \)); \( B_2 \) fails if \( X_{B_2}^{U,e} \leq \sigma^\infty \). Similarly, \( X_{B_1}^{E_i,k,e} \) is the stochastic strength of the segment \( B_1 \) under linear stress concentrations, characterised by a variable remote stress \( \sigma^\infty \) and constant factor \( k \); \( B_1 \) fails if \( X_{B_1}^{E_i,k,e} \leq \sigma^\infty \).

The sequences of events leading to bundle failure (\( E_1, E_2 \) and \( E_3 \)) can now be formally defined as:

\( E_1 \): **Unstable bundle failure** at \( \sigma^\infty = X_{U}^{[1]} \). All 4 segments survive the uniform stress field for \( \sigma^\infty < X_{U}^{[1]} \). \( A_1 \) fails when \( \sigma^\infty = X_{U}^{[1]} \), triggering failure of \( B_1 \) due to stress concentrations. Formally,

\[
E_1 = \{ \sigma^\infty : [X_{U,e}^{A_1} = \sigma^\infty] \land [X_{U,e}^{A_2} > \sigma^\infty] \land [X_{U,e}^{B_1} > \sigma^\infty \land X_{k,e}^{B_1} \leq \sigma^\infty] \land [X_{U,e}^{B_2} > \sigma^\infty] \}.
\]

\( E_2 \): **Stable bundle failure due to stress concentrations** at \( \sigma^\infty = X_{U}^{[1]} \). \( A_1 \) fails when \( \sigma^\infty = X_{U,e}^{A_1} < X_{U,e}^{[1]} \), and (from the assumption \( A(ii) \)) \( A_2 \) survives \( \sigma^\infty \leq X_{U,e}^{A_2} \). \( B_2 \) withstands the stress field for \( \sigma^\infty \leq X_{U,e}^{[1]} \), but \( B_1 \) fails under stress concentrations.
Appendix F

at $\sigma^\infty = X_{u,e}^{[1]}$. Formally,

$$E_2 = \left\{ \sigma^\infty : [X_{u,e}^{A_1} < \sigma^\infty] \land [X_{u,e}^{A_2} > X_{u,e}^{A_1}] \land [X_{K,e}^{E_1} = \sigma^\infty] \land [X_{u,e}^{E_2} > \sigma^\infty] \right\}. \quad (F.2)$$

$E_3$: Stable bundle failure due to independent fibre flaws at $\sigma^\infty = X_{u,e}^{[1]}$. $A_1$ fails when $\sigma^\infty = X_{u,e}^{A_1} < X_{u,e}^{[1]}$, and $A_2$ survives $\sigma^\infty \leq X_{u,e}^{A_1}$. $B_1$ withstands the stress concentrations field for $\sigma^\infty \leq X_{u,e}^{[1]}$, but $B_2$ fails under uniform stresses at $\sigma^\infty = X_{u,e}^{[1]}$, either due to a stress increment $d\sigma^\infty$ or domain extension $dl_e(\sigma^\infty)$ (from Equation [6.6]):

$$E_3 = \left\{ \sigma^\infty : [X_{u,e}^{A_1} < \sigma^\infty] \land [X_{u,e}^{A_2} > X_{u,e}^{A_1}] \land [X_{K,e}^{E_1} > \sigma^\infty] \land [X_{u,e}^{E_2} = \sigma^\infty] \right\}. \quad (F.3)$$

The events above assume the weakest segment in the control length is $A_1$ which (without loss of generality) represents 1/4 of the cases. Therefore, the level–[1] bundle strength distribution within the control length is:

$$\Pr(X_{u,e}^{[1]} = \sigma^\infty) = 4 \cdot \left[ \Pr(E_1) + \Pr(E_2) + \Pr(E_3) \right]. \quad (F.4)$$

The probability for each sequence of events $E_1$, $E_2$ and $E_3$ is defined from the single–fibre strength distributions. All fibre segments have independent and identically distributed strengths; therefore, failure probabilities (cumulative distribution functions) under uniform stresses and under linear stress concentrations are represented respectively as $F_{u,e}^{[0]}(\sigma^\infty) = \Pr(X_{u,e}^{E_2} \leq \sigma^\infty)$ and $F_{K,e}^{[0]}(\sigma^\infty) = \Pr(X_{K,e}^{E_1} \leq \sigma^\infty)$. Consequently:

