ABSTRACT

Intralaminar failure in fibre reinforced polymer (FRP) composites has been investigated by experimental measurement of material properties and through the characterisation of fracture surfaces by time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Strength data for the HTA/F922 carbon-fibre/epoxy composite system, under different combinations of tension and shear loading, have been measured experimentally using un-cracked obliquely tabbed off-axis tensile coupons. Fracture mechanics properties have been investigated using compact tension coupons and obliquely tabbed cracked off-axis coupons. Failure envelopes in K and G space have been established for a glass-fibre/epoxy composite system and an HTA/F927 carbon-fibre/epoxy composite system under combinations of mode I and mode II loadings. The failure envelope for the glass-fibre composite system is dominated by the mode I fracture mechanics component of loading, whereas there is significant interaction of the mode I and mode II components shown in the failure envelope for the carbon-fibre composite system. The failure envelopes have been compared with other published data, notably for delamination fracture.

The preparation of microtomed sections is shown to be a convenient and reliable method for the production of samples of heavily cross-linked polymeric materials for analysis by ToF-SIMS. ToF-SIMS has been used to interrogate composite fracture surfaces with a view to establishing failure loci. A stage has been developed that is able to generate fracture surfaces under either a pure tensile mode I loading or a shear dominated mode II loading in-situ, within the ultra high vacuum confines of the ToF-SIMS spectrometer. ToF-SIMS analysis of fracture surfaces from composite systems with an optimised interface has shown that failure is matrix dominated, regardless of the loading mode, while conventional SEM analysis shows morphological differences. A ToF-SIMS study
has been conducted to establish whether the failure surface chemistry alters when fracture occurs after a period of environmental ageing. A comparison of failure surface chemistries from ToF-SIMS analyses has also been made between a standard composite and varieties that had been produced with different levels of fibre electrochemical surface pre-treatment. A new technique (Gentle-SIMS or G-SIMS) for processing ToF-SIMS spectra has been applied; the technique is believed to simplify the characterisation and interpretation of spectra. A preliminary study has been made of this technique.
ACKNOWLEDGMENTS

Special thanks go to Professors Paul Smith and John Watts for their continued support, enthusiasm and excellent supervision throughout the course of this study. I would like to acknowledge BAE SYSTEMS for provision of materials and financial support and Dr. Amir Rezai for guidance and technical information. I must also acknowledge the financial support of the EPSRC and the input of Dr. Anna Belu at Physical Electronics and Dr. Birgit Hagenhoff at TASCON.

I am very grateful to all members of both the surface and interface reactions group (SIRG) and the composites group for their enlightening discussions and input. Especial thanks go to Mr Andy Brown for his expertise and advise in all matters concerning ToF-SIMS, Mr Reg Whattingham for his patience and counsel on topics of composite fabrication (and golf) and not least Dr. Phil Vickers for his endless supply of information. It would also be remiss of me not to mention Penny Briggs, Margaret Morgan, Shirley Hankers, Dave Lawrence and Julie Gilbert who ensured the smooth running of the project and also Mr Nigel Hooker for his work in constructing the in-situ fracture stubs.

My appreciation also goes to my very good friends and housemates Tim Mitchell, David Booth, Kristian Steel and Peter Kench and also to Mr Edward Heardman and Dr. Matthew Fitzpatrick and to my office colleagues Anne, Sam, Jae and Tom for their continued friendship and assistance.

Finally, a very special thank you to Katie and to my family, for always supporting me and for their encouragement and endurance.
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<th>Description</th>
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<tr>
<td>CFRP</td>
<td>Carbon fibre reinforced polymer</td>
</tr>
<tr>
<td>CT</td>
<td>Compact tension</td>
</tr>
<tr>
<td>DDS</td>
<td>Diamino diphenyl sulphone</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl ether of Bisphenol A</td>
</tr>
<tr>
<td>EMSE</td>
<td>Ecole des Mines de Saint – Etienne</td>
</tr>
<tr>
<td>ENF</td>
<td>End notch flexure</td>
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<tr>
<td>EPSRC</td>
<td>Engineering and Physical Sciences Research Council</td>
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<tr>
<td>ESD</td>
<td>Electron stimulated desorption</td>
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<tr>
<td>FAB-SIMS</td>
<td>Fast-atom-bombardment secondary ion mass spectrometry</td>
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<tr>
<td>FRC</td>
<td>Fibre reinforced composite</td>
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<td>FRP</td>
<td>Fibre reinforced polymer</td>
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<td>GFRP</td>
<td>Glass fibre reinforced polymer</td>
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<tr>
<td>G-SIMS</td>
<td>Gentle secondary ion mass spectrometry</td>
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<tr>
<td>HM</td>
<td>High modulus</td>
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<tr>
<td>HT</td>
<td>High strength</td>
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<tr>
<td>HV</td>
<td>High vacuum</td>
</tr>
<tr>
<td>K61B</td>
<td>2,4,6-tris((dimethylamino)methyl)phenoltri(2-ethylhexanoate)</td>
</tr>
<tr>
<td>NMA</td>
<td>Nadic methyl anhydride</td>
</tr>
<tr>
<td>PAN</td>
<td>Polycrylonitrile</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PEEK</td>
<td>Polyehteretherketone</td>
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<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
<td>SAM</td>
<td>Scanning Auger microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SI</td>
<td>Secondary ion</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
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<td>SNMS</td>
<td>Secondary neutral mass spectrometry</td>
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<td>TASCON</td>
<td>ToF Analytical Services and Consulting</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TFS</td>
<td>Transverse flexure strength</td>
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<tr>
<td>TGDDM</td>
<td>Tetruglycidyl diamino diphenyl methane</td>
</tr>
<tr>
<td>TGMDA</td>
<td>Tetruglycidyl methylene dianiline</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time-of-flight secondary ion mass spectrometry</td>
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<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
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<tr>
<td>XPS</td>
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1.1. SCOPE OF WORK

A composite is a multiphase material that contains two or more distinct constituents or phases. The purpose behind a composite material is an optimisation of the individual component properties by the process of combination. The best mechanical properties are associated with composites based on continuous fibre reinforcement. For most purposes laminates are assembled comprising plies at various orientations. In order that such composite materials may be utilised more widely and efficiently in structural applications, a more detailed understanding of their deformation and fracture behaviour is required than is available currently. One particular failure mechanism is intralaminar matrix cracking, which is the topic of the current study, described below.

In composite laminates containing plies at various orientations to the applied stress, the behaviour of off-axis ply properties are normally matrix-dominated for systems with optimised interfaces [1]. When either a unidirectional composite laminate is loaded transversely or a 90° ply contained within a laminate is loaded in tension, matrix cracking occurs under pure mode I (tensile) loading. Much work, over recent years, has focused on understanding this type of cracking in fibre reinforced polymer (FRP) laminates and the use of both strength-based and fracture-mechanics-based failure criteria have been explored. Boniface et al [2] give a summary of the current understanding of transverse ply cracking for brittle (i.e. low toughness) polymer matrix composite systems. As indicated above, this understanding relates primarily to unidirectional laminates (or 90° plies) loaded transversely, a pure mode I loading situation. In service, however, laminates contain plies that are at an angle to the applied load and matrix cracking will occur therefore under a mixed-mode (tension and shear)
loading. This phenomenon is much less well understood than the corresponding mode I problem.

The identification of the different modes of fracture in a material originates from the work of Irwin [3] in the 1950s. Irwin proposed a general theory of fracture based upon the existence of three distinct fracture modes that could occur at the tip of a crack, Figure 1.01.

![Figure 1.01. Crack opening modes.](image)

These fracture modes are: (1) an opening mode I, where the crack faces undergo opening displacements relative to one another as the crack grows, (2) an in-plane sliding mode II, where the crack faces slide relative to one another in a direction of the crack growth, and (3) an out-of-plane tearing mode III, where the crack faces slide relative to one another in a direction normal to the direction of crack growth.

The resistance of a material to failure can be characterised either by strength measurements, taken from un-cracked coupons, or if there is a crack present by the fracture mechanics properties, i.e. the toughness (G_C) or fracture toughness (K_C), which are measured from pre-cracked coupons. Early solutions for cracked bodies with specific configurations and loadings were developed and applied to structural problems; however, most of these problems consisted of cracks in homogeneous materials.
(typically metallic materials). In homogeneous materials, cracks that may have been originally loaded by all three fracture modes will typically turn as soon as the crack grows so as to assume a pure opening mode I orientation [4]. Hence, attempts are made to characterise the resistance to fracture of such materials in terms of the opening mode I material properties. The problems associated with fracture are more complex in composite materials. In continuous fibre reinforced composite materials the situation exists where cracks are constrained to grow in resin-rich regions between composite plies or between fibre reinforcements. Hence cracks may grow macroscopically in a self-similar manner under mixed-mode loadings. This self-similar crack growth may apply for intralaminar matrix cracking and interlaminar (delamination) cracking see Figure 1.02. Interlaminar or delamination failure under mixed-mode loading has been extensively studied in the literature. However the intralaminar problem has not generally been considered in such a systematic way.

![Diagram showing the interlaminar and the intralaminar fracture planes of a unidirectional continuous fibre reinforced composite laminate.](image)

**Figure 1.02.** *Schematic representation showing the interlaminar and the intralaminar fracture planes of a unidirectional continuous fibre reinforced composite laminate.*

Work on delamination has concentrated on the generation of empirical failure envelopes which describe the locus of failure in terms of the mode I and mode II loading
components. At the micro-mechanical level it has been shown that failure proceeds as a result of the linkage of micro-cracks, which form at the crack tip under the action of the local principal remote stress [5]. While this phenomenon has been modelled in a semi-empirical way [6] it has not led to an accepted form of universal failure criterion for mixed-mode delamination growth [4].

The aim of the present work is to gain a better understanding of failure of off-axis plies under a mixed mode loading, through a contribution of mechanical characterisation and surface analytical techniques. Surface analytical techniques will be used in order to establish if there are any locus of failure differences associated with the different fracture surface morphologies.

This study has the following objectives:

1) To measure experimentally strength-based and, in particular, fracture-mechanics-based material properties relating to intralaminar fracture in fibre reinforced polymer composite materials under different modes of loading.

2) To use the experimental measurements from (1) above to generate fracture mechanics failure envelopes for intralaminar fracture under combinations of mode I and mode II loadings and to compare these with interlaminar data from the literature.

3) The development of improved sample preparation techniques for the ToF-SIMS analysis of thermosetting polymer materials and fibre reinforced polymer composite fracture surfaces.

4) To characterise fracture surfaces of fibre reinforced polymer composite materials through a combination of microscopic and spectroscopic analyses and to relate the findings to the mode of loading.
1.2. STRUCTURE OF THIS THESIS

The first three chapters of this thesis are concerned with providing the reader with an introduction to the aims and objectives of this project (Chapter 1), a review of some of the more general aspects of FRP composites (Chapter 2) and details of the material systems of study and their fabrication (Chapter 3). The report is then split into two major sections.

The first section deals with the mechanical testing of FRPs. It begins with a literature review of the various intralaminar test methods available (Chapter 4), which is then followed by an account of the technique development for the materials tested in the present study (Chapter 5). The section concludes with the detailed mechanical characterisation of the selected glass-fibre reinforced polymer (GFRP) and carbon-fibre reinforced polymer (CFRP) laminates (Chapter 6).

The second major section of this thesis deals with the surface analysis aspects of the project. A detailed appraisal of the techniques to be used is given along with a literature review of previous fractography studies (Chapter 7). Novel techniques for the sample preparation of thermosetting polymeric materials and the in-situ fracture of composite coupons are presented (Chapter 8). Developed techniques are then used to characterise material systems and composite fracture surfaces (Chapter 9).

The final section of this thesis draws conclusions from both aspects of the project and presents possible further work (Chapters 10).
2.1. INTRODUCTION

This project is concerned with the failure of fibre reinforced polymer composites; it is a study involving experimental measurement of mechanical properties and the interrogation of fracture surface morphology and chemistry. In order to understand failure better and to interpret chemical information from the fracture surface, some knowledge of the composite material and its constituents is necessary. The present chapter covers aspects of fibre reinforced polymer composites. A review of the manufacturing process of each component is given as well as some basic mechanical and chemical properties.

2.2. REINFORCEMENTS

2.2.1. Introduction

Many different types of reinforcements are available for the production of composite materials, including fibres, whiskers and particulates. The material properties of the reinforcing phase as well as its size, distribution and architecture will have a marked effect on the final properties of the composite. Fibre reinforced composite (FRC) technology utilises the high stiffness and strength of filamentary materials. The properties of unidirectional FRCs are highly dependent upon the orientation of the fibre
reinforcement. Short fibres may be distributed randomly to produce more uniform material properties; in sheet form, however, the through-thickness strength may still be poor. The ability of the matrix to transfer load to the fibres is controlled by the interface or interphase between them. For this reason fibre reinforcements generally undergo surface treatments to improve adhesion before incorporation into the matrix. Factors other than mechanical properties also play a part in the selection of composites, the most critical being cost. Boron fibres, while processing good properties, especially in compression, are expensive and seldom used except in applications requiring their special properties [7]. Glass fibres are widely available and relatively cheap and so glass fibre reinforced composites are found in a large variety of applications. However, the specific strength of glass fibre reinforced material is generally too low for industries that require high structural performance such as the aerospace industry. Commonly a compromise between structural performance and cost results in aircraft components being made from carbon fibre reinforced composite materials.

2.2.2. Carbon Fibres

Carbon fibres were developed simultaneously in the UK and Japan in the 1960's. Their high elastic constants and strength make them extremely effective as a fibre reinforcement.

In the graphite single crystal, the carbon atoms are arranged in hexagonal arrays (basal planes) within which the bonding is covalent and strong [7]. The basal planes are stacked in a regular ABABAB.... sequence with only weak van der Waals forces between them. The basic crystal units are therefore highly anisotropic; the in-plane Young's modulus is about 1000 GPa, while that perpendicular to the basal planes is only 35 GPa [8].

Carbon fibres consist of small crystallites of 'turbostratic' graphite [8]. Turbostratic graphite closely resembles graphite single crystals, except that the layer planes are not regularly packed. Good alignment of the basal planes parallel to the fibre axis is required for high axial modulus and strength, whereas the arrangement of the layer
planes in the cross section governs the transverse and shear properties of the fibre. The three-dimensional structure and orientation of the basal planes of graphite in a carbon fibre is shown schematically in Figure 2.01.

![Schematic three-dimensional representation of structure in HM type PAN based carbon fibres, after [9].](image)

There are three main routes to producing carbon fibres i.e. from poly(acrylonitrile) (PAN) fibres, from mesophase pitch and by pyrolytic deposition. This project makes use of fibres produced from PAN.

Producing carbon fibres from PAN is the preferred industrial route. Bulk PAN is drawn down to a fibre and stretched to produce alignment of the molecular chains. The stretched fibre is then heated; the active nitrile groups react to produce a ladder polymer, consisting of a row of six-membered rings. While still under tension, the fibre is heated in an oxygen-containing environment which causes further chemical reaction and the formation of cross-links between the ladder molecules. The oxidised PAN is then reduced, by heating in an inert atmosphere such as nitrogen or argon at temperatures above 1000 °C to give the carbon ring structure [8]. This is converted to ‘turbostratic’ graphite by heating at higher temperatures. The process of thermal decomposition of PAN is shown schematically in Figure 2.02.
This method of heat treatment has a strong bearing on the mechanical properties of the fibres (Young’s modulus and tensile strength) because an increase in the pyrolysis temperature results in a more ordered crystalline structure of the graphitic planes [10]. Fibres are classified in accordance with the temperature that they are exposed to during the final high temperature graphitisation stage; the classification gives an indication of the effect that this stage has on their final structure and properties. Fibres that have been subjected to temperatures of 2000 °C and above have a high modulus and are sometimes designated Type I or HM (high-modulus) fibres; those produced in the region 1000 – 1600 °C have a higher strength but lower stiffness and are labelled Type II or HT (high-strength) fibres; fibres manufactured at temperatures below 1000 °C are referred to as Type III (high-strain) fibres and possess lower strength and modulus but are considerably cheaper to produce [9].
2.2.3. Glass Fibres

Glass is a non-crystalline material with a short-range network structure. Its mechanical properties are isotropic and are determined mainly by composition and surface finish [7]. There are several groups of glasses, for example silica, oxynitride, phosphate and halide glasses; however only those based upon silica (SiO₂) are used to any extent in composite technology. Within the silica based glass family, the composition may be altered to yield a variety of mechanical properties of which a number of compositions are commonly used for the production of glass fibres. The most widely used fibre is E-glass (E denotes electrical, as in good electrical insulators). E-glass draws well and has good strength, stiffness, electrical, and weathering properties. Typical properties of a single E-glass fibre are: fibre diameter 8 – 15 µm, strength 3.45 GPa and Young’s modulus 76 GPa [8]. Different compositions of silica glass are available which result in fibres for more specialist applications. For higher mechanical performance R- or S-glass can be used; this type of fibre has a higher strength (4.6 GPa), Young’s modulus (85.5 GPa) and temperature resistance, although costs can be higher [8]. C-glass fibres (C denotes corrosion) offer improved resistance to corrosion over E-glass but have a slightly lower strength (3.3 GPa) [8]. GFRP laminates used in this project have been produced using E-glass fibres.

Glass fibres are produced by melting the raw materials in a reservoir, which feeds several bushings; molten glass is then extruded under gravity through many small holes within the bushings. The fine filaments are drawn mechanically down to a fibre approximately 10 µm in diameter and wound onto a drum. Control of the fibre diameter is achieved through several parameters including the head of the glass in the tank, the viscosity of the glass (composition and temperature), the diameter of the holes and also the winding speed [8]. Fibres are cooled in a spray of water immediately after being drawn. Because surface defects largely govern the strength of glass fibres, a size is usually applied at an early stage of production. The size is crucial to the handle-ability of the fibres; it protects them from damage, binds them together for ease of processing and provides lubrication enabling fibres to withstand abrasion during subsequent processing operations [11]. The size is also important in providing a chemical link between the fibre surface and the matrix material; this is essential for matrix
compatibility and for good interfacial bond strength. The composition of the fibre size is a commercially sensitive aspect of glass fibre manufacture.

2.3. MATRICES

2.3.1. Introduction

In order to utilise the high stiffness and strength of fibre reinforcements it is necessary to combine them with a matrix material that bonds well to the fibre surface and which transfers stress effectively to the fibres. The matrix also stabilises the fibre in compression, contributes to the resistance of damage due to impact by exhibiting plastic deformation, and (in the absence of through-thickness reinforcement) provides out-of-plane properties to the laminate.

The most widely used matrix materials for composites are organic polymers. The main disadvantages of polymer matrix composites are their low maximum working temperatures, high coefficients of thermal expansion and associated dimensional instability, and sensitivity to radiation and moisture. The absorption of water from the environment may have many harmful effects that degrade mechanical performance, including swelling, formation of internal stresses and lowering of the glass transition temperature. There are of course exceptions to these general disadvantages due to the wide range of polymeric materials available; for example, CFRPs may be designed to have very low coefficients of thermal expansion and epoxy matrices are radiation resistant [7]. Polymer matrices may be classified into thermosets, thermoplastics and rubbers. Thermosets generally have much lower strains to failure than thermoplastics. Thermosets are essentially brittle materials, a result of the high level of cross-links within the structure, while thermoplastics can undergo appreciable plastic deformation. Within each class there are many different polymers e.g. epoxy, polyester, polyimide and phenolic are all thermosets. This project is concerned with composites based on epoxy matrix materials.
2.3.2. Epoxy Resins

2.3.2.1. Introduction

An epoxy is a thermosetting polymer. Its chemistry is based on the ability of the epoxide group, Figure 2.03, to react with a wide range of other organic radicals to effect cross-linking without the evolution of a condensate [11]. The epoxy group is also referred to as the oxime, oxirane or ethoxyline group.

![Figure 2.03. The epoxide ring.](image)

Chemical cross-linking is the formation of strong covalent bonds between the polymer chains resulting in the formation of a tightly bound three-dimensional network. The mechanical properties of the final polymer depend upon the molecular units making up the network, a result of the chemical ingredients of the polymer, and upon the length and density of the cross-links, a result of the cure procedure. Curing usually involves the application of heat and pressure and/or the addition of a curing agent or hardener. The rate of the cure reaction is often controlled by use of catalysts and accelerators. Curing can occur at room temperature, but it is usual to use a cure schedule which involves heating at one or more temperatures for pre-determined times to achieve optimum cross-linking and hence optimum properties. Additional post curing stages may also be included within the cure schedule.

Epoxy resins are difunctional or polyfunctional, in terms of the epoxide groups, and may be based on either aliphatic or aromatic backbone structures [11]. The majority of epoxies used for matrices in composite technology are aromatic because of their superior performance; however, blends of aromatic and aliphatic material are available. Commercial systems may be a complex blend of resin, curing agents,
catalysts/accelerators, thermoplastic modifiers, and other additives; this is in order to meet the often-conflicting demands of high performance and ease of processing. Epoxy resins used for matrices in CFRPs are required to have a low viscosity for fibre impregnation, a high reactivity on curing without volatile formation, low shrinkage and good mechanical and thermo-mechanical properties [8]. A major advantage also with epoxies is that they may be cured in two or more stages. This allows preforms to be pre-impregnated with the epoxy in a partially cured state. These preforms are known as pre-pregs.

2.3.2.2. Types of Epoxy Resins

The general-purpose resins for both adhesives and composites are formed from the difunctional diglycidyl ether of bisphenol A. This epoxy resin is formed from the reaction of epichlorohydrin with bisphenol A (Figure 2.04) in the presence of sodium hydroxide. The molar ratio of these two monomers dictates the degree of polymerisation and the molar mass of the final epoxy resin. When \( n = 0 \) the resin is referred to as the diglycidyl ether of bisphenol A (DGEBA) [9]. Other related oligomers are possible with degrees of polymerisation \( (n) \) up to four. The polymers with a higher value of \( n \) are more viscous and thus are less useful in high performance composite applications.

The majority of resins for aerospace composites are formed from glycidyl amines, which have a higher functionality and potentially higher cross-link densities and glass transition temperatures than those based upon the diglycidyl ether of bisphenol A. These resins are often used as pre-pregs. The first generation of epoxies were essentially single-phase un-toughened systems commonly based upon the tetrafunctional epoxy tetruglycidyl methylene dianiline (TGMDA), Figure 2.05. TGMDA based systems possess a useful set of physical characteristics. These include good processability as a pre-pregging resin, high glass transition temperature, low creep and high modulus. Single-phase TGMDA based systems however have relatively low toughness properties compared to later systems.
Figure 2.04. Figure showing the reaction of (i) epichlorohydrin with (ii) bisphenol A and the resultant final epoxy resin (iii), after [9]

Figure 2.05. Tetraglycidal methylene dianiline (TGMDA).

Thermoplastic modifiers may also be added to the epoxies to give a two-phase matrix material. These modifiers, such as polyethersulphone, can be used to control process variables such as viscosity and tack. The molecular weight of the thermoplastic and the end-groups contribute to the processing and performance. For example amine end-groups terminated polyethersulphones ensure chemical bonding with the epoxy resin. These thermoplastic additives can also act so as to toughen the matrix, providing
resistance to micocracking. High temperature performance and durability may be improved with thermosetting modifiers such as bismaleimide and cyanurate resin [9].

The final choice of resin blend can be a complex mixture including hardeners, plasticisers, modifiers and filler materials which will all aid storage, facilitate processing and lead to improved final properties.

2.4. FABRICATION

High performance fibre reinforced composite laminates, especially those based upon CFRP, are frequently manufactured by consolidating pre-preg material in an autoclave or a laboratory pressclave. A composite laminate is essentially a sandwich construction made-up from layers of individual laminae or plies. Unidirectional pre-preg is cut to appropriate dimensions to form the individual laminae.

Pre-preg consists of collimated fibres pre-impregnated with epoxy resin. The pre-preg has a designed level of tack that allows the laminae to be stacked together. For ease of handling and cleanliness the pre-preg is stored between two release films and is usually kept in a container within a freezer to prevent further curing of the resin. To avoid condensation on the pre-preg and moisture ingress, the pre-preg is removed from the freezer and allowed to reach thermal equilibrium before use.

The stacking sequence of the laminae is defined by the required laminate properties. It is usual that laminates are kept 'balanced' and 'symmetric'. A laminate is balanced in order to eliminate shear-coupling forces, which could otherwise distort the final laminate. Balancing requires that there are as many $+9^\circ$ plies as there are $-9^\circ$ plies. The term symmetric is used to indicate that the laminate is symmetric about its mid-plane in geometry this is in order to eliminate extension-bending coupling.