$$\begin{align*}
\Pr(E_1) & \overset{\text{Eq.}[F.3]}{=} \int_{\sigma^\infty} dF_{u,e}^{[0]}(\sigma^\infty) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ F_{K,e}^{[0]}(\sigma^\infty) - F_{u,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] \\
\Pr(E_2) & \overset{\text{Eq.}[F.2]}{=} \int_{\sigma^\infty} f_{\sigma^\infty} \left( \left[ dF_{u,e}^{[0]}(\sigma) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] \right] \cdot \left[ dF_{K,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] ight) = \\
& = \left[ F_{u,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] / 2 \cdot \left[ dF_{K,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] \\
\Pr(E_3) & \overset{\text{Eq.}[F.3]}{=} \int_{\sigma^\infty} F_{u,e}^{[0]}(\sigma^\infty) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma^\infty) \right] / 2 \cdot \left[ 1 - F_{K,e}^{[0]}(\sigma^\infty) \right] \cdot \left[ dF_{u,e}^{[0]}(\sigma^\infty) \right]. \quad (F.5)
\end{align*}$$

The level–[1] bundle strength distribution $F_{u,e}^{[1]}(\sigma^\infty)$ is calculated by replacing the probabilities above in Equation [F.4] and integrating $\Pr(X_{u,e}^{[1]} = \sigma)$ for all $\sigma \leq \sigma^\infty$:

$$F_{u,e}^{[1]}(\sigma^\infty) = 4 \cdot \int_{\sigma^\infty} dF_{u,e}^{[0]}(\sigma) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] \cdot \left[ F_{K,e}^{[0]}(\sigma) - F_{u,e}^{[0]}(\sigma) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] + \\
+ \ F_{u,e}^{[0]}(\sigma) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] / 2 \cdot \left[ dF_{K,e}^{[0]}(\sigma) \right] \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] + \\
+ \ F_{u,e}^{[0]}(\sigma) \cdot \left[ 1 - F_{u,e}^{[0]}(\sigma) \right] / 2 \cdot \left[ 1 - F_{K,e}^{[0]}(\sigma) \right] \cdot \left[ dF_{u,e}^{[0]}(\sigma) \right]. \quad (F.6)$$

F.2
Recalling that $F^N dF = d(F^{N+1})/(N + 1)$ and re-arranging the equation (omitting the integration variable $\sigma$ and the single–fibre superscript $[0]$ for readability) yields:

$$F_{[1]}^{[\mu,c]}(\sigma) = -F_{[0]}^{[\mu,e]}(\sigma)^4 + 2 \cdot F_{[0]}^{[\mu,e]}(\sigma)^3 + 2 \cdot \left[ \int F_{[3]}^{[\kappa,e]} d(F_{[3]}^{[\mu,e]}) + \int F_{[3]}^{[\mu,e]} dF_{[\kappa,e]} \right]_{\sigma=0}^\sigma +$$

$$- 6 \cdot \left[ \int F_{[2]}^{[\kappa,e]} d(F_{[2]}^{[\mu,e]} + \int F_{[2]}^{[\mu,e]} dF_{[\kappa,e]} \right]_{\sigma=0}^\sigma.$$

Integrating by parts each pair of integrals results into:

$$F_{[1]}^{[\mu,c]}(\sigma) = -F_{[0]}^{[\mu,c]}(\sigma)^4 + 2 \cdot F_{[0]}^{[\mu,c]}(\sigma)^3 + 2 \cdot F_{[0]}^{[\mu,c]}(\sigma)^3 \cdot F_{[0]}^{[\kappa,e]}(\sigma) +$$

$$- 6 \cdot F_{[0]}^{[\mu,e]}(\sigma)^2 \cdot F_{[0]}^{[\kappa,e]}(\sigma) + 4 \cdot F_{[0]}^{[\mu,e]}(\sigma) \cdot F_{[0]}^{[\kappa,e]}(\sigma). \quad (F.7)$$

Converting all distributions to survival probabilities, $S(\sigma) = 1 - F(\sigma)$, this corresponds to the scaling law proposed in Equation 6.8 of Section 6.2.3.
Appendix G

Proof of asymptotic behaviour for strength distributions

G.1 Right tail asymptote

Assuming single–fibre strength follows a Weibull distribution (thus $\ln(S_{0,k}^{[0]}) = C_k \ln(S_{0,r}^{[0]})$ from Equation E.8), applying the scaling law (Equation 6.14) to $i = 0$ yields:

\[
\ln(S_{1,u,r}^{[1]}) = 2 \cdot \ln(S_{0,u,r}^{[0]}) + \frac{l_x}{2 \cdot l_x^{[0]}} \cdot \ln \left( 1 + 2 \cdot \left[ \frac{S_{0,u,r}^{[0]}}{C_k - 3} C_k - 3 \right]^{\frac{1}{C_k}} - 2 \cdot \left[ \frac{S_{0,u,r}^{[0]}}{C_k - 1} C_k - 1 \right]^{\frac{1}{C_k}} \right) - \frac{l_x}{2 \cdot l_x^{[0]}} \cdot \ln \left( 2 \cdot \left[ \frac{S_{0,u,r}^{[0]}}{C_k - 1} C_k - 1 \right]^{\frac{2}{C_k}} - 2 \cdot \left[ \frac{S_{0,u,r}^{[0]}}{C_k - 1} C_k - 1 \right]^{\frac{2}{C_k}} \right) =
\]

\[
(G.1)
\]

For large stresses, $S_{0,r}^{[0]}(\sigma^\infty) \to 0$ and $l_x^{[0]} \to \infty$ (Equations 6.6 and 6.9), so the contribution of the terms highlighted above vanishes (as long as exponents are positive). Therefore,

\[
\lim_{\sigma^\infty \to \infty} \ln(S_{0,u,r}^{[1]}(\sigma^\infty)) = \psi \cdot \ln(S_{0,u,r}^{[0]}(\sigma^\infty)) \Rightarrow \lim_{\sigma^\infty \to \infty} S_{0,u,r}^{[1]}(\sigma^\infty) = \exp \left[ -\psi \cdot \left( \frac{\sigma^\infty}{\sigma_0^{[0]}} \right)^m \right],
\]

with

\[
\psi = \begin{cases} 
2, & C_k \geq 3, \\
\frac{1 + C_k}{2}, & C_k < 3.
\end{cases}
\]

(G.2)

The right tail asymptote of $S_{0,u,r}^{[1]}$ is recognisably a Weibull distribution. Consequently, the same argument can be applied recursively up to any level–[i] bundle, whose right tail will then tend asymptotically to a Weibull distribution as well ($\psi$ as defined
above):
\[
\lim_{\sigma^\infty \to \infty} \ln \left[ S_{U,r}^{[i]}(\sigma^\infty) \right] = \psi \ln \left[ S_{U,r}^{[i-1]}(\sigma^\infty) \right] \Rightarrow \lim_{\sigma^\infty \to \infty} S_{U,r}^{[i]}(\sigma^\infty) = \exp \left[ -\psi_i \frac{\sigma^\infty}{\sigma^0_0} \right]^m.
\]

(G.3)

\section*{G.2 Left tail asymptote}

The single–fibre survival probabilities at the effective recovery length can be expressed as (Equations 6.6, 6.9 and 6.10):
\[
S_{U,e}^{[0]}(\sigma^\infty) = \exp(-u^{[0]}) \quad \text{and} \quad S_{K,e}^{[0]}(\sigma^\infty) = \exp(-C_K \cdot u^{[0]}), \quad \text{with} \quad u^{[0]} = \frac{l_e^{[0]}}{l_e} \left( \frac{\sigma^\infty}{\sigma^0_0} \right)^m.
\]

(G.4)

According to the scaling law in Equation 6.8, the level–[1] survival probability in the control length becomes:
\[
S_{U,c}^{[1]}(\sigma^\infty) = \exp \left[ -4 \cdot u^{[0]} \right] + 2 \cdot \exp \left[ -(1 + C_K) \cdot u^{[0]} \right] - 2 \cdot \exp \left[ -(3 + C_K) \cdot u^{[0]} \right].
\]

(G.5)

Taking the limit for low stresses, and using the 2nd order Taylor expansion of the exponential function — \( \lim_{\psi \to 0} \exp(\psi) = 1 + \psi + \psi^2/2 \) — then:
\[
\lim_{\sigma^\infty \to 0} S_{U,c}^{[1]}(\sigma^\infty) = \lim_{\sigma^\infty \to 0} \exp \left[ -4 \cdot C_K \cdot u^{[0]} \right] = \lim_{\sigma^\infty \to 0} \exp \left[ -4 \cdot C_K \cdot \frac{l_e^{[0]}}{l_e} \cdot \frac{\sigma^\infty}{\sigma^0_0} \right]^2 \cdot \left( \frac{\sigma^\infty}{\sigma^0_0} \right)^{2-m}.
\]

(G.6)

Scaling from \( l_e^{[1]} \) (Equation 6.7) to the reference length (WLT as in Equation 6.1),
\[
\lim_{\sigma^\infty \to 0} S_{U,r}^{[1]}(\sigma^\infty) = \exp \left[ -2 \cdot C_K \cdot \frac{l_e^{[0]}}{l_r} \cdot \frac{\sigma^\infty}{\sigma^0_0} \right] = \exp \left[ -4 \cdot C_K \cdot \frac{A^f \cdot \sigma^0_f}{l_r \cdot C^{(0)} \cdot \tau_{SL}} \cdot \frac{\sigma^\infty}{\sigma^0_0} \right]^{2-m+1}.
\]

(G.7)