The pre-preg 'stack' is placed within a consolidation lay-up in the autoclave or pressclave, Figure 2.06. The consolidation lay-up may contain absorbers, depending whether or not the composite being fabricated is a bleed or a zero-bleed system. Bleed
systems are used to soak up excess resin incorporated within the pre-preg. Resin bleed aids the removal of air and residual volatile impurities while also helping consolidation of a void-free laminate. Pre-preg is also produced as non-bleed systems where there is the exact proportion of resin to fibre so as to achieve the correct fibre volume fraction. The removal of large volumes of resin can disturb the fibre alignment and hence the flow of resin is an important property of a pre-preg.

The cure schedule is of great importance for optimising the matrix properties. Relevant parameters include the heat up rate, the final cure temperature, the duration at temperature and the cooling rate; each parameter is specific for any given resin system. The pressure cycle involves firstly applying vacuum to the bag to bring the pressure below 1 atmosphere and enhance the removal of air and volatile residues. Pressure is then applied to the bag either with the vacuum maintained or with the bag vented to atmosphere; the exact pressure is again dependent on the composite system being fabricated. Low compaction pressures may result in resin rich regions between the plies.

Figure 2.06.  Schematic showing an autoclave assembly (bleed cloth optional)
whereas excessive pressures can result in fibrous areas devoid of resin. Over-compacting can also lead to a misalignment of the fibres in unidirectional laminates.

2.5. CONCLUDING REMARKS

The present chapter has provided some basic information on carbon and glass reinforced polymers (CFRPs and GFRPs). In the next chapter we look in more detail at the systems to be studied.
Chapter Three

Materials and Fabrication

3.1. INTRODUCTION

This chapter details the fibre reinforced composite systems studied in the project. The matrix in each system was an epoxy polymer and reinforcements were either carbon fibre or glass fibre. The carbon fibre reinforced polymer systems are labelled by the manufacturer's fibre designation followed by the matrix type. Details are given regarding the lamination procedure for systems that were fabricated within this study. The method used for determining fibre volume fractions of the glass fibre reinforced material is given, along with results. The principal elastic properties for each material system have been taken from the literature and are stated.

3.2. CARBON FIBRE SYSTEMS

3.2.1. HTA/F927

HTA/F927 was the main carbon fibre composite system used in this study. Pre-pregs were produced at Hexcel Composites using Akzo HTA carbon fibres and Hexcel Fibredux F927 epoxy resin. Akzo HTA carbon fibre is a high tensile strength fibre with the following typical properties: - modulus (E) 240 GPa, strength (σf) 3.5 GPa and failure strain (εf) 1.5 % [9]. Fibredux F927 epoxy resin is a tough, modified epoxy system with excellent "hot/wet" performance [12]. It is a complex two-phase system that contains a thermoplastic toughening agent. Unidirectional CFRP panels of HTA/F927 were hand layed using 24 plies of pre-preg. The laminates were cured at
BAE SYSTEMS, Sowerby, using an autoclave, under conditions as specified by the manufacturer's standard cure schedule. A post-cure operation was carried out using a fan-assisted oven in accordance with the manufacturer's standard post-cure schedule. During post-cure the laminates were held between two glass plates to prevent warping. The cured panel thickness was nominally 3 mm. Cured bulk resin samples were also made available.

3.2.2. HTA/F922

HTA/F922 material was utilised in the development of testing procedures and analysis techniques. HTA/F922 is a CFRP system containing Akzo HTA carbon fibres and Ciba Fibredux F922 epoxy resin. F922 is a tetra-functional epoxy resin based on tetruglycidyl diamino diphenyl methane (TGDDM) cured with diamino diphenyl sulphone (DDS), a primary di-functional amine-curing agent [1]. Laminates with epoxy-sized fibres at different levels of electrochemical oxidative surface treatment, 0%, 25%, 75%, 100% (standard, HTA 5131) and 200%, were utilised in fracture surface analysis investigations.

3.2.3. XAS/914

Cured laminates of XAS/914 were used in the development of mechanical testing procedures. XAS/914 is a CFRP system with XAS carbon fibre and 914 epoxy resin. 914 epoxy is a two-phase epoxy system containing the thermoplastic polyethersulphone.

3.3. GLASS FIBRE SYSTEM

Unidirectional glass fibre reinforced laminates were manufactured in-house using a fibre winding and wet lay-up technique. An E-glass fibre roving was wound through a tension device onto an open metal frame revolving at a constant speed. The traverse speed of the roving and the number of passes across the frame dictated the thickness of
Chapter Three: Materials and Fabrication

the laminate. To manufacture a laminate nominally 2 mm thick, two passes across the frame were made.

Fibres were impregnated with Astor-Stag Epoxide Resin 300, (bisphenol A epichlorohydrin). The system was cured with a nadic methyl anhydride (NMA) (methyl-5-norbornene-2,3-dicarboxylic anhydride) curing agent and the cure accelerator K61B (-2,4,6-tris((dimethylamino)methyl))phenoltri(2-ethylhexanoate). The formulation was mixed in the ratio 100:60:4 parts by weight of resin:curing-agent:cure-accelerator, respectively. The wet lay-up process was conducted using the following procedure. The resin and curing agents were mixed and degassed to remove entrapped air and then ‘frozen’ on a sheet of release film on top of a cold plate. The frame of wound fibres was placed within a vacuum box on top of a hot plate covered with a sheet of release film. The resin was placed on the fibres and the vacuum box evacuated. The hot plate lowered the viscosity of the resin, which was then drawn through the fibres under vacuum. Once the fibres were fully impregnated, the frame was removed and air bubbles and excess resin were worked out of the laminate by hand. Laminates were cured between thick glass plates under 80 lbs weight for 3 hours at 100 °C. A post-cure operation was conducted at 150 °C for 3 hours. Bulk resin samples were also fabricated by casting the degassed resin into moulds prior to curing.

Fibre volume fractions for each fabricated laminate were measured using a matrix burn off technique. Small samples were cut from different regions of each laminate and placed within crucibles in a muffle furnace at 450 °C for 3 hours. Weighing before and after burn-off enables the mass of the glass fibres ($M_f$) and the mass of the resin ($M_m$) to be determined. Densities of the glass fibre ($\rho_f$) and resin ($\rho_m$) were 2.56 g/cm$^3$ (provided by Fothergill Engineering) and 1.21 g/cm$^3$ [13], respectively. The volume fraction ($V_f$) of glass fibres in each laminate was calculated using Equation (3.01). Results are given as the average from four separate measurements in Table 3.01.

$$V_f = \frac{M_f / \rho_f}{M_f \rho_f + M_m / \rho_m} \quad (3.01)$$
Table 3.01. *GFRP laminate fibre volume fractions*

<table>
<thead>
<tr>
<th>Laminate</th>
<th>Average $V_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>51</td>
</tr>
</tbody>
</table>

### 3.4. PRINCIPAL MATERIAL PROPERTIES

The principal elastic properties of each of the composite systems used in this project are given in Table 3.02. Values for the carbon fibre systems have been taken from previous work conducted at the University; the longitudinal modulus ($E_1$) has been verified experimentally using unidirectional tensile coupons. Glass fibre/epoxy material properties, for a composite with an average fibre volume fraction of 52%, have been taken from Sih [14].

Table 3.02. *Principal material properties*

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_1$ (GPa)</th>
<th>$E_2$ (GPa)</th>
<th>$G_{12}$ (GPa)</th>
<th>$\nu_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAS/914</td>
<td>145</td>
<td>9.50</td>
<td>5.60</td>
<td>0.31</td>
</tr>
<tr>
<td>HTA/922</td>
<td>136</td>
<td>9.50</td>
<td>6.50</td>
<td>0.31</td>
</tr>
<tr>
<td>HTA/927</td>
<td>110</td>
<td>7.68</td>
<td>4.00</td>
<td>0.30</td>
</tr>
<tr>
<td>Glass/DGEBA</td>
<td>40</td>
<td>10.00</td>
<td>3.75</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Chapter Three: Materials and Fabrication

3.5. USE OF MATERIAL

In later chapters the materials described in the present chapter are characterised. The qualification and development of mechanical testing methods has utilised material from the XAS/914 and HTA/F922 systems (chapter 5). Failure has been characterised through strength measurements for the HTA/F922 system and through fracture mechanics property measurement for the HTA/F927 and glass fibre systems (chapter 6).

The matrix material of the glass fibre composite system has been used in the development of novel sample preparation methods for ToF-SIMS characterisation of thermosetting polymeric materials (chapter 8). This material has also been utilised in a cure study by ToF-SIMS and a GSIMS study (chapter 9). Composite fracture surface investigations have been based around the HTA/F922 and the HTA/F927 material systems (chapter 9).

The next chapter is the first of three concerned with mechanical characterisation and comprises a review of relevant test methods.
Chapter Four

A Review of Mechanical Characterisation of Matrix Fracture

4.1. INTRODUCTION

The aim of this project is to study the intralaminar failure of unidirectional laminates under combined tension and shear loadings. In addition to studying failure under combined stress states, failure at either end of the intended spectrum must also be considered, i.e. pure tensile (mode I) fracture and shear-dominated (mode II) fracture.

The present chapter begins with a review of the various mechanical test methods available to study fracture under a single stress component. A number of material properties may be measured through mechanical testing including strength and toughness. The toughness of a material may be characterised through fracture mechanics parameters [14]. Strength data are generated from un-cracked coupons whereas fracture mechanics studies are performed on cracked samples. Expressions used to calculate strength and fracture mechanics data from the mechanical test methods considered are given.

In order to characterise composite failure under general in-plane loadings, it is necessary to use a failure criterion. For an un-cracked sample, a failure criterion should be strength-based whereas for a cracked sample it should be fracture mechanics based. For pure mode I or pure mode II, the fracture mechanics approach is, in principal, straightforward. Considering energetics parameters, crack advance is assumed to occur when the strain energy release rate exceeds critical values (\( G_I = G_{IC} \) or \( G_{II} = G_{IIIC} \)). Considering stress based parameters, crack propagation is assumed to occur when the...
stress intensity becomes critical ($K_I = K_{IC}$ or $K_{II} = K_{IIc}$). The mixed-mode loading situation is more complex for both un-cracked and cracked laminates. It is difficult to quantify the interaction between the two modes and to derive a failure criterion from simple physical models [15]. A review of some of the more commonly used failure criteria is given; this includes those based upon fracture mechanics parameters and also those based upon strength measurements.

### 4.2. INTRALAMINAR TENSILE FRACTURE

#### 4.2.1. Transverse Tensile Strength

Measurement of transverse tensile strength is not a part of the present work. We note in passing that Rezaifard et al [16] have characterised the transverse tensile strength of HTA/F927 and HTA/F922, two of the materials to be used in the present study, from experiments on coupons cut from (90)$_{16}$ laminates.

#### 4.2.2. Fracture Mechanics Property Measurement

One test method for measuring intralaminar toughness is using a pre-cracked unidirectional composite coupon with a fibre orientation $90^\circ$ to the applied load. This test is standardised, ASTM D-5045-91a [17], with a coupon geometry known as a compact tension specimen, as shown in Figure 4.01. The compact tension test enables both mode I fracture mechanics parameters, the mode I critical stress intensity factor $K_{IC}$ and the mode I strain energy release rate $G_{IC}$, to be measured. Fracture testing involves loading a pre-cracked specimen so that the induced crack propagates under tension.
Figure 4.01. Schematic of a compact tension specimen configuration, dimensions as set by ASTM-5045-91a [17]

The maximum load ($P_{\text{max}}$) or a determined value of load ($P_q$) that the sample is able to sustain prior to crack propagation is used to calculate the mode I fracture toughness (critical stress intensity factor, $K_{\text{IC}}$) of the material. The mode I strain energy release rate ($G_{\text{IC}}$) may be determined by a method which takes into account a displacement correction for sample compliance, loading pin penetration, and sample compression. Prior to fracture testing un-notched samples are loaded in tension, although not to failure, in order that a corrected displacement may be obtained and thus a corrected energy term. Expressions for the measurement of the critical stress intensity and the strain energy release rate in mode I, $K_{\text{IC}}$ and $G_{\text{IC}}$, respectively, are given for the compact tension sample geometry in the standard ASTM D-5045-91a [17]. The expressions are shown in Equations (4.01) and (4.02).

$$K_{\text{IC}} = \left( \frac{P_q}{BW^{1/2}} \right) f(x)$$  \hspace{1cm} (4.01)
Chapter Four: A Review of Mechanical Characterisation of Matrix Fracture

\(P_Q\) is the peak load to fracture, \(B\) is the coupon thickness, \(W\) is the coupon width and \(f(x)\) is a function of the ratio crack length to coupon width, values of which are tabulated within the standard.

\[
G_{IC} = \frac{U}{BW\phi} \tag{4.02}
\]

\(B\) is the coupon thickness, \(W\) is the coupon width, \(\phi\) is an energy calculation factor calculated from the ratio of crack length to coupon width, values of which are tabulated within the standard and \(U\) is a corrected energy term. \(U\) is determined through mechanical testing methods, which are described in more detail in Section 5.2.

Note that the mode I stress intensity factor and the mode I energy release rate are related for an orthotropic material by Equation (4.03) [18].

\[
G_I = K_I^2 \left( \frac{b_{11} b_{22}}{2} \right)^{\frac{1}{2}} \left[ \frac{b_{22}}{b_{11}} \right]^{\frac{1}{2}} + \left( \frac{2b_{12} + b_{66}}{2b_{11}} \right) \right]^{\frac{1}{2}} \tag{4.03}
\]

\(K_I\) is the mode I stress intensity factor, \(G_I\) is the mode I strain energy release rate and \(b_{ij}\) are the elastic coefficients, which are related to the principal material constants \((E_1, E_2, G_{12}, \nu_{22} \text{ and } \nu_{23})\) according to:

\[
b_{11} = S_{11} - \frac{(S_{11})^2}{S_{22}} \quad b_{12} = S_{12} - \frac{S_{12}S_{23}}{S_{22}} \quad b_{22} = S_{22} - \frac{(S_{23})^2}{S_{22}} \quad b_{66} = S_{66} \tag{4.04}
\]

Where:

\[
S_{11} = \frac{1}{E_1} \quad S_{12} = \frac{-\nu_{12}}{E_1} \quad S_{23} = \frac{-\nu_{23}}{E_2} \quad S_{22} = \frac{1}{E_2} \quad S_{66} = \frac{1}{G_{12}} \tag{4.05}
\]
4.3. INTRALAMINAR SHEAR FRACTURE

4.3.1. Introduction

The correct measurement of the intralaminar, or in-plane, shear strength of a composite material is still an unresolved open problem. A criterion for a model test, given by Lee and Munro [19], states that the ideal quantitative shear test method should provide a region of pure, uniform, shear stress and that there should be a unique relationship between the applied load and the magnitude of the shear stress in the test section. Further, for accurate determination of the shear stress/strain response, the test section should be one of maximum shear stress relative to all other regions of the specimen.

A range of the available different test methods for the characterisation of intralaminar shear have been reviewed and evaluated by Lee and Munro [19]. In this work the authors score each test method on a number of different aspects, including specimen processing and preparation, testing equipment and accuracy of results. The accuracy of each test method is taken as a comparison to the results obtained from the thin-walled tube torsion test. A thin-walled tube subjected to torsion is the most desirable specimen for determining shear stress/strain response from an applied mechanics standpoint. There are however several drawbacks to this experimental method that make it impractical for normal laboratory testing. Tubes do not represent the true material manufactured as panels, the fabrication of tubes is extremely complex and sophisticated equipment is required for testing. Of the test methods evaluated by Lee and Munro, the Iosipescu and the 10° off-axis test appear to be the most advantageous for determining shear characteristics. A more detailed review of these two test methods is given in the following sections.

4.3.2. The Iosipescu Test Method

This test method, also known as the double V-notch test, was first proposed by Nicoline Iosipescu in 1967 [20] to characterise the in-plane shear properties of metallic materials. Walrath and Adams first published the application of the test method to composite
Chapter Four: A Review of Mechanical Characterisation of Matrix Fracture

materials in 1982 [21]. The test is now an ASTM Standard, D-5379M-98 [22]. This test method has advantages that it is relatively simple to conduct, employs easily fabricated specimens and is capable of measuring both shear strength and stiffness. The test is, however, complicated by its required use of a special testing fixture. This test is not limited to in-plane shear measurements of composite materials. It could be used to determine interlaminar shear properties of laminates and would also appear to be useful for measuring the shear strength of adhesive joints [19].

The principle of the test is to apply a set of counteracting force couples to a double V-notched specimen in order to create a state of pure and homogeneous shear stress between the notches. The applied force couples result in counteracting moments being produced within the specimen and thus a shear stress state along the specimens midpoint. Figure 4.02 shows a schematic of the Iosipescu specimen and ASTM standard testing fixture. Iosipescu [20] showed that by cutting 90° notches on both edges of each test specimen, the shear stress distribution within the test specimen could be altered from the parabolic shear stress distribution present in beams of constant cross-section, to a constant shear stress distribution in the region between the two notches.

![Figure 4.02. Schematic of the Iosipescu testing fixture and specimen, after [21]](image-url)
Chapter Four: A Review of Mechanical Characterisation of Matrix Fracture

The two most common specimen configurations in the Iosipescu test are with fibres orientated along the longitudinal axis (0° specimens) or the vertical axis (90° specimens).

Although this test method has been used to measure the shear modulus, shear strength measurements that can be obtained are limited and there seems to be confusion within the literature as to the definition of this parameter. These contradictions are possibly because the apparent shear strength values measured from the 0° and 90° specimens are usually different, with different modes of failure [23]. Within the literature Broughton et al [24] report a failure stress of 58 MPa, without quoting it as a failure strength, whereas, Morton et al [25] report a shear strength of 68 MPa, from the same material AS4/3501-6 0° carbon/epoxy, and the same definition of failure point. Adams and Lewis [26] report a shear strength of 115 MPa, again from the same material and test, but not the same definition of the failure point. The correct definition of a failure point is something therefore that needs to be addressed before accurate measurement of shear strength can take place.

Although in isotropic materials the notches were shown not to cause stress concentrations within the test specimens [20, 21], in orthotropic materials this is not the case [21, 23, 24, 25, 26]. It is stated in several publications [23, 24, 26] that in 0° specimens longitudinal cracks frequently propagate prematurely from the notch roots due to the associated stress concentration. Broughton et al [24] state that the shear stress distribution in the test section of both isotropic and orthotropic specimens is not uniform and that shear and normal stress distributions have been shown to be highly dependent on the orthotropic ratio $E_{11} / E_{22}$, fibre orientation, notch geometry and loading boundary conditions.

The use of the Iosipescu coupon is further complicated by contention within the literature as to the correct testing fixture. The ASTM standard [27] recommends the "Modified Wyoming test fixture" as developed by Adams and Walrath [21]. This test fixture however has been documented to suffer from significant out-of-plane movements [28], which result in parasitic twisting of the coupon, as described by Morton et al [25]. Pierron [28] states that if the shear strains are averaged over the two faces of the specimen, shear modulus measurement can be obtained but the effect of these parasitic
movements on failure cannot be accounted for when shear strength measurement is required. In a review of the Iosipescu test, as applied to unidirectional carbon/epoxy composites, Pierron and Vautrin [29] show that provided careful attention is given to the test fixture, failure under a homogeneous stress state can be achieved. This has been attained with the use of a different fixture than the standard, Modified Wyoming test fixture, named by the authors as the “Ecole des Mines de Saint-Etienne” (EMSE) fixture. This alternative fixture utilises the same coupon geometry but has a different load-introduction system. The fixture avoids pre-loading and ensures that the load is applied in the middle plane of the sample resulting in the suppression of any parasitic twisting. Pierron [25] shows that no significant in-plane bending moment exists when using the EMSE fixture.

If the stress state within the composite is indeed homogeneous it is quoted as not being one of pure shear. Vautrin and Pierron [29] highlight the importance that must be paid to the transverse compressive stress that would also be present within the test specimen. In this work [28] a comparison is made between the value of shear strength obtained from the EMSE test fixture, after the use of a quadratic failure criterion taking into account the transverse compressive stress, and that obtained from a $10^\circ$ off-axis test, using the same analysis with transverse tensile stress instead of compressive. The authors conclude that the in-plane shear strength of unidirectional composites may, to date, be rather grossly underestimated due to inappropriate mechanical testing.

### 4.3.3. The Ten Degree Off-Axis Test Method

The use of various angle off-axis test coupons was first proposed by the IIT Research Institute [30].

Off-axis tests are relatively simple to conduct because they use conventional tensile testing equipment without the need for extra testing fixtures. The coupon consists of a unidirectional laminate cut such that the fibres are oriented at an angle $\theta^\circ$ to the applied load direction. Figure 4.03 shows a schematic of a typical coupon. The notation used in Figure 4.03 and that which will be used in the text is as follows: $\sigma$ denotes stress; $\theta$ is
the orientation angle between applied stress (load direction) and the fibre direction; the subscripts \(x\) \(y\) and \(1\) \(2\), refer to orthogonal right-hand co-ordinate systems with \(x\) taken along the applied stress direction and \(1\) taken along the fibre direction.

\[
\begin{align*}
Y & \quad 2 \\
\text{load} & \quad \text{load} \\
\text{fibre direction} & \\
\text{theta} & \\
1 & \\
\end{align*}
\]

**Figure 4.03.** *Off-axis coupon notation.*

When a \(\theta^\circ\) off-axis specimen is subjected to a uniaxial tensile load, a two-dimensional stress state is induced in the material principal directions. This stress state consists of three stresses: longitudinal \((\sigma_{11})\), transverse \((\sigma_{22})\) and in-plane shear \((\tau_{12})\) on the \(\theta^\circ\) plane. The magnitudes of these stresses as a function of the applied stress \(\sigma_x\) are given by the standard transformation equations.

\[
\begin{align*}
\sigma_{11} &= \sigma_x (\cos \theta)^2, \\
\sigma_{22} &= \sigma_x (\sin \theta)^2, \\
\tau_{12} &= \sigma_x \sin \theta \cos \theta 
\end{align*}
\] (4.06)

Chamis and Sinclair's [31] theoretical and experimental investigations led to the conclusion that when failure occurs in off-axis coupons orientated at \(10^\circ\), the in-plane shear stress is near its critical value. This conclusion led to the recommendation that the \(10^\circ\) off-axis tensile specimen be used for the measuring of in-plane shear strength of unidirectional fibre composites. When \(\theta = 10^\circ\) the stress values become:
\[ \sigma_{11} = 0.970 \sigma_x, \quad \sigma_{22} = 0.030 \sigma_x, \quad \tau_{12} = 0.170 \sigma_x \quad (4.07) \]

The values of \( \sigma_{22} \) and \( \tau_{12} \) are used to assess the relative magnitudes of the transverse and intralaminar shear stresses, respectively.

Previous work on 10° off-axis specimens, Chamis and Sinclair [31], found that the predicted results for elastic properties based on composite mechanics were in very good agreement with measured values of modulus and Poisson's ratio. However, they found that a highly in-homogeneous state of deformation was induced within the specimen because of the constant imposed displacement. Pindera and Herakovich [32] have underlined the problems of an imposed constant displacement at the grips. Because the ends of the specimen are constrained by the rigid grips of the testing machine, the application of constant end displacement induces shearing forces and bending moments in the specimen, resulting in stress concentrations and non-uniform deformation. These shearing forces and bending moments are such that tested specimens become S shaped under load, rather than remaining rectangular. One method to accommodate the coupling effect is to use specimens which are long compared with their width. Sun and Berreth [33] successfully used end tabs made from fibreglass knit and a compliant silicon rubber to achieve a uniform strain field within the test specimen. However, these tabs were very time consuming to create and could not sustain an applied load at elevated temperatures. Recently the use of oblique ends tabs has become the accepted method of creating a state of uniform stress in the off-axis specimen under uniaxial loading.

Sun and Chung [34] first proposed the use of oblique end tabs in 1992. The idea behind oblique end tabs for off-axis coupons is to impose displacements along a theoretical line of iso-displacements. The effects of oblique end tabs over rectangular end tabs have been analysed by Pierron and Vautrin [35]; in this study, the authors claim to prove that oblique end tabs are beneficial for the measurement of the ultimate shear stress from the 10° off-axis tensile test.
Sun and Chung calculated the angle $\phi$ between the iso-displacement line and the x-axis (applied load axis) to be given by:

$$\cotan \phi = -\left(\frac{\bar{S}_{16}}{\bar{S}_{11}}\right)$$  \hspace{1cm} (4.08)$$

$\bar{S}_{ij}$ are components of the stiffness tensor in the x-y axes, which are related to the principal elastic constants of the material.