This shows that the left tail asymptote of a level–[1] strength distribution preserves the Weibull nature of the single–fibre distribution (although with different parameters). Consequently, the same argument can be applied recursively up to any level–[i] bundle, hence its left tail Weibull parameters \( m_{LTA}^{[i]} \) and \( \sigma_{LTA}^{[i]} \) are related to those of a level–[i – 1] bundle by:

G.2
Proof of asymptotic behaviour for strength distributions

\[ m_{LTA}^{[i]} = 2 \cdot m_{LTA}^{[i-1]} + 1 \quad \text{and} \quad \sigma_{0,LTA}^{[i]} = \sigma_{0,LTA}^{[i-1]} \left( 4 \cdot C_{K,LTA}^{[i-1]} \frac{\eta^{[i-1]} \cdot A_f \cdot \sigma_{0,LTA}^{[i-1]}}{C^{[i-1]} \cdot \tau_{SL} \cdot l_f} \right)^{-1/m_{LTA}^{[i]}} \]

with \( C_{K,LTA}^{[i]} = \frac{k^{m_{LTA}^{[i]}} + 1}{(m_{LTA}^{[i]} + 1) \cdot (k - 1)} \) and \( m_{LTA}^{[0]} = m \), \( \sigma_{0,LTA}^{[0]} = \sigma_f \). (G.8)
Appendix H

Stress concentrations and equilibrium crack length before level–[i] failure of a fractal fracture surface

The hierarchical failure process considered in the development of the toughness model (defined in Section 7.2.2 and Figure 7.4) implies that, as failure progresses down the hierarchy, fibres and bundles bridging the two fracture faces feel progressively higher stress concentrations. Consider a surface immediately before level–[i] failure; each surviving level–[i] bundle (with \( n^i \) fibres) is surrounded by \( c_G^i - 1 \) partially broken ones; each of the latter contains a level–[i − 1] surviving bundle (with \( n^{i-1} \) fibres), and \( c_G^i - 1 \) partially broken ones. Repeating this recursively down to level [0] (which then contributes with \( (c_G^0 - 1)^i \) bridging fibres), the fraction of surviving fibres is:

\[
1 \cdot c_G^i + (c_G^i - 1) \cdot c_G^{i-1} + (c_G^i - 1)^2 \cdot c_G^{i-2} + \cdots + (c_G^i - 1)^i \cdot 1 = \frac{1}{c_G} \cdot \sum_{j=0}^{i} \left( \frac{c_G - 1}{c_G} \right)^j .
\]  

(H.1)

The sum in the right hand side of Equation (H.1) represents a geometric series with ratio \( r = (c_G - 1)/c_G \), and sum equal to \( \Sigma = (1 - r^{i+1})/(1 - r) \). Assuming the remote load is equally shared by all surviving fibres, the stress concentration factor seen by a level–[i] bundle prior to its failure is then:

\[
k_G^{[i]} = \frac{1}{1 - \left( 1 - \frac{1}{c_G} \right)^{i+1}} .
\]  

(H.2)
Appendix H

The debonding distance of a level–-[i] bridging bundle under the remote stress $\sigma^\infty$ (Figure 7.5 in Section 7.2.2.2) can be calculated through fracture mechanics. Let $U$ be the internal energy, $W^\infty$ the work of the remote load $P$, $W_\mu$ the work done by friction forces, and $G_{sl}$ the debonding fracture toughness. Under load control, the equilibrium debonding distance $a^{[i]}$ verifies:

$$\frac{1}{C^{[i]}} \left[ - \frac{dU}{da^{[i]}} + \frac{dW^\infty}{da^{[i]}} + \frac{dW_\mu}{da^{[i]}} \right] = G_{sl}.$$  \hspace{1cm} (H.3)

Neglecting the contribution of matrix deformation, the internal energy of the linear–
elastic fibres (modulus $E^f$) in the (half–) domain $x \in [0, \ell]$ is:

$$U = \frac{A^{[i]}}{2 \cdot E^f} \cdot \int_{x=0}^{\ell} \left[ \sigma^A(x) \right]^2 + (c_G - 1) \cdot \left[ \sigma^B(x) \right]^2 \, dx.$$  \hspace{1cm} (H.4)

Replacing the stress fields as in Equation 7.6, differentiating and re-arranging,

$$\frac{dU}{da^{[i]}} = \frac{c_G \cdot A^{[i]}}{2 \cdot (c_G - 1) \cdot E^f} \cdot \left[ (k_G^{[i]} - 1) \cdot \sigma^\infty - \lambda_\mu^{[i]} \cdot a^{[i]} \right]^2.$$  \hspace{1cm} (H.5)