Pierron and Vautrin [35] show with the use of finite element stress analysis, that the stress field within a 10° off-axis specimen with normal straight edges is significantly heterogeneous with a large amount of parasitic shear around the end tabs. The equivalent stress field within an oblique end tabbed specimen is much more homogeneous. These findings are backed by experimental results in which all the straight tabbed coupons failed in the tabbed area whereas all the oblique end tabbed coupons failed in the gauge section. An additional conclusion made by this report was that oblique tabs made from +/- 45° glass/epoxy were more effective than conventional aluminium tabs, probably because of their lower longitudinal stiffness. In a further study [36] of the effects of boundary conditions on the strain field in a unidirectional CFRP off-axis tensile test, the use of oblique end tabs was shown to result in a homogeneous strain field over the whole specimen. It was also concluded that the tab oblique angle is not very sensitive to the exact values of elastic moduli, hence only estimates of the materials elastic properties are required. Finite element analysis showed that a 3° error on the oblique angle was acceptable in terms of stress concentrations near the tabs, but that a 7° error leads to significant stress concentrations for the particular CFRP system used.

If the stress field within the oblique end tabbed 10° off-axis specimen is indeed homogeneous, it is not one of pure shear, as shown by Equations (4.06), therefore the influences of the normal stresses must be taken into account. Pierron and Vautrin [35] state that measurement of the ultimate shear stress from 10° off-axis coupons, even when obliquely tabbed, cannot directly be interpreted as the in-plane shear strength. At best it can be said that it gives a lower bound for the shear strength.
4.3.4. Intralaminar Shear Fracture Method Selected For The Current Work

The 10° off-axis tensile test was chosen as the method most appropriate to measure the intralaminar shear characteristics of FRPs. The ideal shear test method would be one where the specimen fails under a homogeneous pure shear stress. It was concluded that, to date, such an ideal shear test method does not exist. Both the Iosipescu and the 10° off-axis test can produce failure under a homogeneous stress state [37], however neither achieves pure shear. The 10° off-axis test was considered the simpler choice due to the complex testing fixture required by the Iosipescu test, as well as the contention within the literature as to which test fixture is more appropriate: the modified Wyoming test fixture or the EMSE fixture. Additional reasons for the choice of the off-axis specimen are that it offers the possibility to measure fracture mechanics properties from cracked coupons and also that failure under various mixed mode conditions may be studied by simply changing the orientation of the fibres, with respect to the applied load. The coupon may also be miniaturised in order that in-situ fractured samples may be generated for fracture surface analysis studies. Off-axis tensile coupons have been used in a number of previous studies on the mixed-mode failure of unidirectional composite laminates [38, 39, 40, 41, 42].

4.3.5. Cracked Off-Axis Specimens

In a cracked off-axis coupon (Figure 4.04), oriented at θ° to an applied far-field axial stress, \( \alpha \), the stress intensity factors, \( K_I \) and \( K_{II} \) for a crack length \( 2a \), are given by [43, 44, 38].

\[
K_I = \sigma_x \sqrt{\pi a} (\cos \theta)^2
\]

\[
K_{II} = \sigma_x \sqrt{\pi a} (\sin \theta \cos \theta)
\]
4.4.2 Strength Based Failure Criteria

Figure 4.04. Cracked off-axis coupon oriented at $\theta^\circ$ to an axial stress $\sigma_3$.

The highlighted area shows the induced two-dimensional stress state within the coupon, as given by Equations (4.06).

The relationship between $K_1$ and $G_1$ for an orthotropic material has been shown previously, (4.03). $K_1$ and $G_1$ are related for an orthotropic material by Equation (4.11) [18].

\[
G_1 = K_1^2 \left[ \left( \frac{b_{11}}{b_{22}} \right)^2 + \left( \frac{2b_{12} + b_{66}}{2b_{11}} \right) \right]^{1/2}
\]

(4.11)
4.4. FAILURE CRITERIA

4.4.1. Introduction

There are a number of failure criteria that have been proposed over the years and there is still a great deal of controversy as to which, if any, are appropriate for the prediction of failure of orthotropic composite materials [45]. The main issue is whether or not the critical stress to trigger one mechanism of failure is affected by the stresses tending to cause the others, i.e. whether there is any interaction between the modes of failure [8].

Failure criteria may either be based upon strength measurements, in which the input parameters are material properties measured using un-cracked coupon geometries, or upon fracture mechanics parameters generated from pre-cracked coupons.

4.4.2. Strength Based Failure Criteria

4.4.2.1. Maximum Stress Criterion

The maximum stress criterion is the most simple failure criterion. If we consider a composite lamina subjected to an in-plane stress, then failure is assumed to occur when a stress parallel or normal to the fibre axis reaches the appropriate critical value, i.e. when one of the following conditions is satisfied:

\[ \sigma_{11} \geq \sigma_{11u}, \quad \sigma_{22} \geq \sigma_{22u}, \quad \tau_{12} \geq \tau_{12u} \quad (4.12) \]

This is shown schematically in Figure 4.05.
Figure 4.05  Schematic illustration of how an arbitrary stress state in a lamina gives rise to failure as a result of exceeding critical values of (a) axial tensile stress $\sigma_{11u}$, (b) transverse stress $\sigma_{22u}$ and (c) shear stress $\tau_{12u}$ after [8]

For any stress system ($\sigma_x$, $\sigma_y$, $\tau_{xy}$) applied at an angle $\theta$ to the principal directions (1-2) of an off-axis lamina, stress evaluations can be carried out from transformation equations, which are derived from force equilibrium considerations:

\[
\begin{pmatrix}
\sigma_{11} \\
\sigma_{22} \\
\tau_{12}
\end{pmatrix} =
\begin{pmatrix}
c^2 & s^2 & 2cs \\
s^2 & c^2 & -2cs \\
-cs & cs & -s^2
\end{pmatrix}
\begin{pmatrix}
\sigma_x \\
\sigma_y \\
\tau_{xy}
\end{pmatrix}
\]  (4.13)

(c = $\cos\theta$, s = $\sin\theta$)
As the applied stress is increased, monitoring of $\sigma_{11}$, $\sigma_{22}$ and $\tau_{12}$ allows the onset of failure to be identified as the point when one of the inequalities in Equation (4.12) is satisfied. Taking the applied stress to be simple tension, the magnitude of $\sigma_x$ necessary to cause failure can be plotted as a function of loading angle $\phi$ between the axis and the fibre direction, for each of the three separate failure modes.

$$\sigma_{xu} = \frac{\sigma_{11u}}{\cos^2 \phi} \quad \sigma_{xu} = \frac{\sigma_{22u}}{\sin^2 \phi} \quad \sigma_{xu} = \frac{\tau_{12u}}{\sin \phi \cos \phi}$$ (4.14)

The three curves in Figure 4.06 represent the three modes of failure. The solid line indicates the predicted variation of the failure stress as $\phi$ increases, according to the maximum stress criterion.

**Figure 4.06** Predicted dependence on loading angle $\phi$ of the applied stress for the onset of different failure modes for a polyester/50% glass lamina, according to the maximum stress criterion, after [8]
4.4.2.2. Polynomial Criteria

Some composite failure criteria are based upon adaptations of yield criteria developed for metals. The most common yield criteria for metals are those of Tresca and von Mises. The Tresca criterion assumes that yielding occurs when a critical value of the maximum shear stress is reached. If $\sigma_p$, $\sigma_q$ and $\sigma_r$ are the principal stresses and $\sigma_y$ is the yield stress, under a uniaxial load the in-plane stress ($\sigma_r = 0$) reduces to:

$$\sigma_p - \sigma_q = \sigma_y \quad \text{or} \quad \sigma_p = \sigma_y \quad (4.15)$$

Assuming:

$$\sigma_p > \sigma_q$$

The von Mises criterion corresponds to yield occurring when the distortional strain energy stored in the material reaches a critical value. This may be expressed as:

$$\left(\sigma_p - \sigma_q\right)^2 + \left(\sigma_q - \sigma_r\right)^2 + \left(\sigma_r - \sigma_p\right)^2 = 2(\sigma_y)^2 \quad (4.16)$$

Both the von Mises and the Tresca yield criteria were developed for the yielding of metallic materials. Any adaptation of these criteria to describe failure of composites must take account of the inherent anisotropy of a fibre composite and of the differences between the mechanisms of metal yielding and of composite failure. The effect of anisotropy in metals was studied by Hill [8], who derived a modified von Mises yield criterion for metals with orthotropic symmetry (three orthogonal planes of symmetry). The adaptation of this criterion to failure of unidirectional composites by replacing the yield stresses by the appropriate measured failure stresses was first proposed by Azzi and Tsai [6]. The formulation they proposed is:
This equation is commonly termed the Tsai-Hill criterion. The criterion defines an envelope in stress space, if the stress state lies outside of this envelope, i.e. the sum of the terms on the left hand side is equal to or greater than unity, failure is predicted.

Although modification of Hill's anisotropic yielding criterion by Tsai is strongly contested within the literature by authors such as Hart-Smith, it still remains, however, one of the most quoted in composite textbooks \[7, 8\]. Hart-Smith \[45, 46\] states that there is no similarity between Hill's theory and Tsai's, because Hill's theory refers to the yielding of a homogeneous material under various states of combined stress by a single mechanism, while Tasi's theory refers to failures by five different mechanisms of a distinctly heterogeneous composite.

The Tsai-Wu failure criterion is another failure criterion that has received extensive use \[47\]. This criterion is similar to the Tsai-Hill criterion but is now a generalised second order polynomial with additional stress terms. Under plane-stress conditions, this failure criterion may be written:

\[
F_{xx} \sigma_{11}^2 + F_x \sigma_{11} + F_{yy} \sigma_{22}^2 + F_y \sigma_{22} + F_{xy} \sigma_{11} \sigma_{22} + F_{ss} \tau_{12}^2 = 1
\]  

(4.18)

The coefficients are related to the material strength properties according to:

\[
F_{xx} = \frac{1}{\sigma_{11}\sigma_{11}}, \quad F_x = \frac{1}{\sigma_{11}} - \frac{1}{\sigma_{11}}, \quad F_{ss} = \frac{1}{\tau_{12}}
\]

\[
F_{yy} = \frac{1}{\sigma_{22}\sigma_{22}}, \quad F_y = \frac{1}{\sigma_{22}} - \frac{1}{\sigma_{22}}, \quad F_{xy} = \frac{F_{xy}}{\sqrt{\sigma_{11}\sigma_{11}\sigma_{22}\sigma_{22}}}
\]
Chapter Four: A Review of Mechanical Characterisation of Matrix Fracture

\( \sigma_{11U}, \sigma_{22U}, \tau_{12U} \) and \( \sigma_{11U}, \sigma_{22U}, \tau_{12U} \) are the lamina longitudinal, transverse and shear strengths in tension and compression, respectively. The \( F_i \) and \( F_{ij} \) terms are second and fourth order lamina strength tensors. The linear stress terms account for possible differences in tensile and compressive strengths. The quadratic stress terms are similar to those in the Tsai-Hill formulation, and describe an ellipsoid in stress space. The \( F_{ij} (i \neq j) \) terms are new to those in the Tsai-Hill criterion. Off-diagonal terms of the strength tensor provide independent interactions among the stress components [47]. The term \( F_{ij}^* \) can only be determined by conducting a biaxial test and is deemed an interaction term.

The Tsai-Wu failure criterion is a strength-based criterion; it predicts the occurrence of failure but nothing about the failure mode (tensile or compressive, longitudinal, transverse or shear). The determination of the \( F_{ij} \) term complicates the criterion, as it is difficult to measure [47]. Indeed Hart-Smith [45] states that the Tsai-Wu failure model contains the interaction term \( F_{ij}^* \) for which no reliable measurement has been found and hence is customarily assigned the value of 0.5 or zero.

4.4.3. Fracture Mechanics Based Failure Criteria

As has previously been stated, for pure mode I and pure mode II the fracture mechanics approach to failure is, in principal, relatively straightforward. Matrix cracking in laminates, however, frequently involves mixed opening and shearing modes. The application of fracture mechanics based criteria for mixed-mode cracking has not been as firmly established as for the single mode case. In the following review, failure criteria are based on off-axis and delamination geometries.

A common route to failure criterion development is the partitioning of the applied load into mode I and mode II components. Whitney [38] suggests that fracture characterisation should concentrate on pure mode I and pure mode II and that under mixed-mode loading a linear criterion for failure should be used, Expression (4.19).
Binienda et al [42] conducting tests on off-axis laminates from a graphite/epoxy system suggested a criterion based upon $G_{I} + G_{II}$ was appropriate for mixed-modes with a ratio of $G_{II}/G_{I} < 3$, Figure 4.07.

![Figure 4.07](image)

**Figure 4.07.** Linear interaction diagram showing mixed-mode strain energy release rate data recorded from off-axis laminates, after [42].

For similar intra-laminar studies on graphite/epoxy and graphite/PEEK composites as reported by Donaldson [41], the linear criterion represents a lower bound (most of the data lie outside of the failure surface) to measured toughness values. Results plotted as the mode II versus mode I components of $G_{C}$ show that the best-fit mixed-mode failure criterion to the data is in the form:

$$\left( \frac{G_{I}}{G_{IC}} \right)^{m} + \left( \frac{G_{II}}{G_{IC}} \right)^{n} = 1$$  \hspace{1cm} (4.20)
In inter-laminar failure studies, Carlsson et al [48] and Hwu et al [49] have also included the addition of empirical constants \((m\text{ and } n)\) into the linear mixed-mode failure criterion, again to provide a better fit to experimental data.

For highly mode II-dominated mixed modes, friction effects may be important and lead to a high apparent fracture toughness [50]. Wang et al [39] observed that the critical energy release rate for mixed-mode loading increases with an increasing mode II loading component. O'Brien [4] reports from a literature review on the comparison of \(G_{IIc}\) to \(G_{IC}\) that the general trend is that brittle materials (lower \(G_{IC}\) values) have \(G_{IIc}\) values much greater than the corresponding \(G_{IC}\), whereas tougher matrix materials (higher \(G_{IC}\) values) have \(G_{IIc}\) values that are close to, but still greater than, the corresponding \(G_{IC}\).

Failure loci have been established by Hashemi et al [51, 52] based on a critical crack opening displacement or with an interaction parameter \((I)\), which varies linearly between 0 and 1 and is a function of the ratio \(G_{I}/G\), Expression (4.21).

\[
\left( \frac{G_{I}}{G_{IC}} - 1 \right) \times \left( \frac{G_{II}}{G_{IIc}} - 1 \right) \times I = 0
\]

O'Brien [4] states that in both brittle and tough matrix composite materials, the complex failure process under mode II loading is far removed from the idealised sliding of two crack planes relative to one another as postulated in the fracture mechanics elasticity solutions. Hence, a mechanistic explanation of mode II fracture is needed. Physical considerations of the failure micro-mechanisms such as the appearance of the fracture surface have been taken into account in the development of some failure criteria. A general mixed-mode criterion including an experimentally measured parameter \(\omega\) to represent the slope of the fracture surface roughness has been proposed by Charalambides et al [53], Expression (4.22). This fracture mechanics based failure criteria was postulated based on the observation that for brittle homogeneous materials subjected to mixed-mode loading, fracture occurs when the total mode I component experienced is equal to a critical value, \(G_{\theta}\).
\[ G_0 = G_C \left[ \cos^2(\psi - \psi_0) + \sin^2 \omega \sin^2(\psi - \psi_0) \right] \quad (4.22) \]

\( G_C \) is the measured fracture energy \( (= G_I + G_{II}) \), \( \psi \) is the phase angle of the applied loads \( [= \text{tan}^{-1}(G_{II}/G_I)^{1/2}] \), \( \psi_0 \) is the phase angle which arises from the elastic mismatch across a bi-material interface (e.g. fibre/matrix interface), also determined empirically. A good description of delamination failure loci using this criterion has been obtained by Kinloch \textit{et al} [6] for PEEK and epoxy composites, Figure 4.08.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.08.png}
\caption{Delamination failure locus for composites (a) epoxy (b) PEEK. Solid line represents theoretical Equation (4.22), after \cite{6}.}
\end{figure}

Charalambides \textit{et al} [53] note that if \( G_{II} = G_{IIIC} \) when \( G_I = 0 \), then \( G_{IIIC} \) may be estimated on a measured \( G_{IC} \) and value of omega. For the worst case of \( \omega = 45^\circ \) the value of \( G_{IIIC} \) is shown to be twice that of \( G_{IC} \). O'Brien [4] states that this is consistent with the postulated initial damage mechanism; the formation of tension micro-cracks ahead of the fracture front. However, that it does not account for the bending and fracture of the ligaments formed by the micro-cracks that releases much of the energy required to create the perceived macroscopic mode II failure growth. Charalambides \textit{et al} [53] cite an epoxy matrix composite example where \( G_{IIIC} = 2.22 \ G_{IC} \). O'Brien [4] gives further
examples from the literature where $G_{IC}$ values are greater than twice the corresponding $G_{IC}$, although states that the basic premise for the development of Expression (4.22) is sound, i.e. that the actual failure mechanism is due to tension, but a complete description of failure was missing.

### 4.5. CONCLUDING REMARKS

Fracture under a pure mode I or pure mode II loading may be characterised using either strength or fracture mechanics properties as measured from un-cracked or cracked coupons, respectively.

Although strength measurements from mode I failed coupons are not part of this study, literature has been identified that characterises mode I failure from strength measurements. The compact tension test method has been identified from the literature for the experimental measurement of mode I fracture mechanics properties.

A review of the available literature has identified various test methods for the characterisation of mode II failure. A 10° off-axis coupon geometry has been chosen as the most favourable sample for predominantly mode II (shear dominated) characterisation. The coupon may be used un-cracked for strength measurements or cracked to generate fracture mechanics data. Variation of the off-axis angle allows loadings with differing intensities of the mode I to mode II ratio to be studied; again strength measurements may be made from un-cracked coupon whereas cracked coupons may be used to generate fracture mechanics data.

In order to characterise composite failure under general in-plane loadings it is necessary to use a failure criterion. Failure criteria may be based upon strength measurements or upon fracture mechanics properties. A review of some of the more commonly used failure criteria (both strength and fracture mechanics based) has shown that there is still a degree of controversy within the literature as to which if any, best characterises failure of a composite under general in-plane loadings.
Chapter Five

Mechanical Testing Development

5.1. INTRODUCTION

The present chapter documents the development of mechanical testing methods used in the present study for the measurement of both strength and fracture mechanics based properties.

Failure of cracked samples under a pure mode I loading has been characterised from measurement of fracture mechanics properties using a compact tension specimen. It has been necessary to establish a notching methodology that leads to a sharp, natural pre-crack of controlled length.

An obliquely tabbed, off-axis tensile coupon geometry has been chosen from the literature as the most appropriate for the characterisation of failure under mixed-mode and predominantly mode II loadings. Calculation of the oblique end tab angle with respect to fibre off-axis angle is given for each of the material systems studied. A 10° off-axis tensile coupon has been used for characterisation of failure under a predominantly mode II, shear dominated loading. Variation of the fibre off-axis angle has enabled failure under loadings of different mode I to mode II ratio to also be characterised. Un-notched coupons have been used for strength measurements and cracked coupons have been used to measure fracture mechanics properties. The method of pre-cracking is described.
5.2. MODE I TENSILE TESTS

5.2.1. Test Procedure

Mode I intralaminar toughness and fracture toughness tests were carried out in accordance with the ASTM standard D-5045-91a [17]. Coupons were loaded in tension, using a screw-driven quasi-static Instron (5500R), at crosshead speeds of 0.5 mm/min.

A number of samples were tested in tension prior to being notched (Figure 5.01a) in order to obtain the load-displacement curve, the un-notched coupon load-displacement curve was then used to correct load-displacement curves recorded from notched specimens (Figure 5.01b). Coupons were tested to loads slightly in excess of the cracked sample failure loads. An extensometer was used to record displacement. The corrected energy term (\(U\)), required in the direct calculation of \(G_{IC}\), was measured from the difference in the areas of the load/displacement plots for cracked and un-cracked coupons. This energy term is given by:

\[
U = \frac{1}{2} P_Q \left[ u_Q - u_i \right]
\]

\(U\) is the corrected energy, \(P_Q\) is the peak load and \(u_Q\) and \(u_i\) are the displacements in the fracture and indentation tests, respectively, (Figure 5.01). Toughness values \((G_{IC})\) were calculated from the corrected energy \((U)\) using Expression (4.02).

Mode I fracture toughness values \((K_{IC})\) were calculated from the maximum loads which coupons sustained prior to unstable crack propagation, using Expression (4.01).
5.2.2. Method Development

Initial mode I fracture toughness results are shown in Table 5.01 for the HTA/F922 composite system. The average measured value of $K_{IC}$ for the HTA/F922 material was 2.80 MN m$^{3/2}$, with a standard deviation of 0.19 MN m$^{3/2}$. This initial value of $K_{IC}$ was compared to that given by Rezaifard et al [16] for the same material and testing procedure. Rezaifard et al report an average $K_{IC}$ value for HTA/F922 CFRP with a 100% fibre surface treatment level (standard fibre surface treatment level), of 1.51 MN m$^{3/2}$. This value is significantly lower than that measured here (2.80 MN m$^{3/2}$).
Table 5.01. Initial HTA/F922 mode I fracture toughness results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a/W = x</th>
<th>f(x)</th>
<th>B (mm)</th>
<th>P_{max} (N)</th>
<th>K_{IC} (MNm^{-3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.5</td>
<td>9.65</td>
<td>2.09</td>
<td>130</td>
<td>3.00</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>9.65</td>
<td>2.17</td>
<td>118</td>
<td>2.62</td>
</tr>
<tr>
<td>D</td>
<td>0.5</td>
<td>9.65</td>
<td>2.20</td>
<td>121</td>
<td>2.65</td>
</tr>
<tr>
<td>E</td>
<td>0.5</td>
<td>9.65</td>
<td>2.17</td>
<td>123</td>
<td>2.73</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>9.65</td>
<td>2.09</td>
<td>130</td>
<td>3.00</td>
</tr>
</tbody>
</table>

A likely reason for the high measured value of $K_{IC}$ is that samples were not correctly pre-cracked prior to testing. If a blunt notch feature was generated, rather than the required sharp crack, the sample would be able to sustain a greater load before unstable crack propagation and thus the calculated value of $K_{IC}$ would be high. A new sample notching and pre-cracking procedure was therefore implemented.

The ASTM standard (D-5045-91a) [17] for compact tension coupons states that the depth of the natural crack generated by tapping must be at least twice as long as the width of the sawed-in slot or machined notch tip radius. In initial experiments the sawed-in slot had been relatively wide, approximately 3 mm, a result of the thickness of the saw blade. The required natural crack therefore needed to be of a length over 6 mm. It was found that longer natural cracks were considerably more difficult to propagate accurately than shorter ones. A method for cutting very thin sawed notches was devised using a powered fretsaw and a piercing saw (jewellery) blade. The blades were very thin, approximately 0.5 mm, thus allowing the length of the natural crack to be considerably shorter than that used previously. Minimising the possibility of fibre bridging was another driving force for the use of short natural cracks.

In order to generate a sharp natural crack, a fresh razor blade was tapped into the tip of the cut notch; during this operation coupons were clamped edge-wise in an engineering vice so as to generate a region of compression. It is proposed that the natural crack generated will propagate through the sample until it reached this region of compression, thus the length of the crack may be controlled. Figure 5.02 shows a schematic of the experimental set-up.
The results, obtained using the improved method of coupon pre-cracking, are shown in Table 5.02.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a/w = x$</th>
<th>$f(x)$</th>
<th>$B$ (mm)</th>
<th>$P_{\text{max}}$ (N)</th>
<th>$K_{IC}$ (MN m$^{-3/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.5</td>
<td>9.65</td>
<td>2.14</td>
<td>57.2</td>
<td>1.29</td>
</tr>
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<td>O</td>
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</tr>
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<td>2.08</td>
<td>55.5</td>
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</tr>
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</tr>
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<td>2.13</td>
<td>76.2</td>
<td>1.73</td>
</tr>
<tr>
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<td>2.20</td>
<td>76.9</td>
<td>1.69</td>
</tr>
<tr>
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<td>2.07</td>
<td>71.1</td>
<td>1.66</td>
</tr>
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<td>1.27</td>
</tr>
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<td>2.21</td>
<td>60.0</td>
<td>1.31</td>
</tr>
<tr>
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<td>2.14</td>
<td>60.8</td>
<td>1.37</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.5</td>
<td>9.65</td>
<td>2.16</td>
<td>75.3</td>
<td>1.68</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.5</td>
<td>9.65</td>
<td>2.08</td>
<td>66.0</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Table 5.02. *HTA/F922 mode I fracture toughness results using improved notching technique.*

Figure 5.02. *Schematic of the clamping set-up used during compact tension coupon pre-cracking.*
The average value of $K_{IC}$, measured using the improved method of coupon pre-cracking, for the HTA/F922 material was $1.51 \text{ MN m}^{3/2}$ with a standard deviation of $0.22 \text{ MN m}^{3/2}$. This value compares favourably with that reported by Rezaifard et al [16], $(1.51 \text{ MN m}^{3/2})$. It was decided therefore that the new method of notching and subsequent pre-cracking was satisfactory. This method was used for the HTA/F927 tests reported in the next chapter.

5.3. OFF-AXIS TENSILE TESTS

5.3.1. Oblique End Tab Angle Calculation

In order to minimise shear-coupling effects and so to promote failure under a homogeneous stress state, oblique end tabs were used with all off-axis tensile test coupons.

In an off-axis tensile test the angle between the theoretical iso-displacement line and the applied load is given by Equation (5.02) [34].

$$\cot \phi = -\left( \frac{\bar{S}_{16}}{\bar{S}_{11}} \right) \quad (5.02)$$

The angle ($\phi$) is given as a function of the compliance coefficients of the material, which themselves are related to the principal material elastic properties. The relationship between the compliance coefficients and the principal material elastic properties has been taken from Jones [54] and is shown in Expressions (5.03) and (5.04).

$$\bar{S}_{11} = S_{11} \cos^4 \theta + (2S_{12} + S_{66}) \sin^2 \theta \cos^2 \theta + S_{22} \sin^4 \theta$$

$$\bar{S}_{16} = (2S_{11} - 2S_{12} - S_{66}) \sin \theta \cos^3 \theta - (2S_{22} - 2S_{12} - S_{66}) \sin^3 \theta \cos \theta$$

(5.03)
Chapter Five: Mechanical Testing Development

Where:

\[
S_{11} = \frac{1}{E_1}, \quad S_{12} = -\frac{\nu_{12}}{E_1}, \quad S_{22} = \frac{1}{E_2}, \quad S_{66} = \frac{1}{G_{12}} \quad (5.04)
\]

\(E_1\) is the longitudinal modulus, \(E_2\) is the transverse modulus, \(\nu_{12}\) is Poisson's ratio and \(G_{12}\) is the shear modulus.

Using Equation (5.02) and the principal elastic material properties of each system, as set out in Table 3.02, the oblique angle (\(\phi\)) is presented as a function of fibre orientation (\(\theta\)) for each material system, Table 5.03 and Figure 5.03. The calculated angles are similar for the three CFRP systems. The GFRP angles differ from those in the CFRP systems because of the less marked anisotropy of this system.

### Table 5.03. Oblique end tab angle

<table>
<thead>
<tr>
<th>Fibre orientation ((\theta^\circ))</th>
<th>XAS/914</th>
<th>HTA/F922</th>
<th>HTA/F927</th>
<th>Glass/DGEBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>5</td>
<td>30.35</td>
<td>35.74</td>
<td>28.97</td>
<td>57.71</td>
</tr>
<tr>
<td>10</td>
<td>23.54</td>
<td>26.69</td>
<td>22.81</td>
<td>43.81</td>
</tr>
<tr>
<td>15</td>
<td>24.54</td>
<td>26.56</td>
<td>24.14</td>
<td>39.86</td>
</tr>
<tr>
<td>20</td>
<td>27.88</td>
<td>29.16</td>
<td>27.77</td>
<td>40.23</td>
</tr>
<tr>
<td>25</td>
<td>32.37</td>
<td>33.00</td>
<td>32.56</td>
<td>42.78</td>
</tr>
<tr>
<td>30</td>
<td>37.59</td>
<td>37.56</td>
<td>38.15</td>
<td>46.60</td>
</tr>
<tr>
<td>35</td>
<td>43.31</td>
<td>42.56</td>
<td>44.35</td>
<td>51.23</td>
</tr>
<tr>
<td>40</td>
<td>34.35</td>
<td>47.84</td>
<td>50.96</td>
<td>56.39</td>
</tr>
<tr>
<td>45</td>
<td>55.52</td>
<td>53.22</td>
<td>57.75</td>
<td>61.82</td>
</tr>
<tr>
<td>50</td>
<td>61.58</td>
<td>58.55</td>
<td>64.40</td>
<td>67.30</td>
</tr>
<tr>
<td>55</td>
<td>67.30</td>
<td>63.70</td>
<td>70.60</td>
<td>72.56</td>
</tr>
<tr>
<td>60</td>
<td>72.48</td>
<td>68.54</td>
<td>76.08</td>
<td>77.37</td>
</tr>
<tr>
<td>65</td>
<td>76.98</td>
<td>73.00</td>
<td>80.62</td>
<td>81.50</td>
</tr>
<tr>
<td>70</td>
<td>80.75</td>
<td>77.05</td>
<td>84.14</td>
<td>84.79</td>
</tr>
<tr>
<td>75</td>
<td>83.80</td>
<td>80.70</td>
<td>86.67</td>
<td>87.18</td>
</tr>
<tr>
<td>80</td>
<td>86.24</td>
<td>84.01</td>
<td>88.32</td>
<td>88.71</td>
</tr>
<tr>
<td>85</td>
<td>88.24</td>
<td>87.07</td>
<td>89.33</td>
<td>89.55</td>
</tr>
<tr>
<td>90</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
</tbody>
</table>
5.3.2. Testing of Un-Notched Off-Axis Coupons

5.3.2.1. Shear Strength Measurements

5.3.2.1.1. Introduction

In-plane maximum shear stress tests were carried out using 10° off-axis coupons with oblique +/- 45° glass/epoxy end tabs, as shown schematically in Figure 5.04. Tests were conducted in order to verify the use of oblique end tabs. Results recorded from the XAS/914 material have been compared to previously published data for the same material. Shear strength measurement has also been conducted using the HTA/F927 material.
5.3.2.1.2. Test Procedure

Specimens were cut from a unidirectional panel of material using a diamond impregnated saw. Coupon edges were polished to a 1 µm finish so as to mitigate the effects of any defects that might provide crack initiation sites. Samples were loaded in tension until failure, using a quasi-static Instron (5500R) tensile test machine. The maximum load sustained prior to failure was recorded and used to calculate the applied far-field failure stress, $\sigma_{uy}$.

The fibre orientation with respect to the longitudinal axis, as determined post fracture, was $9^o$ for the XAS/914 system and $10^o$ for the HTA/F927 system. The stress state within the coupon, calculated using the equations as shown in Expression (4.06), was therefore:

\[
\theta = 9^o
\]

\[
\sigma_{11} = 0.98 \sigma_{uy}, \quad \sigma_{22} = 0.02 \sigma_{uy}, \quad \tau_{12} = -0.15 \sigma_{uy}
\]
\[ \theta = 10^\circ \]

\[
\sigma_{11} = 0.97 \sigma_{su}, \quad \sigma_{22} = 0.03 \sigma_{su}, \quad \tau_{12} = -0.17 \sigma_{su}
\]

### 5.3.2.1.3. Results

The results presented in this thesis are quoted as maximum shear stresses rather than shear strengths because the stress state at failure is not one of pure shear. Results are shown in Tables 5.04 and 5.05 for the XAS/914 and HTA/F927 systems, respectively.

#### Table 5.04. XAS/914 Maximum shear stress results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. Load (kN)</th>
<th>Max. Tensile stress ( \sigma_{su} ) (MPa)</th>
<th>Max. Shear stress ( \tau_{12} ) (MPa)</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSA/914-A</td>
<td>20.2</td>
<td>481.0</td>
<td>74.3</td>
<td>Top tab</td>
</tr>
<tr>
<td>XSA/914-B</td>
<td>22.6</td>
<td>517.2</td>
<td>80.0</td>
<td>Gauge length</td>
</tr>
<tr>
<td>XSA/914-C</td>
<td>21.3</td>
<td>488.5</td>
<td>75.5</td>
<td>Gauge length</td>
</tr>
<tr>
<td>XSA/914-D</td>
<td>19.3</td>
<td>465.1</td>
<td>71.9</td>
<td>Top tab</td>
</tr>
</tbody>
</table>

The maximum shear stress for the XAS/F914 material was measured as 75.4 MPa, with a standard deviation of 3.4 MPa.

#### Table 5.05. HTA/F927 Maximum shear stress results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. Load (kN)</th>
<th>Max. Tensile stress ( \sigma_{su} ) (MPa)</th>
<th>Max. Shear stress ( \tau_{12} ) (MPa)</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTA/F927-A</td>
<td>20.2</td>
<td>481.0</td>
<td>74.3</td>
<td>Bottom tab</td>
</tr>
<tr>
<td>HTA/F927-B</td>
<td>22.6</td>
<td>517.2</td>
<td>80.0</td>
<td>Bottom tab</td>
</tr>
<tr>
<td>HTA/F927-C</td>
<td>21.3</td>
<td>488.5</td>
<td>75.5</td>
<td>Top tab</td>
</tr>
<tr>
<td>HTA/F927-D</td>
<td>19.3</td>
<td>465.1</td>
<td>71.9</td>
<td>Top tab</td>
</tr>
</tbody>
</table>

It was noted after the first four tests using HTA/F927 samples that all the coupons had failed within the gripped end tabbed area. HTA/F927 coupons had been cut from the
maximum width of the fabricated panel, so as to utilise as much material as possible. The thickness of the panel tapered down at its edges; a processing feature. Because of the thickness reduction, full-length samples would have a higher fibre volume fraction at their ends. This was thought to be a possible reason for the locus of failure to be always within the same area. Two further 10° off axis samples were prepared with shorter lengths to minimise the taper. The shorter coupons were tested using the same procedure as the previous 10° off-axis samples. The maximum shear results for the shorter coupons are given in Table 5.06.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. Load (kN)</th>
<th>Max. Tensile stress $\sigma_{tn}$ (MPa)</th>
<th>Max. Shear stress $\tau_{12}$ (MPa)</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>19.2</td>
<td>482.5</td>
<td>82.0</td>
<td>Gauge length</td>
</tr>
<tr>
<td>F</td>
<td>19.7</td>
<td>470.1</td>
<td>79.9</td>
<td>Gauge length</td>
</tr>
</tbody>
</table>

The maximum shear stress for the HTA/F927 material was measured as 81.0 MPa, with a range of +/- 1 MPa.

5.3.2.1.4. Concluding Remarks - Shear Testing

The maximum shear stress results obtained using 10° off-axis coupons of the XAS/914 material compare favourably with data obtained by Pierron and Vautrin [35] for the same material and testing procedure, i.e. 75 MPa compared to 78 MPa from Pierron and Vautrin.

The maximum shear stress reported for the HTA/F927 material is an average from the results of samples E and F, the shorter specimens. The value of maximum shear stress is averaged only from the latter two specimens because of their locus of failure, which was within the gauge length. Previously tested samples, with a longer length, failed at
slightly lower stress values, which gave a total average maximum shear stress of 77.3 MPa (s.d. 3.9 MPa).

All of the fracture coupons retained their rectangular geometry. Samples did not appear to deform into the documented S shape [32, 33] and no other extreme deformation as associated with rigid rectangular end tabbed coupons was observed. This validates the development of the oblique tabs and their subsequent use for cracked specimens.

5.3.2.2. Mixed-Mode Strength Measurements

Strength measurements have been made from fracture tests using un-notched off-axis HTA/F922 coupons. Specimens were cut from unidirectional panels, using a diamond impregnated saw, such that the fibre orientation was at 10°, 25°, 45° or 60° to the longitudinal edge. All samples were tabbed with +/- 45° glass/epoxy oblique end tabs. Specimen edges were polished to a 1 µm finish so as to limit the effects of edge defects. The samples were tested in a screw driven Instron (5500R) at a crosshead speed of 0.5 mm/min and the load/time traces were recorded. Results are presented in Section 6.2.

5.3.3. Testing of Cracked Off-Axis Coupons

5.3.3.1. Crack Geometry Investigation

5.3.3.1.1. Introduction

In chapter 4 the use of a centrally cracked off-axis coupon to investigate crack propagation under mixed-mode loading was discussed. An alternative geometry is an off-axis coupon with an edge crack, which might be easier to test experimentally. In this section, these two alternative geometries are considered.
5.3.3.1.2. Centre Cracked

Consider a rectangular sheet of width \(2W\) containing a crack of length \(2a\) subjected to a uniform uniaxial tensile stress \(\sigma_x\) at the ends; the crack is located centrally at an angle \(\theta\) to the direction of the stress \(\sigma_x\), Figure 5.05.

\[
\sigma_x
\]

\[
\theta
\]

\[
2W
\]

\[
2H
\]

\[
\frac{a}{\eta}
\]

**Figure 5.05.** Central slant crack in a rectangular sheet subjected to a uniform uniaxial tensile stress.

If the crack is oriented at an angle of 45° to the applied stress, expressions for the mode I and mode II fracture toughness may be given by resolving the stress perpendicular and parallel to the crack direction, respectively.

\[
K_I = \sigma_x (\cos\theta)^2 \sqrt{(\pi a)} , \quad K_{II} = \sigma_x \sin\theta \cos\theta \sqrt{(\pi a)} \tag{5.05}
\]

When \(\theta = 45°\)

\[
K_I = \sigma_x / 2 \sqrt{(\pi a)} , \quad K_{II} = \sigma_x / 2 \sqrt{(\pi a)} \tag{5.06}
\]
Normalising both expressions to $K_0$, (the mode I stress intensity factor when $\theta = 0^\circ$) gives the ratios:

$$\frac{K_I}{K_0} = 0.5, \quad \frac{K_{II}}{K_0} = 0.5 \quad (5.07)$$

The term $K_0$ is the stress intensity factor for an isolated crack of length $2a$ in a sheet subjected to a uniform uniaxial tensile stress $\sigma_x$, remote from the crack, perpendicular to the crack direction.

$$K_0 = \sigma_x \sqrt{\pi a} \quad (5.08)$$

Values of stress intensity factors for a centre slant cracked rectangular plate subjected to a uniform uniaxial tensile stress in both mode I and mode II are given in [55]. These results, obtained using a modified mapping collocation method, are given as a function of the off-axis angle and the ratio of $a/W$. For a central crack oriented at an off-axis angle of $45^\circ$ in a very large plate ($a/W \to 0$), the ratios of $K_I/K_0$ and $K_{II}/K_0$ are both equal to 0.5. This corresponds to the value from resolving stresses as given in (5.07).

### 5.3.3.1.3. Edge Cracked

Consider a similar rectangular sheet to that with the central slant crack, this time of width $W$ containing a slanted edge crack of length $a$ oriented at an angle $\beta$ to the direction of applied uniaxial tensile stress, $\sigma_x$, Figure 5.06.

Making the assumption that the stress intensity factors take the same form as that in a semi-infinite body, as shown in Expression (5.09).

$$K = 1.12 \sigma_x \sqrt{\pi a} \quad (5.09)$$
Expressions for the mode I and mode II stress intensity factors then follow from resolving the stress perpendicular and parallel to the crack direction, respectively.

\[
\begin{align*}
K_1 &= 1.12 \sigma_x (\cos \theta)^2 \sqrt{\pi a}, \\
K_{II} &= 1.12 \sigma_x \sin \theta \cos \theta \sqrt{\pi a} \quad (5.10)
\end{align*}
\]

When \( \theta = 45^\circ \)

\[
\begin{align*}
K_1 &= 0.56 \sigma_x \sqrt{\pi a}, \\
K_{II} &= 0.56 \sigma_x \sqrt{\pi a} \quad (5.11)
\end{align*}
\]
Normalising the expressions for $K_1$ and $K_{II}$ (5.11) to $K_0$ (5.12), where $K_0$ is the stress intensity factor for an isolated crack in a sheet under a uniform uniaxial tensile stress $\sigma_x$, and is given by:

$$K_0 = \sigma_x \sqrt{\pi a}$$  \hspace{1cm} (5.12)

Gives the ratios:

$$K_1 / K_0 = 0.56, \quad K_{II} / K_0 = 0.56$$ \hspace{1cm} (5.13)

Comparing these Expressions (5.13) to those given in [55] for the case of an edge slant cracked rectangular plate subjected to a uniform uniaxial tensile stress shows a discrepancy in the ratios of $K_1 / K_0$ and $K_{II} / K_0$. When $\theta = 45^\circ$, for the boundary condition of $a/W \to 0$, [55] gives $K_1 / K_0 = 0.65$ and $K_{II}/K_0 = 0.37$. This means that the sample is not amenable to simple analysis.

5.3.3.1.4. Discussion

For a body containing an edge crack slanted at $45^\circ$, [55] states that the magnitude of the mode I stress intensity factor ($K_1$) will be greater than that of the mode II component. When the slanted crack is located within the centre of the body, [55] states that the mode I and mode II components of the stress intensity are equal. A slanted central crack geometry has therefore been chosen because of the even $K_1 / K_{II}$ ratio, consistent with simple analysis.

5.3.3.2. Fracture Toughness Measurement

The mode I and mode II components of $K$ ($K_1$ and $K_{II}$) were measured experimentally using centre notched off-axis obliquely tabbed tensile coupons. Values of $K_1$ and $K_{II}$ were calculated from the maximum load each sample was able to sustain, prior to unstable crack propagation, using Expressions (4.09) and (4.10), respectively.
5.3.3.3. Toughness Measurement

5.3.3.3.1. Introduction

An experimental method has been applied to measure the critical strain energy release rate \( (G_c) \) from centrally notched off-axis tensile coupons. For any given pre-crack length, \( G_c \) may be determined from the Irwin-Kies \([56]\) relationship, which gives the critical strain energy release rate as a function of load and sample compliance, Expression (5.14).

\[
G_c = \frac{P^2}{4B} \left( \frac{dC}{da} \right) \quad \text{(5.14)}
\]

\( P \) is the fracture load, \( B \) is the coupon width and \( (dC/da) \) is the change in elastic compliance \( (C) \) of the sample with respect to crack length \( (a) \).

In order to calculate values of \( G_c \), from Equation (5.14), the compliance of the samples as a function of the crack length is required.

5.3.3.3.2. Elastic Compliance

Initial compliance measurement tests were carried out using obliquely tabbed 10° off-axis coupons from the XAS/914 system. Coupons were tested in a screw driven Instron (5500R) at a crosshead speed of 0.5 mm/min. Samples were tested with an edge crack parallel to the fibre direction. The length of the crack \( (a) \) varied between 0 mm and 47.5 mm with increments of 2.5 mm between each test. A fresh razor blade was carefully “sawed” along the pre-crack tip so as to sharpen it, according to \([17]\). Load/displacement traces were used to calculate the elastic compliance (displacement/load) for each pre-crack increment. Displacements were recorded using an extensometer with a gauge length of 75 mm. Figure 5.07 shows the graph of compliance with respect to crack length.
A fourth order polynomial was fitted to the compliance plot following [57], as indicated in Figure 5.07. The derivative of the polynomial with respect to pre-crack length \((dC/da)\) was then calculated. A plot of \(dC/da\) versus pre-crack length is shown in Figure 5.08.

The expression for the polynomial fit to the compliance data is given by:

\[
C = 1.26E^2 a^4 - 1.00E^4 a^3 + 7.00E^6 a^2 + 1.00E^11 a + 2.30E^8
\]

**Figure 5.07.** Compliance as a function of notch length for edge notched 10\(^\circ\) off-axis XAS/914 coupons.

**Figure 5.08.** Plot showing the derivative of compliance as a function of notch length for edge notched 10\(^\circ\) off-axis XAS/914 coupons.

Edge notches of set length were cut, parallel to the fibre direction, into obliquely tabbed 10\(^\circ\) off-axis coupons of XAS/914. Notches were sharpened using a razor blade.
Cracked coupons were loaded to failure at a crosshead speed of 0.5 mm/min. The maximum load each sample was able to sustain prior to fracture was recorded. Expression (5.14) was used to calculate $G_c$ values from the fracture load and the appropriate value of $dC/da$ as calculated for each specific crack length from Figure 5.08. Experimentally calculated values of the critical strain energy release rate for each pre-crack length are given in Figure 5.09.

![Figure 5.09. Plot showing experimentally obtained values of $G_c$ using XAS/914 10° off-axis samples.](image)

These initial results obtained from the 10° off-axis toughness tests show a large variation in calculated values of $G_c$ for different crack lengths. The variation in results is possibly due to technique used to pre-cracking the coupons. Pre-cracks were implemented by hand sawing a notch along a specified line and then sharpening the notch with the use of a fresh razor blade; the resultant pre-cracks were not totally linear. A new technique to cut the notch has been developed using the same equipment used for the pre-cracking of compact tension coupons. This technique should result in a consistent thin linear notch within each sample. The technique used to sharpen the crack may also be a factor for the variation in the results. A razor blade was "sawed" across the end of the cut notch. It is most likely that, as in the initial compact tension specimen experiments, the sawing of a razor blade did not generate a sharp natural crack at the notch tip. Hence a method
was devised whereby the off-axis sample could be held within an engineering vice, such that a region of compression is produced. An induced crack should propagate through the material until it reaches this region of compression, similar to the revised method of compact tension coupon pre-cracking. The sample is held off-axis so that the region of compression is perpendicular to the fibre direction, as is shown schematically in Figure 5.10.

![Schematic showing the off-axis clamping of an off-axis coupon.](image)

**Figure 5.10.** Schematic showing the off-axis clamping of an off-axis coupon.

### 5.3.3.3.3. Theoretical Compliance

For un-cracked coupons (0 mm notch lengths) a theoretical method has been identified in order to check the experimentally measured elastic compliance values. Compliance is simply a measure of extension with respect to applied load and may therefore be related to the longitudinal elastic response \( E_x \) of the coupon.
Compliance \( = \frac{\delta}{P} \) \hspace{1cm} (5.15)

\[
E_x = \frac{\text{Stress}}{\text{Strain}} = \frac{P \cdot L}{A \cdot \delta}
\]

(5.16)

\( P \) is applied load, \( L \) and \( A \) are the length and cross-sectional area of the coupon, respectively, and \( \delta \) is the extension of the coupon with applied load. Combining Equations (5.15) and (5.16) the compliance may be written in terms of the elastic response \( (E_x) \).

Compliance \( = \frac{\delta}{P} = \frac{L}{E_x A} \)

(5.17)

The longitudinal elastic response \( (E_x) \) may be calculated from the principal elastic material properties of the laminate \( (E_1, E_2, G_{12}) \) by application of a transformed reduced stiffness calculation. This gives the result:

\[
\frac{1}{E_x} = \frac{\cos^4 \theta}{E_1} + \frac{\sin^4 \theta}{E_2} + \left( \frac{1}{G_{12}} - \frac{2v_{12}}{E_1} \right) \sin^2 \theta \cos^2 \theta
\]

(5.18)

Using the relationship between the elastic response of the coupon and the principal material elastic properties, as defined in Table 3.02, a theoretical measurement of the longitudinal compliance of an off-axis coupon may be calculated. This theoretically derived value of compliance may be compared to experimentally measured values (recorded from off-axis coupons with 0 mm notch lengths).
For the 10° off-axis XAS/914 coupons used in initial technique development experiments, theoretical values of compliance at 0 mm notch length have been calculated, Table 5.07. Values are given for an off-axis angle of 9° (fibre orientation measured post-fracture) with a +/- 1° variation. Values of compliance have also been calculated from the experimentally measured longitudinal elastic response ($E_x$) of the coupons, Table 5.08. Modulus values were taken from best-fit lines through experimentally measured stress-strain data, the recorded stress-stain response of the coupons was linear.

**Table 5.07. Variation of $E_x$ with off-axis angle for XAS/914 coupons.**

<table>
<thead>
<tr>
<th>Fibre Angle Degrees</th>
<th>$E_1$ GPa</th>
<th>$E_2$ GPa</th>
<th>$G_{12}$ GPa</th>
<th>$v_{12}$</th>
<th>$1/E_x$ Pa$^{-1}$</th>
<th>$E_x$ GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>145</td>
<td>9.5</td>
<td>5.6</td>
<td>0.31</td>
<td>$9.98E^{-12}$</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>145</td>
<td>9.5</td>
<td>5.6</td>
<td>0.31</td>
<td>$1.08E^{-11}$</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>145</td>
<td>9.5</td>
<td>5.6</td>
<td>0.31</td>
<td>$1.17E^{-11}$</td>
<td>86</td>
</tr>
</tbody>
</table>

The results shown in Table 5.07 are compared to experimentally determined values of the elastic compliance at 0 mm notch lengths, Table 5.08.

**Table 5.08. Comparison of experimental and theoretical XAS/914 compliance results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Off- axis Angle Degrees</th>
<th>X-sectional area m$^2$</th>
<th>Calculated Compliance (m/N)</th>
<th>Experimental Compliance (m/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8</td>
<td>4.04E$^{-5}$</td>
<td>2.47E$^{-8}$</td>
<td>2.38E$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.04E$^{-5}$</td>
<td>2.67E$^{-8}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.04E$^{-5}$</td>
<td>2.89E$^{-8}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.08 shows that there is reasonable correlation between the derived and experimentally determined values of elastic compliance; there is agreement within about 10% for an off-axis angle of 9°.
The calculated value of compliance is obviously highly dependent upon the principal elastic properties of the material. Elastic material properties for the carbon fibre composite systems have been taken from previous studies. It is possible that material used in this study had slightly varying properties; the fibre volume fraction could alter with manufacture. The slight variation in the measured and calculated values of compliance could therefore be a result of differing elastic properties.