The work contribution from the remote load $P$ (with remote displacement $u^A(\ell)$) is:

$$\frac{dW^\infty}{da^{[i]}} = P \cdot \frac{du^A(\ell)}{da^{[i]}} , \text{ where } P = c_G A^{[i]} \sigma^\infty \text{ and } u^A(\ell) = \frac{1}{E^f} \int_{x=0}^{\ell} \sigma^A(x) \, dx.$$  \hspace{1cm} (H.6)

Simplifying,

$$\frac{dW^\infty}{da^{[i]}} = \frac{c_G \cdot A^{[i]}}{E^f} \cdot \sigma^\infty \cdot \left[ (k_G^{[i]} - 1) \cdot \sigma^\infty - \lambda_\mu^{[i]} \cdot a^{[i]} \right].$$  \hspace{1cm} (H.7)

The energy dissipated by the constant frictional stresses $\tau_\mu$ is:

$$W_\mu = -\tau_\mu \cdot C^{[i]} \cdot \int_{x=0}^{a^{[i]}} \|u(x)\| \, dx ,$$  \hspace{1cm} (H.8)

where $\tau_\mu \cdot C^{[i]} = \lambda_\mu^{[i]} \cdot A^{[i]}$ (Equation 7.7) and the displacement jump is:

$$\|u(x)\| = u^B(x) - u^A(x) = \frac{1}{E^f} \cdot \int_{\xi=x}^{a^{[i]}} \sigma^A(\xi) - \sigma^B(\xi) \, d\xi .$$  \hspace{1cm} (H.9)

Using the stress field in Equation 7.6,

$$\|u(x)\| = \frac{c_G \cdot (x - a^{[i]})}{(c_G - 1) \cdot E^f} \cdot \left[ (k_G^{[i]} - 1) \cdot \sigma^\infty - \frac{1}{2} \cdot \lambda_\mu^{[i]} \cdot (x + a^{[i]}) \right].$$  \hspace{1cm} (H.10)
and thus differentiating Equation \[H.8\] yields:

\[
\frac{dW_i}{da[i]} = -\frac{c_G \cdot A[i]}{(c_G - 1) \cdot E^f \cdot \lambda_{ii} \cdot a[i]} \cdot \left[ (k_{ii}^i - 1) \cdot \sigma^\infty - \lambda_{ii} \cdot a[i] \right].
\] (H.11)

Replacing Equations [H.5], [H.7] and [H.11] in Equation [H.8] and simplifying,

\[
\frac{c_G \cdot A[i]}{2 \cdot E^f \cdot C[i]} \cdot \frac{(2 \cdot c_G - k_{ii}^i - 1) \cdot \sigma^\infty - \lambda_{ii} \cdot a[i]}{(c_G - 1) \cdot \left[ (k_{ii}^i - 1) \cdot \sigma^\infty - \lambda_{ii} \cdot a[i] \right]} = G_{SL}.
\] (H.12)

Taking the smallest solution of this quadratic equation in \(a[i]\) (where the left-hand side — a measure of the energy release rate — decreases with increasing \(a[i]\)), the equilibrium crack length at the remote stress \(\sigma^\infty\) is:

\[
a[i](\sigma^\infty) = \frac{1}{\lambda_{ii}^i} \cdot \left[ (c_G - 1) \cdot \sigma^\infty - \sqrt{\left( (c_G - k_{ii}^i) \cdot \sigma^\infty \right)^2 + \frac{2 \cdot (c_G - 1) \cdot E^f \cdot G_{SL} \cdot C[i]}{c_G \cdot A[i]} \cdot \lambda_{ii} \cdot a[i]} \right].
\] (H.13)
Appendix I

Mode-II toughness for debonding

The model developed in Chapter 8 requires the in-situ mode–II toughness $G_{SL}$, associated with debonding between a fibre or bundle and the surrounding material.

The dissipation mechanisms associated with $G_{SL}$ are similar to those contributing to the mode–II delamination toughness ($G_{IIc}$), measured for instance through End Notched Flexure (ENF) tests. However, while the former considers an idealised microscopic texture of the debonded surface (see geometries defined in Appendix D), the latter is usually normalised by the macroscopic (smoothed) delaminated area. The toughnesses $G_{SL}$ and $G_{IIc}$ are thus related by the respective perimeters $C_{micro}$ and $C_{macro}$:

$$G_{SL} = \alpha \cdot G_{IIc} \quad \text{where} \quad \alpha = \frac{C_{macro}}{C_{micro}}.$$  \hspace{1cm} (I.1)

Assuming that debonding follows preferentially the fibre–matrix interface (see Appendix D), and depending on whether fibres are in a quadrangular (superscript $QI$) or hexagonal (superscript $HI$) arrangement, the factor $\alpha$ is:

$$\alpha^{QI} = \frac{s_q + \phi f}{s_q + \frac{\pi}{2} \cdot \phi f} \quad \text{Eq. 6.5} \quad \frac{1}{1 - 2 \cdot \sqrt{\frac{Vf}{\pi}} + \sqrt{Vf \cdot \pi}},$$

$$\alpha^{HI} = \frac{s_h + \phi f}{s_h + \frac{\pi}{2} \cdot \phi f} \quad \text{Eq. D.1} \quad \frac{1}{1 - \sqrt{\frac{2 \cdot \sqrt{3} \cdot Vf}{\pi}} + \sqrt{\frac{3 \cdot Vf}{2} \cdot \pi}}.$$  \hspace{1cm} (I.2)

Because $C_{macro} \leq C_{micro}$, the in-situ toughness $G_{SL}$ is smaller than the macroscopic $G_{IIc}$. 

I.1
Appendix J

Frictional stresses during pull–out

The models presented in Chapters 7 and 8 depend on the in-situ pull–out frictional stress ($\tau_\mu$). Considering Coulomb friction,

$$\tau_\mu = p \cdot \mu,$$

where $p$ is the fibre–matrix interfacial compressive stress and $\mu$ is the friction coefficient. \hfill (J.1)

Frictional stresses are usually measured in model composites, with an extremely high matrix content (e.g. Single–Fibre Pull–Out (SFPO) tests, Chapter 5). In this case, matrix contraction around the fibre interface is not representative of that in a real composite (where $V_f \approx 60\%$), hence it is necessary to find a relation between the frictional stresses in both cases.

Consider the two–cylinders model in Figure J.1(a) representing a fibre (diameter $\phi^f$) surrounded by a matrix ring (with external diameter $\phi^m = \phi^f / \sqrt{V_f}$). The curing process induces stress–free deformations represented by $\varepsilon_{\Delta T}$ and $\varepsilon_{\Delta T}^m$; these are different due to the mismatch of thermal expansion coefficients in the two constituents, and to the chemical contractions of the matrix.

This mismatch generates elastic stresses in the system to ensure compatibility of radial deformation between fibres and matrix at their interface, represented by $\varepsilon_{\theta}(\phi^f / 2)$. Considering only radial ($r$) and circumferential ($\theta$) stresses (hence neglecting Poisson’s effects due to loading in the axial direction), a linear thermo–elastic analysis yields:

$$\varepsilon_{\theta}^r(\phi^f / 2) = \varepsilon_{\theta}^m(\phi^f / 2) \Rightarrow$$

$$\Rightarrow \varepsilon_{\Delta T} + \frac{\sigma_{\theta}^r(\phi^f / 2)}{E_f^2} - \nu_{21} \cdot \frac{\sigma_{r}^r(\phi^f / 2)}{E_f^2} = \varepsilon_{\Delta T}^m + \frac{\sigma_{\theta}^m(\phi^f / 2)}{E_m^2} - \nu_m \cdot \frac{\sigma_{r}^m(\phi^f / 2)}{E_m^2}. \hfill (J.2)$$

J.1
Here the matrix is isotropic (Young’s modulus $E^m$, Poisson’s ration $\nu^m$), while the fibre is transversely orthotropic (transverse elastic modulus $E^f_2$ and Poisson’s ratio $\nu^f_{23}$). Radial ($\sigma_r$) and circumferential ($\sigma_\theta$) stresses are related by Lamé’s equations for thick–walled cylinders of internal radius $r_i$ and external radius $r_e$, under internal ($p_i$) and external ($p_e$) pressure,

$$
\begin{align*}
\sigma_r(r) &= C_0 + C_1 \cdot \frac{1}{r^2} \\
\sigma_\theta(r) &= C_0 - C_1 \cdot \frac{1}{r^2}
\end{align*}
$$

with

$$
\begin{align*}
C_0 &= \frac{p_i \cdot r_i^2 - p_e \cdot r_e^2}{r_e^2 - r_i^2} \\
C_1 &= \frac{r_i^2 \cdot r_e^2 \cdot (p_e - p_i)}{r_e^2 - r_i^2}.
\end{align*}
$$

The boundary conditions are represented in Figure J.1(a). The interference pressure at the fibre–matrix interface is $p$, and no external pressure is applied to the matrix ring. This is valid both for the SFPO test (with $\phi^m \gg \phi^f$), and as an axi–symmetric representative cell of a composite with the specified $V^f$ (as the fibre–matrix cylinder must be in equilibrium with the homogenised surrounding). Applying Equation J.3 to the model in Figure J.1(a) yields:

$$
\sigma_r^f(\phi^f/2) = \sigma_\theta^f(\phi^f/2) = \sigma_m^r(\phi^f/2) = -p, \quad \sigma_m^\theta(\phi^f/2) = p \cdot \frac{1 + V^f}{1 - V^f}.
$$