Comparison of un-cracked compliance values, from experimental measurements and as calculated from the longitudinal modulus, is reported for all off-axis coupons tested in chapter 6.

5.4. Concluding Remarks

Experimental methods have been developed for the characterisation of failure under mode I and mixed-mode loadings. Strength measurements made using obliquely tabbed off-axis tensile coupons have been shown to compare well with published data. A method for the generation and control of a sharp natural crack in both compact tension and off-axis coupons has been established. Initial mechanical testing of notched coupons has resulted in the measurement of fracture mechanics data that conforms to previously published results. A methodology has been established from compliance experiments for the determination of toughness from off-axis tensile coupons. Experimentally measured values of compliance have been verified by comparison to theoretically calculated values.

The techniques developed for the characterisation of fracture properties can now be applied with confidence to the material systems of main interest in the present study, as reported in chapter 6.
Chapter Six

Mechanical Properties

Characterisation

6.1. INTRODUCTION

The experimental procedures developed within the previous chapter have been used to characterise fracture of a number of composite material systems. Stress states at failure for several off-axis geometries have been determined from strength measurements and failure envelopes have been derived experimentally using fracture mechanics properties.

The present chapter is split into three parts, each characterising a different material system. The HTA/F922 material system has been characterised through strength measurements whereas the GFRP and HTA/F927 material systems have been characterised through fracture mechanics properties.

6.2. HTA/F922

6.2.1. Introduction

The HTA/F922 composite system has been characterised using strength measurements. Obliquely tabbed off-axis coupons have been loaded in tension to failure following the procedure described in Section 5.3.2.2.
6.2.2. Strength Properties

The results from mixed-mode off-axis strength tests are shown in Table 6.01. The magnitude of each of the three stresses acting within the test coupons, \((\sigma_{11}, \sigma_{22}, \tau_{12})\) as given by Equation (4.06), has been calculated from the applied tensile stress at fracture \((\sigma_{tu})\).

The results show that there is a significant degree of interaction between the stresses at failure. The transverse stress, \(\sigma_{22}\) (perpendicular to the fibre direction) increases as the angle of fibre orientation to the applied load increases. The rise in \(\sigma_{22}\) is accompanied by a drop, similar in magnitude, of the value of \(\tau_{12}\). The most significant change in value is that of \(\sigma_{11}\); as the angle of fibre orientation is increased the value of \(\sigma_{11}\) drops dramatically.

Table 6.01. Off-axis coupon strength measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angle ((\theta^\circ))</th>
<th>Load ((kN))</th>
<th>Applied Fracture Stress (\sigma_{tu}) ((MPa))</th>
<th>(\sigma_{11}) ((MPa))</th>
<th>(\sigma_{22}) ((MPa))</th>
<th>(\tau_{12}) ((MPa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTA/F922-A</td>
<td>10</td>
<td>16.00</td>
<td>396</td>
<td>384</td>
<td>12</td>
<td>68</td>
</tr>
<tr>
<td>HTA/F922-B</td>
<td>10</td>
<td>16.70</td>
<td>414</td>
<td>402</td>
<td>13</td>
<td>71</td>
</tr>
<tr>
<td>HTA/F922-A</td>
<td>25</td>
<td>7.33</td>
<td>179</td>
<td>147</td>
<td>32</td>
<td>69</td>
</tr>
<tr>
<td>HTA/F922-B</td>
<td>25</td>
<td>7.22</td>
<td>178</td>
<td>146</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>HTA/F922-C</td>
<td>25</td>
<td>7.52</td>
<td>184</td>
<td>151</td>
<td>33</td>
<td>71</td>
</tr>
<tr>
<td>HTA/F922-D</td>
<td>25</td>
<td>6.19</td>
<td>154</td>
<td>126</td>
<td>27</td>
<td>59</td>
</tr>
<tr>
<td>HTA/F922-A</td>
<td>45</td>
<td>2.51</td>
<td>62</td>
<td>31</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>HTA/F922-B</td>
<td>45</td>
<td>3.73</td>
<td>92</td>
<td>46</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>HTA/F922-A</td>
<td>60</td>
<td>3.09</td>
<td>78</td>
<td>20</td>
<td>58</td>
<td>34</td>
</tr>
<tr>
<td>HTA/F922-B</td>
<td>60</td>
<td>3.22</td>
<td>75</td>
<td>19</td>
<td>56</td>
<td>33</td>
</tr>
<tr>
<td>HTA/F922-C</td>
<td>60</td>
<td>3.06</td>
<td>75</td>
<td>19</td>
<td>56</td>
<td>32</td>
</tr>
</tbody>
</table>

The results are shown graphically as the change in applied tensile fracture stress with off-axis angle, Figure 6.01. Experimental data points are plotted as an average of the measured values for each off-axis angle. Figure 6.01 also shows the change in
magnitude of the predicted failure stress ($\sigma_{\text{fu}}$) with off-axis angle for the individual transverse and shear failure modes, calculated using the failure strengths of the material in the 1-2 coordinate (fibre orientation), given in Table 6.02, using Equations (4.14). Predictions are also plotted for the dependence on loading angle of the applied stress for the onset of different failure modes according to the maximum stress criterion and the Tsai-Hill failure criterion. Both the maximum stress criterion and the Tsai–Hill failure criterion have been calculated from the failure strengths of the material, given in Table 6.02.

<table>
<thead>
<tr>
<th>$\sigma_{11u}$ (MPa)</th>
<th>$\sigma_{22u}$ (MPa)</th>
<th>$\tau_{12u}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>71.6</td>
<td>90</td>
</tr>
</tbody>
</table>

**Table 6.02.** Failure stresses of HTA/F922 [58].

**Figure 6.01.** Experimentally measured applied failure stresses of off-axis HTA/F922 coupons and prediction of failure according to the maximum stress failure criterion and the Tsai-Hill failure criterion.
6.2.3. Discussion

Failure strength measurements from HTA/F922 off-axis coupons show that there are significant interactions between the transverse normal and shear components of stress at failure, this can be emphasised by plotting a graph of the transverse normal stress component ($\sigma_{22}$) against the shear stress component ($\tau_{12}$), Figure 6.02.

![Plot showing the transverse normal ($\sigma_{22}$) and shear ($\tau_{12}$) components of stress at failure, in off-axis HTA/F922 coupons, calculated from experimental results and as predicted by the Maximum Stress failure criterion and the Tsai-Hill failure criterion.](image)

Figures 6.01 and 6.02 show that some interaction of the stress components is predicted by the Tsai-Hill polynomial failure criterion, although this interaction is less than that indicated by the experimental results. Figures 6.01 and 6.02 also show that the Maximum Stress failure criterion does not account for any interaction between the stress components.
Further off-axis coupon strength data have been taken from [59], for a glass-fibre/epoxy composite system. The magnitudes of the transverse normal ($\sigma_{22}$) and shear ($\tau_{12}$) components of stress at failure have been calculated for this composite system from the applied longitudinal failure stress ($\sigma_{33}$), using Equation 4.06, the results are shown in Figure 6.03. Figure 6.03 also shows the results predicted by the Tsai-Hill polynomial failure criterion and the Maximum Stress failure criterion.

![Graph showing stress components](image)

**Figure 6.03.** Plot showing the magnitude of the transverse normal ($\sigma_{22}$) and shear ($\tau_{12}$) components of stress at failure, in off-axis glass-fibre/epoxy composite coupons, calculated from the applied longitudinal failure stress [59] and as predicted by the Maximum Stress and Tsai-Hill failure criteria.

The experimental data shown in Figure 6.03 shows a similar trend to that shown in Figure 6.02, indicating that for this brittle composite system (glass-fibre/epoxy) there is also significant interaction between the transverse normal and shear components of stress at failure.
6.3. GLASS-FIBRE / EPOXY

6.3.1. Introduction

Characterisation of mixed-mode crack propagation has been undertaken using fracture mechanics parameters. Mixed-mode intralaminar fracture tests have been performed on obliquely tabbed, centrally notched, off-axis tensile coupons. Samples were cut from unidirectional laminates using a diamond impregnated saw; five different off-axis angles were chosen, 10°, 15°, 25°, 45° and 75°. The compliance was measured as a function of crack length for each off-axis angle. Experimentally measured compliance values for un-cracked samples have then been compared to those from theoretical calculations. Coupons with differing crack lengths and off-axis angles have been tested to failure.

Toughness data for each mixed-mode loading ratio has been calculated from the fracture load experiments and compliance measurements. The mode I and mode II components of the stress intensity factor have been determined from the failure stress and crack length. Relationships between the fracture toughness and the toughness have been used to determine the mode I and mode II components of toughness. The total critical value of toughness calculated as a sum of its partitioned components has been compared to the measured value obtained from compliance results.

A failure envelope has been determined in both K and G space for mixed-mode loadings.

6.3.2. Elastic Compliance

6.3.2.1. Experimental Determination of Compliance

Tensile tests were conducted using a quasi-static Instron (5500R) tensile test machine; tests were run at a crosshead speed of 0.5 mm/min. Elastic compliance measurements were made by loading and unloading notched coupons in tension. Displacements were
measured using an extensometer, the gauge length of which varied depending upon the off-axis angle of the coupon. In these compliance tests the maximum load applied was insufficient to cause crack propagation. A centre notch was cut into coupons by first drilling a 1 mm diameter hole into their centre. A fine jewellery blade was inserted through the hole. Notches were cut parallel to the fibre direction using a powered fretsaw. The length of the notch (2a) ranged from 0 mm to a maximum as dictated by the coupon width, compliance measurements were made at notch length intervals of 2.5 mm. Figures 6.04 to 6.08 show plots of the elastic compliance as a function of notch length for each of the off-axis coupon geometries.

Figure 6.04. Compliance as a function of notch length for centre notched 10° off-axis GFRP coupons.

![Figure 6.04](image)

\[ C = 0.21844a^4 - 5.6202E^3a^3 + 4.7242E^4a^2 + 2.1539E^7a + 7.398E^8 \]

Figure 6.05. Compliance as a function of notch length for centre notched 15° off-axis GFRP coupons.

![Figure 6.05](image)

\[ C = 0.29921a^4 + 1.6176E^3a^3 + 1.0622E^5a^2 + 1.2477E^7a + 5.7478E^8 \]
$C = 0.41697a^4 - 7.9516E^{-3}a^3 + 7.5125E^{-5}a^2 + 3.8051E^{-7}a + 6.7518E^{-8}$

**Figure 6.06.** Compliance as a function of notch length for centre notched 25° off-axis GFRP coupons.

$C = 2.7579a^4 - 3.3839E^{-2}a^3 + 1.6278E^{-4}a^2 + 4.8989E^{-7}a + 1.0126E^{-7}$

**Figure 6.07.** Compliance as a function of notch length for centre notched 45° off-axis GFRP coupons.

$C = -8.7265E^{-2}a^4 + 5.8941E^{-2}a^3 - 8.0636E^{-5}a^2 + 9.1954E^{-7}a + 8.6647E^{-8}$

**Figure 6.08.** Compliance as a function of notch length for centre notched 75° off-axis GFRP coupons.
A fourth order polynomial was fitted to each set of compliance results. Each polynomial equation is shown with its respective compliance plot. The derivative of the polynomial with respect to crack length \((dC/da)\) was then calculated. Figures 6.09 to 6.13 show the variation of \(dC/da\) as a function of crack length \((a)\) for each off-axis angle.

**Figure 6.09.** Plot showing the derivative of compliance as a function of notch length for centre notched 10° off-axis GFRP coupons.

**Figure 6.10.** Plot showing the derivative of compliance as a function of notch length for centre notched 15° off-axis GFRP coupons.

**Figure 6.13.** Plot showing the derivative of compliance as a function of notch length for centre notched 75° off-axis GFRP coupons.
Figure 6.11. Plot showing the derivative of compliance as a function of notch length for centre notched 25° off-axis GFRP coupons.

Figure 6.12. Plot showing the derivative of compliance as a function of notch length for centre notched 45° off-axis GFRP coupons.

Figure 6.13. Plot showing the derivative of compliance as a function of notch length for centre notched 75° off-axis GFRP coupons.
6.3.2.2. Theoretical Determination of Compliance

Values of the elastic compliance at 0 mm notch lengths may be determined from theory, as described in Section 5.3.3.3.3. The elastic compliance may be resolved from the longitudinal modulus using Equation (5.17). The longitudinal modulus $E_x$ has been calculated for each off-axis angle, with a variation of $\pm 1^\circ$, Table 6.03.

<table>
<thead>
<tr>
<th>Fibre Angle (Degrees)</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x$ (GPa)</td>
<td>33.5</td>
<td>32.3</td>
<td>31.0</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>27.5</td>
<td>26.3</td>
<td>25.2</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>24</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>18.2</td>
<td>17.5</td>
<td>16.9</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>44</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>10.7</td>
<td>10.6</td>
<td>10.5</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>74</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>9.7</td>
<td>9.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>

6.3.2.3. Comparison of Compliance Results

Experimental and calculated values of elastic compliance for un-cracked off-axis coupons have been compared, Table 6.04. The results show that there is good agreement between the measured and calculated compliance values. For both the 10° and 15° off-axis coupons there is less than 5% variation between experimental and calculated values, agreement for both the 25° and 75° coupon geometry is within 10%. There is a greater difference between the average experimental and calculated value of compliance for the 45° off-axis coupons, approximately 20%.

Variations between the measured and calculated compliance values could possibly be attributed to the different off-axis coupon geometries. 45° off-axis coupons were wider
(~ twice as wide) and shorter (~ 25 %) than the lower angle off-axis samples. The increased width was necessary in order to accommodate a similar range of pre-crack lengths and the reduced length was a constraint of the material available. The smaller experimental compliance may be associated with fibre restraint at the grips.

Table 6.04. Comparison of experimental and theoretical compliance results for the GFRP system.

<table>
<thead>
<tr>
<th>Angle Degrees</th>
<th>Ave. Calculated Compliance (m/N)</th>
<th>Ave. Experimental Compliance (m/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>7.56E-08</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.84E-08</td>
<td>7.47E-08</td>
</tr>
<tr>
<td>11</td>
<td>8.14E-08</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>5.70E-08</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>5.94E-08</td>
<td>5.78E-08</td>
</tr>
<tr>
<td>16</td>
<td>6.20E-08</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>7.51E-08</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>7.76E-08</td>
<td>7.32E-08</td>
</tr>
<tr>
<td>26</td>
<td>8.05E-08</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>1.24E-07</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>1.25E-07</td>
<td>1.05E-07</td>
</tr>
<tr>
<td>46</td>
<td>1.27E-07</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>9.64E-08</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>9.61E-08</td>
<td>8.75E-08</td>
</tr>
<tr>
<td>76</td>
<td>9.58E-08</td>
<td></td>
</tr>
</tbody>
</table>

6.3.3. Fracture tests

Samples were tested to failure in tension using a quasi-static Instron (5500R); loads were applied using a crosshead speed of 0.5 mm/min. Coupons were centrally cracked. The crack was sharpened and its length controlled using techniques as presented within the previous chapter. The length of the pre-crack was varied such that a range of crack conditions were tested for each off-axis coupon geometry. Load versus % Strain plots were recorded during fracture testing in order to verify that compliance was consistent.
with previously determined calibration curves. Strain measurements were recorded using an extensometer.

A summary of all the data used in fracture mechanics property measurements is given in Tables 6.05 to 6.09, including coupon dimensions and results from mechanical testing experiments.

**Table 6.05. Summary of fracture test data for 10° off-axis GFRP coupons.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness m</th>
<th>Width 2W m</th>
<th>Cross sectional Area m²</th>
<th>Crack length 2a m</th>
<th>a/W</th>
<th>Failure Load N</th>
<th>Failure Stress MPa</th>
<th>dC/da 1/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.0023</td>
<td>0.0130</td>
<td>2.97E-05</td>
<td>0.014</td>
<td></td>
<td>5937</td>
<td>20</td>
<td>4.39E-07</td>
</tr>
<tr>
<td>O</td>
<td>0.0023</td>
<td>0.0130</td>
<td>3.00E-05</td>
<td>0.015</td>
<td></td>
<td>5442</td>
<td>18</td>
<td>4.45E-07</td>
</tr>
<tr>
<td>Q</td>
<td>0.0023</td>
<td>0.0130</td>
<td>3.00E-05</td>
<td>0.024</td>
<td></td>
<td>4201</td>
<td>14</td>
<td>6.90E-07</td>
</tr>
<tr>
<td>R</td>
<td>0.0023</td>
<td>0.0130</td>
<td>3.00E-05</td>
<td>0.023</td>
<td></td>
<td>4572</td>
<td>15</td>
<td>6.39E-07</td>
</tr>
<tr>
<td>T</td>
<td>0.0022</td>
<td>0.0129</td>
<td>2.81E-05</td>
<td>0.026</td>
<td></td>
<td>4088</td>
<td>15</td>
<td>8.18E-07</td>
</tr>
<tr>
<td>Z</td>
<td>0.0022</td>
<td>0.0130</td>
<td>2.84E-05</td>
<td>0.026</td>
<td></td>
<td>4037</td>
<td>14</td>
<td>8.18E-07</td>
</tr>
<tr>
<td>S</td>
<td>0.0022</td>
<td>0.0130</td>
<td>2.78E-05</td>
<td>0.027</td>
<td></td>
<td>3640</td>
<td>13</td>
<td>8.96E-07</td>
</tr>
<tr>
<td>U</td>
<td>0.0023</td>
<td>0.0129</td>
<td>2.93E-05</td>
<td>0.031</td>
<td></td>
<td>3361</td>
<td>12</td>
<td>1.32E-06</td>
</tr>
<tr>
<td>V</td>
<td>0.0023</td>
<td>0.0130</td>
<td>2.99E-05</td>
<td>0.031</td>
<td></td>
<td>3175</td>
<td>11</td>
<td>1.32E-06</td>
</tr>
<tr>
<td>W</td>
<td>0.0022</td>
<td>0.0130</td>
<td>2.90E-05</td>
<td>0.034</td>
<td></td>
<td>3010</td>
<td>10</td>
<td>1.76E-06</td>
</tr>
<tr>
<td>Y</td>
<td>0.0022</td>
<td>0.0130</td>
<td>2.88E-05</td>
<td>0.036</td>
<td></td>
<td>2553</td>
<td>89</td>
<td>2.13E-06</td>
</tr>
</tbody>
</table>

**Table 6.06. Summary of fracture test data for 15° off-axis GFRP coupons.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness m</th>
<th>Width 2W m</th>
<th>Cross sectional Area m²</th>
<th>Crack length 2a m</th>
<th>a/W</th>
<th>Failure Load N</th>
<th>Failure Stress MPa</th>
<th>dC/da 1/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0022</td>
<td>0.01485</td>
<td>3.25E-05</td>
<td>0.012</td>
<td></td>
<td>3940</td>
<td>12</td>
<td>6.85E-07</td>
</tr>
<tr>
<td>D</td>
<td>0.0022</td>
<td>0.01493</td>
<td>3.31E-05</td>
<td>0.015</td>
<td></td>
<td>3268</td>
<td>99</td>
<td>1.06E-06</td>
</tr>
<tr>
<td>C</td>
<td>0.0020</td>
<td>0.01485</td>
<td>3.27E-05</td>
<td>0.015</td>
<td></td>
<td>2980</td>
<td>91</td>
<td>1.06E-06</td>
</tr>
<tr>
<td>B</td>
<td>0.0022</td>
<td>0.01487</td>
<td>3.32E-05</td>
<td>0.016</td>
<td></td>
<td>2554</td>
<td>77</td>
<td>1.22E-06</td>
</tr>
<tr>
<td>E</td>
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<td>0.01485</td>
<td>3.18E-05</td>
<td>0.020</td>
<td></td>
<td>2153</td>
<td>68</td>
<td>2.02E-06</td>
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### Table 6.07. Summary of fracture test data for 25° off-axis GFRP coupons.

<table>
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<tr>
<th>Sample</th>
<th>Thickness (m)</th>
<th>Width (2W m)</th>
<th>Cross sectional Area (m²)</th>
<th>Crack length 2a (m)</th>
<th>a/W</th>
<th>Failure Load (N)</th>
<th>Failure Stress (MPa)</th>
<th>dC/da (1/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0024</td>
<td>0.0246</td>
<td>5.81E-05</td>
<td>0.013</td>
<td>0.0065</td>
<td>2914</td>
<td>50</td>
<td>8.07E-07</td>
</tr>
<tr>
<td>D</td>
<td>0.0021</td>
<td>0.0243</td>
<td>5.18E-05</td>
<td>0.018</td>
<td>0.0090</td>
<td>2420</td>
<td>47</td>
<td>1.02E-06</td>
</tr>
<tr>
<td>H</td>
<td>0.0022</td>
<td>0.0251</td>
<td>5.50E-05</td>
<td>0.019</td>
<td>0.0095</td>
<td>2554</td>
<td>46</td>
<td>1.08E-06</td>
</tr>
<tr>
<td>E</td>
<td>0.0021</td>
<td>0.0243</td>
<td>5.08E-05</td>
<td>0.022</td>
<td>0.0110</td>
<td>1770</td>
<td>35</td>
<td>1.37E-06</td>
</tr>
<tr>
<td>I</td>
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<td>0.0251</td>
<td>5.67E-05</td>
<td>0.022</td>
<td>0.0110</td>
<td>2257</td>
<td>40</td>
<td>1.37E-06</td>
</tr>
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<td>M</td>
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<td>0.0249</td>
<td>5.34E-05</td>
<td>0.027</td>
<td>0.0135</td>
<td>1728</td>
<td>32</td>
<td>2.16E-06</td>
</tr>
<tr>
<td>K</td>
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<td>0.0252</td>
<td>5.55E-05</td>
<td>0.029</td>
<td>0.0145</td>
<td>1487</td>
<td>27</td>
<td>2.63E-06</td>
</tr>
<tr>
<td>F</td>
<td>0.0023</td>
<td>0.0245</td>
<td>5.72E-05</td>
<td>0.030</td>
<td>0.0150</td>
<td>1547</td>
<td>27</td>
<td>2.90E-06</td>
</tr>
<tr>
<td>J</td>
<td>0.0022</td>
<td>0.0251</td>
<td>5.53E-05</td>
<td>0.030</td>
<td>0.0150</td>
<td>1451</td>
<td>26</td>
<td>2.90E-06</td>
</tr>
<tr>
<td>L</td>
<td>0.0022</td>
<td>0.0252</td>
<td>5.47E-05</td>
<td>0.035</td>
<td>0.0175</td>
<td>1094</td>
<td>20</td>
<td>4.64E-06</td>
</tr>
</tbody>
</table>

### Table 6.08. Summary of fracture test data for 45° off-axis GFRP coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (m)</th>
<th>Width (2W m)</th>
<th>Cross sectional Area (m²)</th>
<th>Crack length 2a (m)</th>
<th>a/W</th>
<th>Failure Load (N)</th>
<th>Failure Stress (MPa)</th>
<th>dC/da (1/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.0022</td>
<td>0.0252</td>
<td>5.63E-05</td>
<td>0.005</td>
<td>0.0025</td>
<td>1854</td>
<td>33</td>
<td>8.42E-07</td>
</tr>
<tr>
<td>A</td>
<td>0.0023</td>
<td>0.0252</td>
<td>5.69E-05</td>
<td>0.009</td>
<td>0.0045</td>
<td>1736</td>
<td>31</td>
<td>9.04E-07</td>
</tr>
<tr>
<td>H</td>
<td>0.0022</td>
<td>0.0251</td>
<td>5.57E-05</td>
<td>0.012</td>
<td>0.0060</td>
<td>1395</td>
<td>25</td>
<td>1.17E-06</td>
</tr>
<tr>
<td>E</td>
<td>0.0022</td>
<td>0.0252</td>
<td>5.57E-05</td>
<td>0.015</td>
<td>0.0075</td>
<td>1114</td>
<td>20</td>
<td>1.88E-06</td>
</tr>
<tr>
<td>G</td>
<td>0.0023</td>
<td>0.0251</td>
<td>5.84E-05</td>
<td>0.015</td>
<td>0.0075</td>
<td>1167</td>
<td>20</td>
<td>1.88E-06</td>
</tr>
<tr>
<td>K</td>
<td>0.0023</td>
<td>0.0250</td>
<td>5.66E-05</td>
<td>0.016</td>
<td>0.0080</td>
<td>1034</td>
<td>18</td>
<td>2.25E-06</td>
</tr>
<tr>
<td>C</td>
<td>0.0023</td>
<td>0.0252</td>
<td>5.75E-05</td>
<td>0.018</td>
<td>0.0090</td>
<td>911</td>
<td>16</td>
<td>3.24E-06</td>
</tr>
<tr>
<td>I</td>
<td>0.0024</td>
<td>0.0244</td>
<td>5.76E-05</td>
<td>0.020</td>
<td>0.0100</td>
<td>745</td>
<td>13</td>
<td>4.63E-06</td>
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</tbody>
</table>

### Table 6.09. Summary of fracture test data for 75° off-axis GFRP coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (m)</th>
<th>Width (2W m)</th>
<th>Cross sectional Area (m²)</th>
<th>Crack length 2a (m)</th>
<th>a/W</th>
<th>Failure Load (N)</th>
<th>Failure Stress (MPa)</th>
<th>dC/da (1/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.0022</td>
<td>0.0245</td>
<td>5.45E-05</td>
<td>0.006</td>
<td>0.0030</td>
<td>1008</td>
<td>19</td>
<td>2.02E-06</td>
</tr>
<tr>
<td>H</td>
<td>0.0022</td>
<td>0.0246</td>
<td>5.49E-05</td>
<td>0.006</td>
<td>0.0030</td>
<td>1010</td>
<td>18</td>
<td>2.02E-06</td>
</tr>
<tr>
<td>E</td>
<td>0.0022</td>
<td>0.0246</td>
<td>5.49E-05</td>
<td>0.007</td>
<td>0.0033</td>
<td>964</td>
<td>18</td>
<td>2.25E-06</td>
</tr>
<tr>
<td>D</td>
<td>0.0023</td>
<td>0.0247</td>
<td>5.73E-05</td>
<td>0.007</td>
<td>0.0035</td>
<td>952</td>
<td>17</td>
<td>2.51E-06</td>
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<td>0.0246</td>
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<td>0.0040</td>
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<td>G</td>
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<td>0.0246</td>
<td>5.57E-05</td>
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<td>0.0055</td>
<td>737</td>
<td>13</td>
<td>5.32E-06</td>
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</table>
6.3.4. Fracture Mechanics Properties

The critical strain energy release rate $G_c$ (toughness) has been determined from maximum loads, associated with the onset of unstable crack propagation, and elastic compliance results using Expression (5.14).

Values of $K_1$ and $K_{II}$ have been calculated from resolved stress considerations, Expressions (4.09) and (4.10), and experimentally determined critical loads for the onset of fracture. These results ($K_1$ and $K_{II}$) have been converted to values of $G_I$ and $G_{II}$ by application of Expressions (4.03) and (4.11) in conjunction with the unidirectional material properties listed in Table 3.02. The sum of the partitioned $G$ components (as calculated from fracture toughness results) has been calculated and is compared to the total measured value of $G_c$ obtained from experimental results. Fracture mechanics properties are shown in Tables 6.10 to 6.14. The tables are divided into experimentally measured results and corresponding calculated results.

Table 6.10. Fracture mechanics properties of $10^\circ$ off-axis GFRP coupons.

<table>
<thead>
<tr>
<th>Crack Length mm</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_c$ J/m²</td>
<td>$K_{II}$ MPa m$^{1/2}$</td>
</tr>
<tr>
<td>14</td>
<td>1687</td>
<td>5.07</td>
</tr>
<tr>
<td>15</td>
<td>1428</td>
<td>4.76</td>
</tr>
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<td>23</td>
<td>1446</td>
<td>4.96</td>
</tr>
<tr>
<td>24</td>
<td>1319</td>
<td>4.64</td>
</tr>
<tr>
<td>26</td>
<td>1575</td>
<td>5.04</td>
</tr>
<tr>
<td>26</td>
<td>1522</td>
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<td>4.60</td>
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<td>31</td>
<td>1636</td>
<td>4.33</td>
</tr>
<tr>
<td>31</td>
<td>1441</td>
<td>4.01</td>
</tr>
<tr>
<td>34</td>
<td>1782</td>
<td>4.10</td>
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<tr>
<td>36</td>
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<td>3.61</td>
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</table>
Table 6.11. Fracture mechanics properties of 15° off-axis GFRP coupons.

<table>
<thead>
<tr>
<th>Crack Length (mm)</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_c$ J/m²</td>
<td>$K_{II}$ MPa m$^{1/2}$</td>
</tr>
<tr>
<td>12</td>
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<td>4.16</td>
</tr>
<tr>
<td>15</td>
<td>1278</td>
<td>3.79</td>
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<tr>
<td>15</td>
<td>1179</td>
<td>3.50</td>
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<tr>
<td>18</td>
<td>891</td>
<td>3.05</td>
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<tr>
<td>20</td>
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</table>

Table 6.12. Fracture mechanics properties of 25° off-axis GFRP coupons.

<table>
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<tr>
<th>Crack Length (mm)</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_c$ J/m²</td>
<td>$K_{II}$ MPa m$^{1/2}$</td>
</tr>
<tr>
<td>13</td>
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<td>18</td>
<td>699</td>
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<td>19</td>
<td>808</td>
<td>3.07</td>
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<tr>
<td>22</td>
<td>512</td>
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<td>22</td>
<td>770</td>
<td>2.83</td>
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<tr>
<td>22</td>
<td>755</td>
<td>2.55</td>
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<td>29</td>
<td>660</td>
<td>2.19</td>
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<td>30</td>
<td>740</td>
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<td>30</td>
<td>693</td>
<td>2.18</td>
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<td>35</td>
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</table>

Table 6.13. Fracture mechanics properties of 45° off-axis GFRP coupons.

<table>
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<th>Crack Length (mm)</th>
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<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$G_c$ J/m²</td>
<td>$K_{II}$ MPa m$^{1/2}$</td>
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<tr>
<td>5</td>
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<td>1.46</td>
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<tr>
<td>9</td>
<td>302</td>
<td>1.81</td>
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<td>12</td>
<td>257</td>
<td>1.72</td>
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<td>15</td>
<td>263</td>
<td>1.54</td>
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<td>295</td>
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</tr>
<tr>
<td>20</td>
<td>272</td>
<td>1.15</td>
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</tbody>
</table>
Table 6.14. *Fracture mechanics properties of 75° off-axis GFRP coupons.*

<table>
<thead>
<tr>
<th>Crack Length mm</th>
<th>G\textsubscript{C} J/m\textsuperscript{2}</th>
<th>K\textsubscript{II} MPa m\textsuperscript{1/2}</th>
<th>K\textsubscript{I} MPa m\textsuperscript{1/2}</th>
<th>G\textsubscript{II} J/m\textsuperscript{2}</th>
<th>G\textsubscript{I} J/m\textsuperscript{2}</th>
<th>G\textsubscript{C} Total J/m\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>231</td>
<td>0.45</td>
<td>1.68</td>
<td>10</td>
<td>258</td>
<td>268</td>
</tr>
<tr>
<td>6</td>
<td>231</td>
<td>0.45</td>
<td>1.66</td>
<td>9</td>
<td>255</td>
<td>264</td>
</tr>
<tr>
<td>7</td>
<td>234</td>
<td>0.44</td>
<td>1.66</td>
<td>9</td>
<td>252</td>
<td>261</td>
</tr>
<tr>
<td>7</td>
<td>245</td>
<td>0.44</td>
<td>1.63</td>
<td>9</td>
<td>243</td>
<td>252</td>
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<tr>
<td>8</td>
<td>253</td>
<td>0.45</td>
<td>1.68</td>
<td>10</td>
<td>260</td>
<td>270</td>
</tr>
<tr>
<td>11</td>
<td>320</td>
<td>0.44</td>
<td>1.62</td>
<td>9</td>
<td>242</td>
<td>251</td>
</tr>
</tbody>
</table>

In principle the G\textsubscript{C} values should be equal. To facilitate comparison the results are shown graphically, Figures 6.14 to 6.18. There is reasonably good correlation between G\textsubscript{C} values at short pre-crack lengths for all off-axis geometries. As the pre-crack length is increased there is a general trend of a decrease in the G\textsubscript{C} values derived from fracture toughness results whereas experimentally measured values of G\textsubscript{C} remain reasonably consistent. The trend is visually more obvious for the lower off-axis angle coupon geometries because of the larger range of pre-crack lengths. The value of G\textsubscript{C} for each off-axis angle would be expected to remain constant across the pre-crack length range (as is the case for the results experimentally determined from the compliance method). The decrease in the (fracture toughness derived) values of G\textsubscript{C} with increasing pre-crack length suggests, perhaps not surprisingly, that the stress intensity factors (and the derived G\textsubscript{C} values) need to be modified to account for finite width effects at larger a/W ratios.
Chapter Six: Mechanical Properties Characterisation

10° off-axis

![Graph showing comparison between Gc values for 10° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.]

**Figure 6.14.** *A comparison between Gc values for 10° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.*

15° off-axis

![Graph showing comparison between Gc values for 15° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.]

**Figure 6.15.** *A comparison between Gc values for 15° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.*

25° off-axis

![Graph showing comparison between Gc values for 25° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.]

**Figure 6.16.** *A comparison between Gc values for 25° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.*
Figure 6.17. A comparison between $G_C$ values for 45° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.

Figure 6.18. A comparison between $G_C$ values for 75° off-axis GFRP coupons: experimentally measured or calculated from fracture toughness results.

6.3.5. Failure Envelopes

Failure loci in K and G space are shown in Figures 6.19 and 6.20, respectively. Experimental results measured from 10° off-axis coupons are plotted in Blue, data from 15° off-axis coupons are plotted in Pink, 25° off-axis coupon results are in Brown, 45° off-axis results are in Green, and 75° off-axis results are plotted in Grey. Points representing the pure mode loading situations have been taken from the literature and are shown in Black. The mode I value has been taken from compact tension tests results [60] and the mode II value from interlaminar fracture results using end notch flexure test
coupons [44]. The intensity of each colour reflects the magnitude of crack length; points representative of longer cracks have less colour intensity than those from shorter cracks.

Figure 6.19. Failure locus for the GFRP composite in $K$ space.

Figure 6.20. Failure locus for the GFRP composite in $G$ space.
The data, shown in Figures 6.19 and 6.20, are not corrected for finite-width effects. Finite-width correction factors (calculated from finite element analysis) for a range of geometries of isotropic plates containing off-axis cracks are given in [55]. While this is not ideal, anisotropic correction factors do not appear to be available in the literature for this geometry. There is, however, some evidence in the literature which suggests that finite-width correction factors may not differ too much between isotropic and anisotropic materials [61]. The correction factors for $K_I$ and $K_{II}$ are only given for the $a/W$ range of 0.1 to 0.8. It was therefore not possible to correct all the experimental data for finite-width effects, only the results obtained from coupons with an $a/W$ value between 0.1 and 0.8. Failure envelopes, after modification for coupon finite-width effects, in $K$ and $G$ space are shown in Figures 6.21 and 6.22, respectively. These results are discussed further in Section 6.5.

![Figure 6.21. Failure locus for the GFRP composite in $K$ space.](image)
6.3.6. Discussion

Fracture of this glass fibre/epoxy material appears to be dominated by the mode I fracture mechanics component. For the corrected data failure envelopes in the K and G plane are well described by a linear line of zero gradient such that either $K_I = K_{IC}$ or $G_I = G_{IC}$, until fracture is nominally mode II. Similar trends, for different material systems, may be found within the literature. Figure 6.23 shows failure loci in the $K_o$ ($K_I$) versus $K_t$ ($K_{II}$) plane for two different composite material systems, as measured using off-axis coupons [62] (the x-axis refers to the mode I component and the y-axis to the mode II component). The plots are dominated by the mode I fracture mechanics parameter. Figure 6.24 shows the delamination failure loci in G space for two composite material systems [63]. Linear trend lines are plotted through the data, for one of the materials the trend line follows $G_I = G_{IC}$. 

---

**Figure 6.22.** Failure locus for the GFRP composite in G space.
Chapter Six: Mechanical Properties Characterisation

6.4. HTA/F927

6.4.1. Introduction

In this section, crack propagation in HTA/F927 is characterised under mode I and mixed-mode loadings. Fracture under a pure mode I loading has been studied using compact

Figure 6.23. Off-axis coupon failure loci for the AS4-3501-06 and IM7-8551-7 material systems, after [62].

Figure 6.24. Delamination failure loci for the IM7/5260 and IM7/8320 material systems, after [63].
tension coupons, enabling $G_{IC}$ and $K_{IC}$ to be determined independently. In a similar study to that on GFRP mixed-mode intralaminar fracture tests have been performed on obliquely tabbed, centrally cracked, off-axis tensile coupons. Four different off-axis geometries have been studied: $10^\circ$, $25^\circ$, $45^\circ$ and $75^\circ$. Toughness data ($G_C$) for each mixed-mode loading ratio has been calculated from fracture experiments and compliance measurements. The mode I and mode II components of the stress intensity factor at fracture ($K_I$ and $K_{II}$) have been determined from fracture tests. Relationships between $K$ and $G$ have been used to convert experimentally determined values of $K_I$ and $K_{II}$ into measurements of $G_I$ and $G_{II}$, respectively. The total value of $G$ calculated as a sum of its partitioned components has been compared to the measured value obtained from compliance results. A failure envelope has been determined in both $K$ and $G$ space.

6.4.2. Fracture Under Mode I Loading

6.4.2.1. Method

Compact tension coupons were cut from unidirectional laminates using a diamond impregnated saw. Samples were loaded in tension prior to being notched in order to ascertain the deformation due to loading pin indentation. Each coupon was notched and then pre-cracked following the technique as described in Section 5.2.2. Coupons were then loaded in tension until fracture.

Fracture curves were evaluated according to the ASTM standard [17]. A line was plotted with a gradient 5% less than the initial gradient of the slope. The intercept of this line with the fracture plot was used to determine the validity of the test and the value of failure load to be used in material property calculations. Three different types of fracture curve were measured. Examples of each of these three curve types are given in Figures 6.25 to 6.27 and the differences are discussed below.
Figure 6.25. Compact tension fracture curve type (a).

Figure 6.26. Compact tension fracture curve type (b).

Figure 6.27. Compact tension fracture curve type (c).
Type (a): The maximum load ($P_{\text{max}}$) occurs prior to the intercept of the experimental data with the +5% compliance line ($P_Q$). The value of $P_{\text{max}}$ was used to calculate fracture mechanics data.

Type (b): The maximum load ($P_{\text{max}}$) occurs after the intercept of the experimental data with the +5% compliance line ($P_Q$). However the value of $P_{\text{max}} / P_Q$ is less than 1.1, therefore $P_Q$ was used to calculate fracture mechanics data.

Type (c): The maximum load ($P_{\text{max}}$) occurs after the intercept of the experimental data with the +5% compliance line ($P_Q$). However the value of $P_{\text{max}} / P_Q$ is greater than 1.1, therefore the test is invalid.

Two out of the twelve fracture tests were found to be invalid. The ASTM standard recommends that at least three replicate tests be made for each material. Of the remaining ten results either $P_{\text{max}}$ or $P_Q$ was used to calculate $K_{IC}$. $G_{IC}$ was calculated from corrected energy measurements based on the same load as used for the $K_{IC}$ calculation.

6.4.2.2. Mode I Fracture Mechanics Properties

The mode I fracture mechanics results measured from compact tension (C.T.) coupons are shown in Table 6.15, the average values are given in Table 6.16. These average values (experimentally measured from C.T. coupons) of $K_{IC}$ and $G_{IC}$ have been used to calculate values of $G_{IC}$ and $K_{IC}$, respectively, from the $G_{IC} - K_{IC}$ inter-relationship, Expression (4.03). Calculated values of $K_{IC}$ and $G_{IC}$ are also given in Table 6.16 for comparison along with experimentally measured $K_{IC}$ values from an alternative study [58].

There is good correlation between the experimentally measured fracture mechanics properties and those calculated from the $G_{IC} - K_{IC}$ inter-relationship. The values also correspond well to the results from the previous study.
Table 6.15. *Mode I fracture mechanics properties of HTA/F927.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Fracture Toughness $K_{IC}$ (MPa m$^{1/2}$)</th>
<th>Measured Toughness $G_{IC}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.88</td>
<td>412</td>
</tr>
<tr>
<td>B</td>
<td>1.97</td>
<td>451</td>
</tr>
<tr>
<td>C</td>
<td>1.84</td>
<td>272</td>
</tr>
<tr>
<td>D</td>
<td>1.92</td>
<td>269</td>
</tr>
<tr>
<td>H</td>
<td>1.82</td>
<td>307</td>
</tr>
<tr>
<td>K</td>
<td>1.81</td>
<td>355</td>
</tr>
<tr>
<td>L</td>
<td>1.70</td>
<td>337</td>
</tr>
<tr>
<td>M</td>
<td>1.89</td>
<td>382</td>
</tr>
<tr>
<td>O</td>
<td>1.92</td>
<td>388</td>
</tr>
<tr>
<td>P</td>
<td>1.93</td>
<td>389</td>
</tr>
</tbody>
</table>

Table 6.16. *Summary of the mode I fracture mechanics properties of HTA/F927.*

<table>
<thead>
<tr>
<th>Average Fracture Toughness $K_{IC}$ (MPa m$^{1/2}$)</th>
<th>Average Toughness $G_{IC}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimentally measured from C.T. coupons</td>
<td>1.87 (s.d. 0.08)</td>
</tr>
<tr>
<td>Calculated from the $G_{IC} - K_{IC}$ inter-relationship, Expression (4.03)</td>
<td>1.96 (s.d. 0.17)</td>
</tr>
</tbody>
</table>

6.4.3. Fracture Under Mixed-Mode Loadings

6.4.3.1. Introduction

Mixed-mode intralaminar tests have been performed on obliquely tabbed, centrally notched, off-axis tensile coupons. Four different off-axis geometries have been studied:
10°, 25°, 45° and 75°. Coupons were cut from unidirectional laminates using a diamond impregnated saw. The compliance was measured as a function of crack length for each off-axis angle. Experimentally measured compliance values for un-cracked samples have been compared to values calculated from theory. Additional coupons from each off-axis set have been pre-cracked and loaded to failure. Results have been used to calculate fracture mechanics properties.

6.4.3.2. Elastic Compliance

6.4.3.2.1. Experimental Determination of Compliance

Compliance was determined experimentally using the same tensile testing method as employed with the GFRP system; centre notches were also cut following the same methodology – both procedures are described in Section 6.3.2.1. Compliance measurements were made at notch length intervals of 2.5 mm. Figures 6.28 to 6.30 show plots of the elastic compliance as a function of crack length for 10°, 25° and 45° off-axis coupon geometries.

![Compliance vs. Notch Length](image)

Figure 6.28. Compliance as a function of notch length for centre notched 10° off-axis HTA/F927 coupons
A fourth order polynomial was fitted to each set of compliance results. Each polynomial is shown with its respective compliance plot. The derivative of the polynomial with respect to crack length \((dC/da)\) was then calculated. Figures 6.31 to 6.33 show the variation of \(dC/da\) as a function of crack length \((a)\) for each off-axis angle.
Figure 6.31. Plot showing the derivative of compliance as a function of notch length for centre notched 10° off-axis HTA/F927 coupons.

Figure 6.32. Plot showing the derivative of compliance as a function of notch length for centre notched 25° off-axis HTA/F927 coupons.

Figure 6.33. Plot showing the derivative of compliance as a function of notch length for centre notched 45° off-axis HTA/F927 coupons.
6.4.3.2.2. Theoretical Determination of Compliance

The elastic compliance may be resolved from the longitudinal modulus using Equation (5.17) as described in Section 5.3.3.3.3. For the HTA/F927 material system the longitudinal modulus $E_x$ has been calculated for each off-axis angle, with a variation of $\pm 1^\circ$, Table 6.17.

Table 6.17. Variation of $E_x$ with off-axis angle for the HTA/F927 system.

<table>
<thead>
<tr>
<th>Fibre Angle (Degrees)</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x$ (GPa)</td>
<td>68.6</td>
<td>63.2</td>
<td>58.2</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>24</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>22.9</td>
<td>21.7</td>
<td>20.5</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>44</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>10.7</td>
<td>10.4</td>
<td>10.2</td>
</tr>
<tr>
<td>Fibre Angle (Degrees)</td>
<td>74</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>$E_x$ (GPa)</td>
<td>7.8</td>
<td>7.8</td>
<td>7.8</td>
</tr>
</tbody>
</table>

6.4.3.2.3. Comparison of Compliance Results

Experimental and calculated values of elastic compliance for un-cracked off-axis coupons have been compared, Table 6.18. For off-axis angles of $10^\circ$, $25^\circ$ and $75^\circ$ there is reasonable agreement between the calculated and experimentally determined values of compliance. As was noted with the GFRP system there is less agreement with the $45^\circ$ off-axis coupon results, again this is possibly due to the dimensions of the $45^\circ$ off-axis coupons (shorter and wider).
Table 6.18. Comparison of experimental and theoretical compliance results.

<table>
<thead>
<tr>
<th>Angle Degrees</th>
<th>Ave. Calculated Compliance (m/N)</th>
<th>Ave. Experimental Compliance (m/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2.55E-08</td>
<td>2.39E-08</td>
</tr>
<tr>
<td>10</td>
<td>2.77E-08</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3.01E-08</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>3.28E-08</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.46E-08</td>
<td>3.13E-08</td>
</tr>
<tr>
<td>26</td>
<td>3.66E-08</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>2.83E-08</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>2.90E-08</td>
<td>2.47E-07</td>
</tr>
<tr>
<td>46</td>
<td>2.90E-08</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>3.97E-08</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>3.98E-08</td>
<td>3.21E-08</td>
</tr>
<tr>
<td>76</td>
<td>3.99E-08</td>
<td></td>
</tr>
</tbody>
</table>

6.4.3.3. Fracture tests

Samples were tested to failure in tension following the method described in Section 6.3.3. Coupons were centrally cracked. The crack was sharpened and its length controlled using techniques as presented within the previous chapter.

A summary of all the data used in the calculation of off-axis fracture mechanics properties is given in Tables 6.19 to 6.22, including coupon dimensions and results from mechanical testing experiments.

Table 6.19. Summary of fracture test data for 10° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness</th>
<th>Width</th>
<th>Cross sectional area</th>
<th>Crack length</th>
<th>a</th>
<th>a/W</th>
<th>Failure Load</th>
<th>Failure Stress</th>
<th>dC/da</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.0033</td>
<td>0.0132</td>
<td>4.30E-05</td>
<td>0.025</td>
<td>0.0125</td>
<td>1.90</td>
<td>3905</td>
<td>91</td>
<td>2.99E-07</td>
</tr>
<tr>
<td>Q</td>
<td>0.0033</td>
<td>0.0132</td>
<td>4.27E-05</td>
<td>0.025</td>
<td>0.0125</td>
<td>1.90</td>
<td>4271</td>
<td>100</td>
<td>2.99E-07</td>
</tr>
<tr>
<td>T</td>
<td>0.0033</td>
<td>0.0131</td>
<td>4.35E-05</td>
<td>0.025</td>
<td>0.0125</td>
<td>1.91</td>
<td>4243</td>
<td>97</td>
<td>2.99E-07</td>
</tr>
<tr>
<td>R</td>
<td>0.0033</td>
<td>0.0131</td>
<td>4.32E-05</td>
<td>0.035</td>
<td>0.0175</td>
<td>2.67</td>
<td>2390</td>
<td>55</td>
<td>6.74E-07</td>
</tr>
<tr>
<td>S</td>
<td>0.0033</td>
<td>0.0131</td>
<td>4.32E-05</td>
<td>0.035</td>
<td>0.0175</td>
<td>2.67</td>
<td>2743</td>
<td>64</td>
<td>6.74E-07</td>
</tr>
</tbody>
</table>

100
### Table 6.20. Summary of fracture test data for 25° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [m]</th>
<th>Width 2W [m]</th>
<th>Cross sectional Area [m²]</th>
<th>Crack length 2a [m]</th>
<th>a/W</th>
<th>Failure Load [N]</th>
<th>Failure Stress [MPa]</th>
<th>dC/da [1/N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>0.0033</td>
<td>0.0205</td>
<td>6.69E-05</td>
<td>0.005</td>
<td>0.24</td>
<td>3360</td>
<td>50</td>
<td>1.56E-07</td>
</tr>
<tr>
<td>B</td>
<td>0.0032</td>
<td>0.0205</td>
<td>6.51E-05</td>
<td>0.007</td>
<td>0.35</td>
<td>2499</td>
<td>38</td>
<td>2.99E-06</td>
</tr>
<tr>
<td>E</td>
<td>0.0033</td>
<td>0.0203</td>
<td>6.75E-05</td>
<td>0.012</td>
<td>0.59</td>
<td>1639</td>
<td>24</td>
<td>8.64E-06</td>
</tr>
<tr>
<td>A</td>
<td>0.0033</td>
<td>0.0205</td>
<td>6.66E-05</td>
<td>0.020</td>
<td>0.99</td>
<td>918</td>
<td>14</td>
<td>2.38E-06</td>
</tr>
</tbody>
</table>

### Table 6.21. Summary of fracture test data for 45° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [m]</th>
<th>Width 2W [m]</th>
<th>Cross sectional Area [m²]</th>
<th>Crack length 2a [m]</th>
<th>a/W</th>
<th>Failure Load [N]</th>
<th>Failure Stress [MPa]</th>
<th>dC/da [1/N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0033</td>
<td>0.0255</td>
<td>8.29E-05</td>
<td>0.008</td>
<td>0.31</td>
<td>1388</td>
<td>17</td>
<td>6.22E-07</td>
</tr>
<tr>
<td>E</td>
<td>0.0033</td>
<td>0.0255</td>
<td>8.29E-05</td>
<td>0.009</td>
<td>0.35</td>
<td>1365</td>
<td>17</td>
<td>7.29E-07</td>
</tr>
<tr>
<td>F</td>
<td>0.0033</td>
<td>0.0255</td>
<td>8.31E-05</td>
<td>0.010</td>
<td>0.39</td>
<td>1271</td>
<td>15</td>
<td>8.62E-06</td>
</tr>
<tr>
<td>H</td>
<td>0.0033</td>
<td>0.0255</td>
<td>8.37E-05</td>
<td>0.011</td>
<td>0.43</td>
<td>1161</td>
<td>14</td>
<td>1.02E-06</td>
</tr>
<tr>
<td>B</td>
<td>0.0032</td>
<td>0.0255</td>
<td>8.20E-05</td>
<td>0.011</td>
<td>0.43</td>
<td>1197</td>
<td>15</td>
<td>1.02E-06</td>
</tr>
<tr>
<td>D</td>
<td>0.0033</td>
<td>0.0254</td>
<td>8.36E-05</td>
<td>0.013</td>
<td>0.51</td>
<td>1060</td>
<td>13</td>
<td>1.44E-06</td>
</tr>
</tbody>
</table>

### Table 6.22. Summary of fracture test data for 75° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [m]</th>
<th>Width 2W [m]</th>
<th>Cross sectional Area [m²]</th>
<th>Crack length 2a [m]</th>
<th>a/W</th>
<th>Failure Load [N]</th>
<th>Failure Stress [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0032</td>
<td>0.0253</td>
<td>8.18E-05</td>
<td>0.007</td>
<td>0.28</td>
<td>1096</td>
<td>13</td>
</tr>
<tr>
<td>A</td>
<td>0.0031</td>
<td>0.0254</td>
<td>7.80E-05</td>
<td>0.009</td>
<td>0.35</td>
<td>894</td>
<td>12</td>
</tr>
</tbody>
</table>
6.4.3.4. Mixed-Mode Fracture Mechanics Properties

The critical strain energy release rate $G_C$ (toughness) has been determined from maximum loads, associated with the onset of unstable crack propagation, and elastic compliance results using Expression (5.14).