Replacing these in Equation J.2 and solving to $p$ results in:

$$
p = \frac{(-\varepsilon^m_{\Delta T} + \varepsilon_{\Delta T}) \cdot E^2 \cdot E^m \cdot (1 - V^f)}{E^f_2 \cdot (1 + \nu^m) + E^m \cdot (1 - \nu^f)_{23} + V^f \cdot \{E^f_2 \cdot (1 - \nu^m) - E^m \cdot (1 - \nu^f)_{23}\}}.
$$

Figure J.1: Model for determination of in-situ frictional stresses. Nominal inputs are $E^m = 4$ GPa, $\nu^m = 0.35$, $E^f_2 = 15$ GPa, $\nu^f_{23} = 0.20$ and $V^f = 60\%$; nominal outputs are highlighted as ◆.
In a SFPO test, \( V^f \to 0 \); let the interfacial stress in this case be represented as \( p_0 \). The relation between the latter and the interfacial pressure in a generic composite with fibre content \( V^f \) is:

\[
p = \xi \cdot (1 - V^f) \cdot p_0
\]

where

\[
\xi = \frac{E_f^2 \cdot (1 + \nu_m) + E_m \cdot (1 - \nu_{23}^f)}{E_f^2 \cdot (1 + \nu_m) + E_m \cdot (1 - \nu_{23}^f) + V^f \cdot [E_f^2 \cdot (1 - \nu_m) - E_m \cdot (1 - \nu_{23}^f)]}.
\]

For reasonable values of matrix properties, \( \xi \) is nearly independent of \( E_f^2 \) and \( \nu_{23}^f \) (Figure J.1(b)); this is particularly important because transverse fibre properties are extremely difficult to measure. Moreover, \( \xi \approx 1 \) is a sensible approximation that greatly reduces the number of required inputs (Figure J.1(c)).

Following Equations J.1 and J.6 and if \( \tau_\mu^0 \) is measured during SFPO, the frictional stresses during pull–out can be therefore approximated by:

\[
\tau_\mu = \xi \cdot (1 - V^f) \cdot \tau_\mu^0 \approx (1 - V^f) \cdot \tau_\mu^0.
\]

Alternatively, Equation J.5 can be used to calculate friction coefficient \( \mu \) directly from a SFPO test. Disregarding chemical shrinking, \( \varepsilon_{\Delta T}^m - \varepsilon_{\Delta T}^f = \Delta T (\alpha_m - \alpha_f^f) \); neglecting also the mismatch between transverse elastic properties of the RU and the matrix, the residual interfacial pressure in a model composite with \( V^f \to 0 \) is:

\[
p^0 \approx \frac{\Delta T \cdot (\alpha_m - \alpha_f^f) \cdot E_m}{2}, \quad \text{and} \quad \mu = \frac{\tau_\mu^0}{p^0}.
\]
Appendix K

Derivation of the level–[i] pull–out length distribution in a fractal fracture surface

Consider the pull–out length cCDF \( S_{p_i}(l_{po}) \) defined in Equation 7.16a. Changing the integration variable from \( a_i \) to \( \sigma^\infty \) (unequivocally related in Equation 7.8),

\[
S_{p_i}(l_{po}) = \Pr(L_{po} > l_{po}^{[i]}) = \int_{\sigma^\infty = \sigma^{min}(l_{po})}^{\infty} \Pr(X_{deb} = \sigma^\infty \land L_{po}^{[i]} \geq l_{po}^{[i]}) ,
\]

where the lower integration limit verifies \( a_i^{[i]}(\sigma^{min}) = l_{po}^{[i]} \); following the definition of \( a_i^{[i]}(\sigma^{\infty}) \) in Equation 7.8

\[
\sigma^{min}(l_{po}) = \frac{\lambda^{[i]}_a \cdot l_{po}^{[i]}}{\kappa^{[i]}_a} \left( c_G - 1 + \frac{\psi^{[i]}_a \cdot \kappa^{[i]}_a}{\left(\lambda^{[i]}_a \cdot l_{po}^{[i]}\right)^2} + (c_G - k^{[i]}_G) \right) .
\]