Values of $K_I$ and $K_{II}$ have been calculated from the experimentally determined critical loads for the onset of fracture, using Expressions (4.09) and (4.10). Following Section 6.3.4, these results ($K_I$ and $K_{II}$) have been converted to values of $G_I$ and $G_{II}$, the sum of which has been calculated and is compared to the total measured value of $G_C$ obtained from experimental results. Fracture mechanics properties are shown in Tables 6.23 to 6.26. The tables are divided into experimentally measured results and corresponding calculated results.

Table 6.23. Fracture mechanics properties of $10^\circ$ off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Crack Length mm</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_C$ J/m²</td>
<td>$K_{II}$ MPa m¹/²</td>
</tr>
<tr>
<td>25</td>
<td>351</td>
<td>3.08</td>
</tr>
<tr>
<td>25</td>
<td>420</td>
<td>3.39</td>
</tr>
<tr>
<td>25</td>
<td>405</td>
<td>3.30</td>
</tr>
<tr>
<td>35</td>
<td>384</td>
<td>2.55</td>
</tr>
<tr>
<td>35</td>
<td>293</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Table 6.24. Fracture mechanics properties of $25^\circ$ off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Crack Length mm</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_C$ J/m²</td>
<td>$K_{II}$ MPa m¹/²</td>
</tr>
<tr>
<td>5</td>
<td>135</td>
<td>1.70</td>
</tr>
<tr>
<td>7</td>
<td>146</td>
<td>1.54</td>
</tr>
<tr>
<td>12</td>
<td>176</td>
<td>1.28</td>
</tr>
<tr>
<td>20</td>
<td>153</td>
<td>0.94</td>
</tr>
</tbody>
</table>
### Table 6.25. Fracture mechanics properties of 45° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Crack Length (mm)</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G_c J/m²</td>
<td>K_II MPa m¹/²</td>
</tr>
<tr>
<td>8</td>
<td>92</td>
<td>0.94</td>
</tr>
<tr>
<td>9</td>
<td>104</td>
<td>0.98</td>
</tr>
<tr>
<td>10</td>
<td>107</td>
<td>0.96</td>
</tr>
<tr>
<td>11</td>
<td>114</td>
<td>0.96</td>
</tr>
<tr>
<td>11</td>
<td>105</td>
<td>0.91</td>
</tr>
<tr>
<td>13</td>
<td>123</td>
<td>0.91</td>
</tr>
</tbody>
</table>

### Table 6.26. Fracture mechanics properties of 75° off-axis HTA/F927 coupons.

<table>
<thead>
<tr>
<th>Crack Length (mm)</th>
<th>EXPERIMENTAL</th>
<th>CALCULATED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G_c J/m²</td>
<td>K_II MPa m¹/²</td>
</tr>
<tr>
<td>7</td>
<td>N/A</td>
<td>0.35</td>
</tr>
<tr>
<td>9</td>
<td>N/A</td>
<td>0.34</td>
</tr>
</tbody>
</table>

As was stated in Section 6.3.4, in principle the G_c values should be equal. The results are shown graphically, Figures 6.34 to 6.36. The same trends are noted as were observed with the GFRP system; there is reasonably good correlation between both G_c values at short pre-crack lengths for all off-axis geometries. There is less agreement as the pre-crack length is increased; this is visually more evident in the lower off-axis coupon geometries because of the larger range of pre-crack lengths. As indicated in Section 6.3.4 the value of G_c for each off-axis angle would be expected to remain constant. The decrease in the (fracture toughness derived) values of G_c with increasing pre-crack length suggests that the stress intensity factors (and the calculated G_c values) need to be modified to account for finite width effects at larger a/W ratios.
6.4.4. Failure Envelopes

Failure load envelopes have been calculated from the results from 10° off-axis coupons and plotted in Figure 6.37. The nominal fracture toughness has therefore been applied to the data in order to establish failure load envelopes for the HTA/F927 material. The failure load envelopes presented in Figures 6.37 and 6.38 have been calculated using the method described in Section 5.3.4.

Figure 6.34. A comparison between $G_c$ values for 10° off-axis HTA/F927 coupons: experimentally measured or calculated from fracture toughness results.

Figure 6.35. A comparison between $G_c$ values for 25° off-axis HTA/F927 coupons: experimentally measured or calculated from fracture toughness results.

Figure 6.36. A comparison between $G_c$ values for 45° off-axis HTA/F927 coupons: experimentally measured or calculated from fracture toughness results.
6.4.4. Failure Envelopes

Failure loci in K and G space are shown in Figures 6.37 and 6.38, respectively. Results measured from compact tension coupons are plotted in Yellow. Data obtained from 10° off-axis coupons are plotted in Blue, 25° off-axis coupon results are plotted in Brown, 45° off-axis results are plotted in Green, and 75° off-axis results are plotted in Grey. A point to represent the pure mode II loading situation has been taken from the literature [64] and is plotted in Black. The intensity of each colour reflects the magnitude of crack length; points representative of longer cracks have less colour intensity than those from shorter cracks.

The data, shown in Figures 6.37 and 6.38, are not corrected for finite-width effects. Finite-width correction factors, taken from isotropic considerations [55], have therefore been applied to the data (for the $a/W$ range of 0.1 to 0.8). The failure locus, after modification for coupon finite-width effects, in $K_C$ and $G_C$ space is shown in Figures 6.39 and 6.40, respectively.
Figure 6.37. *Failure locus for the HTA/F927 composite in K space.*

Figure 6.38. *Failure locus for the HTA/F927 composite in G space.*
6.4.5. Discussion

The failure envelope for the HTA/F927 material system, after application of finite-width correction formulae, is shown in Figure 6.39. The locus of failure data for this material, described by an exponential decay curve between measured and literature data, contains similar failure loci to those observed for a PEKK/carbon fibre composite plotted in the $K_s$ versus $G_s$ plane. Further failure loci in $K$ space is the theoretical prediction of Ogden et al. (93) and the data of the present study. The line of best fit is given by the equation $G_s = 10.5K_s^2$. The experimental values of $G_s$ are then in excellent crack propagation for the HTA/F927 composite.

Figure 6.39. Failure locus for the HTA/F927 composite in $K$ space.

Figure 6.40. Failure locus for the HTA/F927 composite in $G$ space.
6.4.5. Discussion

The failure envelope for the HTA/F927 material system, after application of finite-width correction factors, shows a significant interaction between the mode I and mode II stress components in both K and G space. The locus of failure follows an exponential decay curve between the mode I point to the mode II point. The literature also contains similar failure loci plots that follow this trend. Figures 6.41 [53] and 6.42 [6] show the delamination failure loci for a PEEK / carbon fibre composite plotted in the $G_1$ versus $G_{II}$ plane. Indicated on both plots is the theoretical prediction of failure according to Equation (4.22) as proposed by Charalambides et al [53]. If anything the data of the present study show a stronger interaction. This may reflect that in intralaminar crack propagation there is less effect of crack-face friction than in interlaminar crack propagation tests.

![Figure 6.41](image)

**Figure 6.41.** Delamination failure locus for a PEEK-matrix/carbon-fibre composite, solid line is theoretical prediction following Equation (4.22), after [53].
6.5. CONCLUDING REMARKS

Failure strengths have been measured using un-cracked off-axis coupons. A comprehensive study has been carried out using cracked off-axis laminates to investigate intralaminar crack propagation.

Considering brittle composite material systems (HTA/F922 and glass-fibre/epoxy), strength-based measurements conducted on un-cracked coupons as well as results from the literature show that there are clear stress interactions at failure, whereas, fracture-mechanics-based measurements conducted on pre-cracked coupons indicate that crack propagation is nominally mode I controlled. For a tough composite material system (HTA/F927), the failure envelopes in K and G space, measured from pre-cracked coupons after application of finite-width correction factors, show significant interactions between the mode I and mode II stress components.

The main aim of this part of the work was to develop a suitable methodology of determining intralaminar failure envelopes; this has been successful. A better understanding of the origins of the envelope remains unresolved, as for the companion delamination problem.
Chapter Seven

A Review of ToF-SIMS and its Application to Polymers and Composites

7.1. INTRODUCTION

The fractography of fibre polymer composites is known to give a valuable insight into the mechanics of failure. Fractography studies are conventionally carried out using optical and electron microscopy; however, in order to understand failure better it may be necessary to employ surface analysis techniques that can provide detailed chemical information of the material. Examination of fracture surfaces may lead to an improved understanding of the interfacial microchemistry of composite failure.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been recognised as a technique that is both highly surface specific and is capable of providing detailed chemical information, it has an extremely high sensitivity and is, in favourable cases, also capable of excellent spatial resolution.

The present chapter provides a background to the technique of ToF-SIMS, detailing the secondary ion mass spectrometry (SIMS) process as well as aspects of the instrumentation. An outline of sample preparation methods for the ToF-SIMS analysis of insulating materials, such as an FRP thermosetting matrix material, is given. The chapter concludes with a review of previous FRP fracture surface studies.
7.2. THE SIMS PROCESS

SIMS is the mass spectrometry of the secondary ions emitted from a surface after it has been bombarded by a beam of energetic primary ions. During the impact of a primary particle with a surface, energy is transferred from the primary particle to the atoms of the material via a collision process. This process gives rise to a cascade of inter-atomic collisions within the solid matrix. The classic simile is that of a billiard ball type collision [65]. Some of the products of the collision cascades disappear deep into the solid, others return to the surface region causing the emission of secondary particles. Emitted secondary particles include electrons, neutral species, atoms, molecules and atomic and cluster ions. The sputtering process is shown schematically in Figure 7.01.

![Figure 7.01. A schematic representation of the sputtering process.](image)

The majority of the emitted species are neutrals, used in sputtered neutral mass spectrometry (SNMS), however in secondary ion mass spectrometry it is the secondary ions that are collected and mass analysed. The secondary ions not only give the characteristic elemental composition of a surface, but because ions are also emitted in clusters they also give an indication to the chemical structure [66].
The bombardment of a surface by a beam of high-energy primary ions results in a 'cascade' of atomic collisions within the material. The higher the energy of the incident primary ion, the greater the collision cascade within the material and hence the greater the yield of secondary ions. The use of a high flux primary ion beam, however, results in 'damage' of the sample's surface. As the ion beam sputters away the sample's surface layers the analysis becomes less and less surface-specific. Eventually bulk analysis will be taking place. This process known as dynamic SIMS is a destructive process, but can be used to give a depth profile by recording the intensities of chosen mass fragments as a function of time. The application of SIMS to give a true surface representation was first demonstrated by Benninghoven [67]. The use of a very low primary particle flux density allows spectral data to be generated in a time scale which is very short compared to the lifetime of the surface layer. The information gained is characteristic of the chemistry of the surface because the primary particle does not impact any point on the surface more than once during the course of analysis. This process, known as static SIMS, results in a much lower secondary ion yield and hence requires a much higher sensitivity of the detection equipment or longer acquisition times. In the static SIMS mode, parallel rather than series detection of secondary ions is preferred. This is achieved by the use of a spectrometer with parallel detection such as a time-of-flight (ToF) analyser, as described later in this chapter.

7.3. THE INSTRUMENTATION

7.3.1. Introduction

Static SIMS involves the bombardment of a sample with a low-density flux of positive ions (or neutral atoms) and the mass analysis of the positive and negative secondary ions which are emitted from the surface of the samples. Static SIMS experiments are therefore conducted under conditions of ultra high vacuum (UHV) (<10⁻⁸ mbar) to eliminate the possibility of surface contamination, thus at the centre of any SIMS instrument is a vacuum vessel, with its associated pumping systems. The system usually consists of an analysis chamber, with a primary ion source and a mass spectrometer with its associated secondary ion collection optics, a preparation chamber, where samples can
be etched, cleaved, chemically treated or coated, and a fast entry lock. The entry lock allows samples to be rapidly loaded into the system without degrading the vacuum conditions in the analysis chamber. There is also a dedicated data system based on a PC or workstation for control of the spectrometer and processing of the acquired data. The main components will now be considered in turn.

7.3.2. Primary Ion Sources

The various different requirements for static SIMS studies give rise to a variety of primary beam sources. The most important ion source parameters are brightness, extractable current and energy spread. These parameters will determine the final current/spot size characteristics of the beam at the sample surface [65]. There are three types of ion source used for static SIMS these are the electron impact, surface ionisation and liquid-metal field emission sources.

In the electron impact ion source, electrons are produced from a heated filament and accelerated towards an anode by a voltage difference, the electrons gain sufficient energy to ionise supply gas atoms upon impact. Ion guns based on this type are generally small, relatively cheap and ideal for quadrupole static SIMS. The necessary stable, low current density at the sample is easily achieved by using a low gas pressure and a defocused beam.

Surface ionisation is used to produce [Cs]$^+$ beams used for time-of-flight secondary ion mass spectrometers. These sources combine a very high brightness with a very low energy spread. Caesium is fed from a heated reservoir into either a heated porous tungsten plug or via the vapour phase onto a heated filament. The evaporation of the caesium from the tungsten surface occurs as both atoms and ions. The ions are then accelerated away from the emitting surface. The resultant ion beam is generally very pure as no collisions are involved. A pure ion beam means that mass filtering is not required and the high brightness ensures that more ions per pulse can be achieved than with an electron impact source.
In liquid metal ion sources the liquid metal (usually gallium) is drawn from a heated reservoir over the tip of a needle, radius ~ 5 µm. In front of the tip is an extraction electrode biased negatively so as to produce a field strength at the tip. Opposing electrostatic and surface tension forces acting on the liquid film produces a conical shape with a very high radius of curvature cusp protruding from the tip. Field emission occurs from this cusp. The source brightness is exceptionally high, however the energy spread is relatively large and depends on the extracted current. With natural gallium liquid metal ion sources it is usual to use a Wien mass filter [65] within the gun column in order that only pre-selected ions are used as the primary beam. $^{69}$[Ga]$^+$ ions rather than $^{71}$[Ga]$^+$ are preferred (as $^{69}$[Ga]$^+$ is the most intense isotope) hence the $^{71}$[Ga]$^+$ ions will be filtered out. Some current designs of gallium liquid metal ion sources use mono-isotopic $^{69}$[Ga]$^+$ and therefore avoid the need for a mass filter within the gun column [65]. Liquid metal ion source guns are widely used for high resolution ToF-SIMS imaging because of their ability to realise small spot sizes (200nm is readily achievable). The pulsing of the liquid metal ion source as is required by ToF-SIMS does degrade resolution slightly; however, spot sizes are generally below 1 µm.

The majority of ToF-SIMS studies in this project have been conducted using a $^{69}$[Ga]$^+$ primary ion source, as produced from a liquid metal ion gun. Additional experiments, however, have utilised [Cs]$^+$, and [SF$_5$]$^+$ primary ion sources. [Cs]$^+$ primary ion sources have a very high brightness and so may be used to increase high mass secondary ion yield, whereas polyatomic primary ion sources, such as [SF$_3$]$^+$, are thought to be advantageous for the analysis of polymer materials.

### 7.3.3. Mass Analysers

Whichever primary beam system is used in static SIMS studies it is necessary to maximise the information level achieved per unit of surface damage. The analysis and detection system therefore need to be as efficient as possible. The quadrupole mass analyser was, up until the early nineties, favoured because of the ease with which it was incorporated in the ultra high vacuum systems. The quadrupole analyser is however a low transmission device, furthermore it is a serial acquisition instrument so that it only
allows the sequential transmission of ions, all other ions being discarded. The information loss is therefore very high [67].

The time-of-flight (ToF) mass analyser has become of greater importance in the use of static SIMS for the analysis of organic materials. This is because the whole spectrum is acquired in parallel so the primary ion dose is the minimum possible. Transmission is high or constant across a mass range thus there is no discrimination against high mass ions allowing more complex ions to be analysed. The ToF analyser utilises a pulsed primary beam, the resulting pulse or 'packet' of secondary ions are accelerated via an extraction field, thereby giving them all virtually the same kinetic energy, over a very short distance before entering a field-free drift tube. Since ions of different mass will have different velocities mass separation will occur, thus a mass spectrum of all the ions is generated from the flight time spectrum. The secondary ions generated in this manner usually have quite a wide range of kinetic energies, which is generally compensated for by an energy analyser in the flight tube. An example of an energy analyser is the electrostatic ion mirror as used in a reflectron-type ToF-SIMS instrument; this is shown schematically in Figure 7.02. The ion mirror consists of a series of precisely spaced rings acting as an electrostatic lens with a gradually increasing retarding field. Faster moving ions (those with higher kinetic energy) will penetrate deeper into the electric field of the ion mirror and so take a longer path than slower moving, less energetic, ions of the same mass. The result is that all ions of the same mass should arrive at the detector at the same time.
7.3.4. Instruments Employed Within the Current Study

The main instrument used in this study has been a VG Scientific Type 23 ToF-SIMS system equipped with a Poschenrieder-type mass analyser. In this instrument an electric field, produced by electrostatic sectors, is interposed between two linear drift tubes. In this field the secondary ions follow curved trajectories that are longer for the more energetic ions in such a way that the initial energy variation is compensated [69]. Figure 7.03 shows a photograph of the instrument and a schematic showing the main operational components.

Secondary ion mass spectra have also been generated from additional ToF-SIMS instruments. Other ToF-SIMS analysers utilised in this study have been a VG Scientific Type 23 ToF-SIMS system equipped with a two-stage reflectron-type mass analyser, an ION-ToF GmbH ToF-SIMS IV instrument equipped with a single stage reflectron-type mass analyser and a Physical Electronics Trift II instrument equipped with a triple sector mass analyser.
Chapter Seven: A Review of ToF-SIMS and its Application to Polymers and Composite

7.4. TOF-SIMS OF INSULATING MATERIALS

7.4.1. Introduction

The Time-of-Flight Mass Spectrometer

Figure 7.03. Poschenrieder-type ToF-SIMS instrument.

Figure 7.03. Poschenrieder-type ToF-SIMS instrument.
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7.4. ToF-SIMS OF INSULATING MATERIALS

7.4.1. Introduction

In order to characterise composite fracture surfaces and distinguish between species arising from the fibres and those representative of the matrix material, initial ToF-SIMS studies have been conducted on the bulk resin material. Organic insulating materials, such as the polymer matrix in a FRP, are not only chemically complex but also very sensitive to particle bombardment. Under primary ion bombardment the surface potential of the material will rise, known as sample charging, with consequent problems for spectral acquisition.

When a positive ion beam bombards an insulating material the surface potential rises due to the input of positive charge and the emission of secondary electrons. A non-uniform potential develops across the sample's surface, known as differential charging, this is because the charge developed cannot be replaced through ground currents, due to the insulating nature of the sample. The surface potential can rise very rapidly resulting in the kinetic energy of the emitted positive ions rising well beyond the acceptance window of the analyser. This is noted during an analysis by a steep reduction in the secondary ion intensity. In the negative mode the secondary ions are unable to escape the positive potential of the surface, which again may be noted by a lack of secondary ion signal. Solutions to overcome sample charging include the use of low energy electron flood guns, fast atom primary particle sources instead of ion sources and the use of conducting surface grids placed over the analysis material.

7.4.2. Electron Flood Guns

The most widely used solution to compensate for sample charging is to irradiate the sample's surface with a beam of relatively low energy electrons. After a primary ion pulse the extraction field is reduced to almost zero volts and a longer pulse of low energy electrons is directed at the sample. After this pulse a short delay before raising the extraction field for the next primary ion pulse avoids the possibility of extracting any
ions arising from electron induced emission into the spectrometer. The pulsing frequency of the electron source is usually an order of magnitude less than that of the primary ion source. A schematic of the process is shown in Figure 7.04. The theory behind such a method is that the electrons will be attracted to the region of positive charge on the sample’s surface and hence the surface potential will return to neutral. The method is usually successful for the acquisition of positive static SIMS spectra, however, for negative ion detection it is necessary to drive the surface potential negative in order for the negative ion to be released from the surface. This requires a higher flux of electrons. A disadvantage to electron bombardment is that it may give rise to sample degradation and electron stimulated ion emission. In ToF-SIMS these factors may be of less consequence as the electron flood gun is of a very low energy and is pulsed, however, the pulsing means inherently more complicated electronic systems.

![Figure 7.04. Pulse-time diagram of primary ions, extractor voltage and charge compensating electrons as used for ToF-SIMS of insulating materials, after [70].](image-url)
7.4.3. Fast Atom Bombardment

The use of a fast atom primary beam instead of the usual ion beam has been suggested as another method to reduce the effects of sample charging. An ion beam from a noble gas impact source is passed through a cell containing the same gas at high pressure. A proportion of the ions lose their charge by capturing an electron from the atoms randomly moving in the chamber. There is virtually no momentum transfer so that the fast atom beam which emerges has the same energy and spatial characteristics as the original ion beam. The residual ion beam is then deflected away [65].

Unlike an ion beam, a fast atom primary beam does not transfer charge to the sample surface; however, the surface potential does still rise due to the emission of secondary electrons. This potential very quickly reaches a plateau of about 30 eV, because the emitted secondary electrons only have kinetic energies in this range once the plateau is reached no more electrons emerge. The ion acceptance optics may be adjusted to cope with ions in the energy range enabling positive ion spectra to be generated from insulating materials. Disadvantages with this system are that the surface potential still needs to be made negative to allow the acquisition of negative ion spectra, thus some electron input is still required. Measurement of the beam density is also more difficult with fast atom bombardment as the beam cannot be steered [65].

7.4.4. Conducting Grids

The use of a conducting grid either directly deposited, or physically placed over the surface of the sample seems a relatively simple way of eliminating charge build up on a samples surface. In this method the grid should be small enough to allow a high transmission of the secondary ions, but be sufficiently large so as to bleed off any charge build up from the samples surface. In the case of a deposited grid, the deposition process should be such that it does not alter the chemical nature of the analyte’s surface.
An example of a ToF-SIMS experiment using a conducting grid is that by Bletsos and Hercules [71] where a nickel grid has been used to minimise charge accumulation of a thick polymer film.

### 7.5. CATIONISATION

The process of cationisation may be exploited to give high analytical sensitivity. As has been stated previously, the majority of species emitted in the SIMS process are neutrals; the possible analysis of some of these neutrals combined with the secondary ions already detected could be greatly beneficial in the characterisation of a surface. The mechanisms and efficiencies of sputtered species to be cationised are still relatively poorly understood.