The integrand function in Equation K.1 has been defined in Equation 7.15 from the auxiliary probability distributions \( S_{\lambda_1}^{[i]}(\sigma^{\infty}, l_{po}^{[i]}) \) and \( F_{\lambda_1}^{[i]}(\sigma^{\infty}, l_{po}^{[i]}) \). Considering their representation in Figure 7.6, they can be calculated from \( S_{\lambda_0}^{[i]}(\sigma^{\max}) \) (defined in Equation 7.11) as:

\[
S_{\lambda_1}^{[i]}(\sigma^{\infty}, l_{po}^{[i]}) = \frac{S_{\lambda_0}^{[i]}(\sigma^{\infty})}{S_{\lambda_0}^{[i]}(\sigma_{po}(\sigma^{\infty}, l_{po}^{[i]}))} \quad \text{and} \quad F_{\lambda_1}^{[i]}(\sigma^{\infty}, l_{po}^{[i]}) = 1 - \frac{S_{\lambda_0}^{[i]}(\sigma_{po}(\sigma^{\infty}, l_{po}^{[i]}))}{S_{\lambda_0}^{[i]}(\sigma^{\infty})} .
\]
The differential of the latter, omitting the variables $\sigma^\infty$ and $l^{[i]}_{p0}$ in $\sigma^{[i]}_{p0}$ and $\sigma^{[i]}_a$, is:

$$\frac{dF^{[i]}_H}{d\sigma^\infty} = \frac{1}{S^{[i]}_{\lambda_H}(\sigma^{[i]}_a)} \left( \frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\lambda_H}(\sigma^{[i]}_{p0}) \right] - S^{[i]}_{\lambda_H}(\sigma^{[i]}_{p0}) \cdot \frac{d}{d\sigma^\infty} \left[ \frac{S^{[i]}_{\lambda_H}(\sigma^{[i]}_a)}{S^{[i]}_{\lambda_H}(\sigma^{[i]}_a)} \right] \right) d\sigma^\infty. \tag{K.4}$$

Replacing Equations K.3 and K.4 into the definition of $\Pr(X^{[i]}_{\text{deb}} = \sigma^\infty \wedge L^{[i]}_{p0} \geq l^{[i]}_{p0}$) (Equation 7.15) and re-arranging yields:

$$\Pr(X^{[i]}_{\text{deb}} = \sigma^\infty \wedge L^{[i]}_{p0} \geq l^{[i]}_{p0}) = -S^{[i]}_{\text{deb}}(\sigma^\infty) \cdot \frac{2}{l^r \cdot \lambda^{[i]}_H} \cdot \frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\text{deb}}(\sigma^{[i]}_{p0}) \right] - \frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\text{deb}}(\sigma^{[i]}_a) \right] d\sigma^\infty, \tag{K.5}$$

for all $\sigma^\infty > \sigma^{\text{min}}$. The first factor in Equation K.5 is $S^{[i]}_{\text{deb}}(\sigma^{[i]}_a)/S^{[i]}_{\text{deb}}(\sigma^{[i]}_a) = S^{[i]}_{\text{deb}}(\sigma^\infty)$ (Equation 7.12). The derivative terms can be calculated by applying the chain and logarithmic differentiation rules, and the definition of $S^{[i]}_{\lambda_H}(\sigma^{\text{max}})$:

$$\frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\lambda_H}(\sigma^{\text{max}}) \right] = \frac{d\sigma^{\text{max}}}{d\sigma^\infty} \cdot \ln \left[ S^{[i]}_{\lambda_H}(\sigma^{\text{max}}) \right] + \frac{d}{d\sigma^\infty} \left[ \ln \left( S^{[i]}_{\text{deb}}(\sigma^{[i]}_{p0}) \right) \right] \cdot \frac{2}{l^r \cdot \lambda^{[i]}_H}. \tag{K.6}$$

Equation K.5 then simplifies to:

$$\Pr(X^{[i]}_{\text{deb}} = \sigma^\infty \wedge L^{[i]}_{p0} \geq l^{[i]}_{p0}) =$$

$$-S^{[i]}_{\text{deb}}(\sigma^\infty) \cdot \frac{2}{l^r \cdot \lambda^{[i]}_H} \cdot \left( \frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\text{deb}}(\sigma^{[i]}_{p0}) \right] - \frac{d}{d\sigma^\infty} \left[ S^{[i]}_{\text{deb}}(\sigma^{[i]}_a) \right] \right) d\sigma^\infty, \tag{K.7}$$

where, following the definition of $\sigma^{[i]}_a(\sigma^\infty)$ and $\sigma^{[i]}_{p0}(\sigma^\infty)$ in Equations 7.13 and 7.14

$$\frac{d\sigma^{[i]}_a}{d\sigma^\infty} = 1 - \epsilon_g + k^{[i]}_0 + \frac{(c_g - k^{[i]}_0)^2 \cdot \sigma^\infty}{\sqrt{[(c_g - k^{[i]}_0) \cdot \sigma^\infty]^2 + \psi^{[i]}_a}} \quad \text{and} \quad \frac{d\sigma^{[i]}_{p0}}{d\sigma^\infty} = k^{[i]}_0. \tag{K.8}$$

Integrating Equation K.7 for $\sigma^\infty \geq \sigma^{\text{min}}$ finally leads to the pull-out cCDF presented in Equation 7.16b.