Cationisation, under normal circumstances of polymer analysis, is by the attachment of alkali metal ions ([Na]$^+$ or [K]$^+$) or other metals with a high secondary ion yield (most often [Ag]) to sputtered neutrals, molecules or fragments. Many molecules which give [M + H]$^+$ ions will, in the presence of alkali metal cations give [M + A]$^+$ ions (A-alkali metal) instead of, or in addition to, the protonated analogue. This process is very efficient requiring only trace amounts of the alkali ions to be present.

Benninghoven first introduced the deliberate cationisation of polymers with silver [65]. The technique involved the deposition from solution, of a monolayer (or less), of the analyte onto a silver surface. This method has now become an accepted method for the characterisation of polymer molecular weight distributions [72, 73, 74] and high mass fragments [75]. Yields of [M + Ag]$^+$ ions can be very high and because silver has a distinct isotope pattern, $^{107}$[Ag] and $^{109}$[Ag] of almost equal abundance, the cationised species are easily identified. This is not always the case with alkali metal cationisation since the cations are usually mono-isotopic. The thickness of the analyte, monolayer or less, also results in charge build-up being less of a problem as the potential is grounded due to the silver beneath.
This method of polymer analysis has a distinct flaw, the polymer must be cast as a monolayer film onto the silver substrate, and thus the analysis is only of the polymer bulk and is not 'true' surface analysis. The technique is also limited to the analysis of thermoplastic polymer materials, as thermosetting polymers cannot be cast in such a manner.

The reverse of the usual experimental set up has also been undertaken, i.e. casting thin silver films onto the sample's surface instead of vice-versa. In an experiment by Linton et al [76] a ToF-SIMS analysis was undertaken of linear low-density poly(ethylene) with a silver pattern, 150 nm thick deposited upon its surface. The silver was deposited through a transmission electron microscope (TEM) grid onto the polymers surface, resulting in a pattern of individual squares of silver. The polymer in this analysis was however cast onto a substrate, i.e. as a thin film and thus the analysis is again of bulk properties.

The cationisation of thick polymer films has been successfully undertaken, Bletsos and Hercules [71], by the use of a thin silver foil, with a circular hole cut from its centre, placed over the sample. In this experiment detection of ion fragments in the medium mass range m/z \( \leq 4500 \) was possible from a 1 mm thick cross-linked polydimethylsiloxane sample.

### 7.6. FRACTOGRAPHY

#### 7.6.1. Scanning Electron Microscopy Studies

A number of prior studies have considered the relationships between the fracture surface morphology and the mode of failure [15, 41, 77, 78, 79, 80].

Failure surfaces of FRPs from mode I and mode II intralaminar and interlaminar loadings have been documented by Garg [78]. In this study [78] delamination (interlaminar) fracture surfaces are taken from double cantilever beam and cracked lap shear coupons, the fracture surfaces are stated as being generated from mode I and mode
II loadings, respectively. Intralaminar fracture surfaces are taken from compact tension and centre notched tension coupons, which are stated to be mode I and mode II loadings, respectively. Both the intralaminar and interlaminar mode I fracture surfaces show very similar morphologies, which are dominated by matrix cleavage.

The mode I epoxy fracture surface is marked by branched crack structures between fibres and river patterns and chevron markings [77] in resin rich zones within lamina. In addition to the surface features the mode I intralaminar fracture surface has more fibre matrix debonding and some broken fibres.

The mode II interlaminar fracture surface is shown to consist of fibres apparently free of any matrix residue and complex matrix patterns between fibres. Garg [78] reports that the epoxy features have generally been referred to as hackles, lacerations or raised platelets [77]. The observed surface hackles all have similar features such as a pointed structure either near one or both of the fibre matrix boundaries, a bulge in the middle and a tilt towards one end.

The mode II intralaminar fracture surface, as documented by Garg [78], shows varied epoxy features. Fine cracks are observed originating near the fibre matrix boundaries which coalesce to form larger cracks similar to the branched crack structures as seen in the mode I fracture surface. The fine cracks are seen interacting with overlapping platelets which give the appearance of a feather structure [77]. Shear cusps and hackles are observed, however, these are of a smaller size due to the smaller fibre spacing compared with those in the mode II delamination surface.

Several authors [15, 77, 79, 80, 81, 82] have proposed explanation for the formation of shear hackles and cusps. Purslow [77] states that if a band of material is subjected to a shear stress, failure will commence as a series of micro-tensile fractures in the plane of the shear band but which are normal to the resolved tensile component, Figure 7.05a. With increasing shear stress the number of tensile cracks will increase and will individually elongate, Figure 7.05b, and curve over as they approach the limits of the shear band, Figure 7.05c. Ultimately shear failure occurs along the line of cracks when these tensile failures simultaneously coalesce, Figure 7.05d. The limits of the shear band will be dictated by the fibre spacing in a fibre reinforced composite, this is seen by Garg.
[78] where more widely spaced hackles occur in regions where fibres are relatively further apart.

\[\text{Figure 7.05. Schematic showing matrix shear failure and the formation of cusps, after [77].}\]

The differences between mode I and mode II fracture surfaces as documented by Garg [78] have been seen in other studies of FRP composites. Donaldson [41] observes a clean cleavage type mode I fracture surface, as increasing amounts of mode II are introduced hackles are observed, initially regular and shallow they become irregular and nearly vertical with the increased mode II ratio. Hashemi et al [52] using a carbon fibre/PEEK composite system show an SEM analysis of fracture surfaces from mode I, mode II, and mixed-mode tests and note that as the degree of mode II loading increases there is an increasing extent of apparent interfacial failure between the matrix and fibres.
Fractographic results from a mixed mode delamination study by Trakas et al [80] show cleaved matrix mode I fracture surfaces and shear hackle and matrix damage features on a mode II fracture surface.

### 7.6.2. SIMS Studies

Both optical and electron microscopy are limited in their ability to detect very thin polymeric over-layers. To date there has been very little published work on SIMS studies of carbon fibre fracture surfaces. The advantages of a technique such as ToF-SIMS have previously been discussed but can be summarised in its ability to provide a detailed chemical fingerprint which is highly surface specific thus allowing thin over-layers, such as matrix material adhering to fibres, to be analysed. The high sensitivity and small spatial resolution of ToF-SIMS gives it the advantage over alternative surface science techniques such as X-ray photoelectron spectroscopy (XPS) which has an inability to distinguish unambiguously the type and distribution of functional groups and has a lack of spatial resolution.

Alternative surface analysis techniques such as scanning Auger microscopy (SAM) have been used to study the fibre/matrix interface of composites materials. Cazeneuve et al [83] use SAM to identify the components of a continuous CFRP composite fracture surface by appropriate choice of elemental markers for the fibre and the matrix. Cazeneuve et al [83] also use SAM of a short-fibre CFRP fracture surface to show failure takes place at the carbon fibre surface leaving a very thin layer (0.6 to 2nm) of absorbed matrix on the pullout fibres.

The study of CFRP composite fracture surfaces by SIMS has been addressed previously [68, 84, 85]. In a study by Denison et al [84] imaging SIMS, with a quadrupole mass analyser, has been used to characterise the fracture surface of composite laminates produced with varying amount of fibre oxidation. By the use of two negative marker ions, species originating from the fibres have been distinguished from those originating from the matrix. Mass 26 was chosen to represent the fibres; this corresponds to the [CN]⁻ ion. This ion was chosen as it was thought to arise from the incomplete pyrolysis
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of the polyacrylonitrile used to make the fibres. Mass 35 was chosen as a representative of the matrix material, this corresponds to the ion [Cl]⁻, which is reported to be in the resin material as a contaminant due to the use of epichlorohydrin in its synthesis. These marker ions have enabled the detection of thin matrix over-layers (≤ 0.01 µm thick) on the highly oxidised fibres. These over-layers are not present on the untreated fibres. The results from the SIMS analysis have been correlated with the interlaminar shear strength of the various composite laminates, showing that as the fibres underwent higher surface treatments the shear strength increases, and the more evidence there is of matrix over-layers from the surface analysis. The conclusions are that oxidative treatment of fibres improves adhesion at the interface until at high treatment levels it becomes dominant over the limiting, constant resin strength. This paper provides a good example of how mechanical testing and surface analysis may be combined to give a better overview of composite failure mechanisms.

Hearn and Briggs [85] give an example of the images possible from a ToF-SIMS analysis of a fracture surface. This work states that the analysis by a ToF-SIMS instrument of a fracture surface can be carried out with greater confidence than that with a quadrupole instrument due to its higher transmission and parallel detection. In this study the authors analyse the ion mass pattern from carbon fibres, alone, as well as that generated solely from a thick film of the polymer matrix, in order to characterise species specific to either fibres or matrix. The results show that the positive spectrum from the matrix is dominated by the same ions as those found in the spectrum from carbon fibres, thus no distinction is possible. The negative spectrum from the matrix, however, contained a distinct series of cluster ions characteristic only of the matrix material. Unfortunately these molecular cluster ions were deemed to be of too low an intensity to allow high spatial resolution imaging of fracture surfaces to take place. Secondary ion images of the fracture surface were recorded, however, and the [S]⁻ ion was used, because of its high intensity, to identify the matrix material and distinguish it from the fibres. The secondary ion imaging analysis led the authors [85] to conclude that there existed areas of interfacial failure within the fracture surface.

Vickers [68] has conducted detailed studies by ToF-SIMS of both carbon fibres and carbon fibre composite fracture surfaces. In this study [68] positive and negative
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secondary ion mass spectra are presented from carbon fibres that have undergone different levels of oxidative surface treatment, in the range 0 % - 100 %. Qualitatively there is little difference between the spectra from untreated and treated fibres; low mass ion fragments have been assigned to possible groups that could originate from the fibres structure. The positive spectra from the treated fibres are dominated by the inorganic ions [Na]+ and [Ca]+, these ions are thought to be adsorbed onto the fibre surface during the oxidative procedure which occurs within an aqueous electrolyte. ToF-SIMS analysis of carbon fibre pre-preg material by Vickers [68] has revealed an amount of release agent left on the uncured sheet material's surface after the removal of the protective release film. The effect of siloxane-type release agents on the interlaminar toughness of CFRP is presented by Vickers et al [86]. This paper concludes that the addition of a very low molecular weight polydimethylsiloxane (PDMS) appears to improve the interlaminar fracture resistance of a composite. SIMS spectra from cured composite fracture surfaces are presented by Vickers [68]; species believed to be representative of fibres and of matrix material are identified. Both positive and negative ion composite fracture surface spectra show large amounts of contaminant siloxane based molecules. Contaminant molecules were thought to originate from the release films that pre-preg material comes supplied with, or from contamination from the atmosphere. The only way to completely avoid the possibility of contamination from the atmosphere is to fracture the composite in the UHV confines of the spectrometer. Vickers [68] conducted in-situ fracture of CFRP coupons within the confines of the spectrometer. In this study [68] a commercial (VG Scientific) fracture stage, originally designed for metallurgical studies was used. Failure was induced within a 'matchstick' coupon held within the preparation chamber of the spectrometer. The stage brought about fracture by impacting the test coupon in a method that resembled an Izod impact test, although failure did not conform to any conventional mechanical test standards for fracture. ToF-SIMS analysis of the resultant fracture surfaces still reveals ions representative of the contaminant PDMS although in greatly reduced intensity. Both positive and negative secondary ion mass spectra are characterised by peaks representative of aliphatic hydrocarbons and also of aromatic species, all of which can be assigned to either the matrix material or fibres or both. Ions believed characteristic of uncured DGEBA were observed, this is reported to be a function of the carbon fibre size material and as such representative that in some cases fracture was through the fibre matrix interface.
7.6.3. Concluding Remarks

A considerable amount of work has focused on FRP fractography studies by electron microscopy. Variations in surface morphology as a consequence of the loading mode of failure have been documented previously. Within the literature there is a good agreement as to the relationship between the visual appearance of FRP fracture surfaces and their respective mode of failure. The most important fractographic feature for characterisation of a mode II fracture surface is the cusp or hackle. It should, therefore, be possible to make a visual distinction between fracture surfaces and to comment on the possible loading mode of failure, this is applicable to both interlaminar and intralaminar fracture planes.

The application of ToF-SIMS to FRP fractography studies has resulted in an increased chemical knowledge of the fracture surface and the identification (or absence) of matrix over-layers adhering to pulled-out fibres. ToF-SIMS has the potential to determine the precise locus of failure, whether interfacially between fibre and matrix, cohesively within the matrix or perhaps even within the fibre-matrix interphase. However, commercially available epoxy matrix FRP systems are based upon intricate formulations, as discussed previously (Chapter 2), the spectra of the fracture surface are therefore highly complex and thus a systematic approach to characterisation is required. In addition, if meaningful data are to be generated all post fracture contamination must be eliminated from the fracture surface and hence from the associated surface spectra. The difficulties in choosing marker fragmentation ions that are characteristic of the individual components of an FRP composite system have been highlighted. The ToF-SIMS studies of FRP fracture surfaces identified within the literature all use very different ions to represent both fibre and matrix material.
Chapter Eight

The Development of ToF-SIMS for the Analysis of FRP Composites

8.1. CHARGE COMPENSATORY METHODS

8.1.1. Introduction

Some aspects of FRPs have been addressed previously (Chapter 2). Modern commercial FRP systems are generally complex materials; in addition to fibres and bulk matrix material they may incorporate a fibre size as well as hardeners, plasticisers, modifiers and fillers all of which will contribute to the storage, processing and final properties. In order to aid the interpretation of ToF-SIMS spectra recorded from FRP fracture surfaces, it would be advantageous to be able to distinguish between species representative of the fibres and those representative of the matrix material. A starting point to the surface analysis investigation was, therefore, to obtain fingerprint analyses of the bulk matrix materials. The difficulties in achieving an analysis from a thick block of insulating material such as a cured thermosetting polymer have been addressed previously, Section 7.4. ToF-SIMS analyses were attempted on thick plaques of epoxy resin, however the secondary ion yield was observed to decrease considerably a few seconds into the analysis, resultant spectra were of very poor quality in terms of both mass resolution and secondary ion yield. The insulating nature of the polymer matrixes meant that an appropriate method of charge compensation was required. The first aim of this part of the experimental work was therefore to establish such a method.
8.1.2. Fixed Grids

8.1.2.1. Methodology

The first charge compensatory method to be investigated was the use of conducting grids. Conducting grids were seen as a method that minimised any external influences on the SIMS process. In an experiment resembling that by Bletsos and Hercules [71], conducting grids were placed over thick, ~ 2.8 mm, samples of polymethylmethacrylate (PMMA) in order to establish their charge neutralising potential. PMMA was chosen because it is a thermoplastic and hence should provide a high yield of secondary ions and also because its secondary ion spectra is well documented in both the positive and negative ion mode. The grids used were (i) a tungsten mesh, obtained from V.G. Scientific (ii) a copper TEM grid and (iii) a nickel TEM grid. The TEM grids were 100 mesh in size; this corresponds to 100 lines per inch or 39 lines per centimetre. Samples were mounted in spring-loaded stubs with the grid placed over the sample and a niobium cover plate over the grid. The niobium cover plates had a 10 mm diameter circular hole cut in them through which the analysis could take place. Cover plates were used so as to keep the grid in place and also to provide good contact between the grid and the stub.

8.1.2.2. Results

During the analysis, regardless of the pulse frequency and width, all three grids showed good charge compensation at a magnification of 200, corresponding to a field of view of approximately 1.3 mm. Efficient charge compensation was noted by the fact that there was no reduction in secondary ion intensity during the analysis and no use of the electron flood was required. At a higher magnification (500) all three grids were less effective at compensating for charge build up, this was noted by the loss in secondary ion signal during the analysis, a magnification of 500 corresponds to a field of view of approximately 0.5 mm. The reduction in signal, however, was still far less than during an analysis of the polymer alone i.e. without any charge compensation methods. Experiments using the copper grid showed the lowest fall in secondary ion intensity.
during an analysis. When used in conjunction with an electron flood gun, all three grids showed high secondary ion count rates with no reduction with time.

Positive fragment ions representative of PMMA occur at mass/ionic charge values (m/z) of 59, 69 and 121 \[87\], corresponding to the following ions, respectively.

\[
\begin{align*}
\text{CH}_3 - \text{O} - \text{C} &\equiv \text{O}^+ \\
\text{m}/\text{z} = 59
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 = \text{C} &\equiv \text{O}^+ \\
\text{m}/\text{z} = 69
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - \text{O} - \text{C} &\equiv \text{O}^+ \\
\text{m}/\text{z} = 121
\end{align*}
\]

Negative fragment ions representative of PMMA occur at m/z values of 31, 55 and 85 \[87\], corresponding to the following ions, respectively.

\[
\begin{align*}
\text{CH}_3 - \text{O}^- \\
\text{m}/\text{z} = 31
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 = \text{C} &\equiv \text{CH} - \text{O}^- \\
\text{m}/\text{z} = 55
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - \text{O}^- \\
\text{m}/\text{z} = 85
\end{align*}
\]

An imaging analysis was undertaken with ions representative of copper and PMMA, Tables 8.01 and 8.02 list the ions selected for this analysis.

**Table 8.01.** Positive ions selected for a ToF-SIMS image from a PMMA sample covered with a copper grid.

<table>
<thead>
<tr>
<th>Material Selected</th>
<th>Ion</th>
<th>m/z</th>
<th>Representative colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>$^{63}\text{[Cu]}^+$</td>
<td>63</td>
<td>Red</td>
</tr>
<tr>
<td>Copper</td>
<td>$^{65}\text{[Cu]}^+$</td>
<td>65</td>
<td>Red</td>
</tr>
<tr>
<td>PMMA</td>
<td>$\text{[C}_2\text{H}_3\text{O}_2]^+$</td>
<td>59</td>
<td>Green</td>
</tr>
<tr>
<td>PMMA</td>
<td>$\text{[C}_4\text{H}_5\text{O]}^+$</td>
<td>69</td>
<td>Green</td>
</tr>
</tbody>
</table>
Table 8.02. Negative ions selected for a ToF-SIMS image from a PMMA sample covered with a copper grid.

<table>
<thead>
<tr>
<th>Material Selected</th>
<th>Ion</th>
<th>m/z</th>
<th>Representative colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>$^{35}[\text{Cl}]^+$</td>
<td>35</td>
<td>Red</td>
</tr>
<tr>
<td>Chloride</td>
<td>$^{37}[\text{Cl}]^+$</td>
<td>37</td>
<td>Red</td>
</tr>
<tr>
<td>PMMA</td>
<td>$[\text{CH}_3\text{O}]^-$</td>
<td>31</td>
<td>Green</td>
</tr>
<tr>
<td>PMMA</td>
<td>$[\text{C}_3\text{H}_2\text{O}]^-$</td>
<td>55</td>
<td>Green</td>
</tr>
<tr>
<td>PMMA</td>
<td>$[\text{C}_4\text{H}_5\text{O}_2]^{-}$</td>
<td>85</td>
<td>Green</td>
</tr>
<tr>
<td>PMMA</td>
<td>$[\text{C}<em>9\text{H}</em>{13}\text{O}_4]^{-}$</td>
<td>135</td>
<td>Green</td>
</tr>
</tbody>
</table>

Experimental conditions in the positive mode were as follows: primary beam energy 20 kV, pulse frequency 5 kHz, pulse width 30 ns, magnification at 200. Negative mode acquisitions were made with a 22 kV primary ion beam; hence the field of view is slightly smaller. An electron flood gun was also employed for charge neutralisation during ToF-SIMS analyses. In the negative ion mode the chloride ions, $^{35}[\text{Cl}]^-$ and $^{37}[\text{Cl}]^-$ were used to identify the copper grid, as copper ions do not appear in the negative spectrum. The positive and negative ion images obtained are shown in Figures 8.01 and 8.02, respectively.

![Image of ToF-SIMS images](image)

Red (copper)  Green (PMMA)  Addition of maps

Scale: 1.3 mm

Figure 8.01. ToF-SIMS images of positive ions from a thick PMMA sample covered with a Cu grid.
8.1.2.3. Discussion

The charge reducing effects using fixed grids during the ToF-SIMS analysis of thick blocks of polymer was found to be satisfactory. The grids had a shadowing effect upon the resultant secondary ions; this can be seen in the mass selected images of Figures 8.01 and 8.02. As a result of the geometry of the instrument, secondary ions are extracted normal to the sample’s surface but primary ions are incident at an angle of 45°. Ions representative of the polymer are only visible from one side of the exposed polymer surface. These images demonstrate the topographical limitations of a SIMS analysis without any correctional methods. During the SIMS process, ions are emitted from the sample’s surface at a variety of angles; only those able to clear the surface grid will be collected for analysis. The angle of incident of primary ion beam (45°) on the sample’s surface combined with the thickness of the grid will also contribute to the shadowing effects evident in the images of Figures 8.01 and 8.02.
8.1.3. Deposited Silver Grids

8.1.3.1. Methodology

The process of analysis enhancement through the cationisation of sputtered neutrals with silver has been discussed previously, Section 7.5. Experiments were undertaken in an attempt to combine the advantages of silver cationisation with the charge neutralisation of metal grids. Silver was deposited through a grating to produce an in-situ grid. This experiment was similar to that carried out by Linton et al [76], except that rather than isolated islands of silver being deposited upon the samples surface a grid pattern was achieved. The grid pattern was used as isolated islands are not grounded and hence could "float" at different potentials. Depositing through the grating produced parallel lines of silver. The silver was first deposited transversely, the sample was then rotated around 90° and silver deposited longitudinally, the resultant silver pattern was that of a grid. The grating consisted of bars, 500 µm in width with a 200 µm spacing. The resulting pattern was therefore 500 µm by 500 µm blank squares separated by 200 µm wide bands of silver.

Silver was deposited by entwining silver wire around the tungsten filament of a resistance heater. The filament of the heater was contained within a nozzle, thus enabling the silver to be aimed along a set pathway; the evaporator assembly was then mounted onto the preparation chamber of the Poschenrieder ToF-SIMS instrument. The grating was fixed onto a stub, which enabled it to be placed beneath line of sight of the resistance heater. A small stage for holding sample stubs was attached to a linear drive, which in turn was connected to the preparation chamber. The linear drive enabled samples to be raised up beneath the grating into the path of the depositing silver; Figure 8.03 shows a schematic of the apparatus. A linear drive was used as it was thought necessary to manipulate the sample as close to the grating as possible. The closer the sample to the grating, the less diffuse the resultant pattern of silver.
Chapter Eight: The Development of ToF-SIMS for the Analysis of FRP Composites

8.1.3.2. Results

Initial investigations were conducted using an optical microscope. This was to establish whether or not the deposition process had worked and to assess the resultant silver pattern. Figure 8.04 shows light photomicrographs of an epoxy sample that had undergone the silver deposition process. From Figure 8.04 it may be seen that silver deposition process was successful, the resultant pattern is that of a sharp grid.

![Diagram of ToF-SIMS instrument showing configuration for depositing silver on a sample](image)

**Figure 8.03.** *Schematic showing the configuration used for depositing silver on to a sample within the preparation chamber of the ToF-SIMS instrument.*
In order that secondary ions associated with the silver and the deposition process were not confused with those emitted from the samples, initial experiments using a deposited silver grid were conducted upon samples of aluminium foil. A ToF-SIMS analysis of the aluminium was performed, a silver grid was then deposited and the resultant spectra compared to that of the pure aluminium. Any ions associated purely with the silver and/or the deposition process could be recorded and eliminated from future analysis.

The spectrum from a sample of aluminium foil was dominated an intense peak at m/z = 27, this corresponds to the aluminium ion $^{27}\text{[A]^{+}}$ although the peak could have a contribution from the $[\text{C}_2\text{H}_3]^{+}$ ion as well. There is a peak of low intensity observed at m/z = 29, which corresponds to the organic ion fragment $[\text{C}_2\text{H}_5]^{+}$. The occurrence of this ion fragment (m/z = 29) indicates that the peak at m/z = 27 does have a contribution from the related $[\text{C}_2\text{H}_3]^{+}$ organic ion, although the contribution is thought to be minimal. High resolution of the peak at m/z = 27 would distinguish between the two ions although such analyses was not conducted in the present study. Other peaks within the spectrum were those representative of inorganic contaminants such as $[\text{Na}]^{+}$ and very low mass organic fragments such as $[\text{C}]^{+}$, $[\text{CH}_2]^{+}$, $[\text{CH}_3]^{+}$, $[\text{C}_2\text{HO}]^{+}$.

A positive ion spectrum typical of spectra recorded from the aluminium foil after silver grid deposition is shown in Figure 8.05. The spectrum is dominated by a peak at m/z =
27, corresponding to the aluminium ion $^{27}\text{[Al]}^+$, there are also intense peaks at $m/z = 107$ and 109 which are representative of the silver ions $^{107}\text{[Ag]}^+$ and $^{109}\text{[Ag]}^+$, respectively. Peaks from multiple configurations of silver ions are also present, such as $2\text{Ag}$ at $m/z = 214, 216, 218$ and $3\text{Ag}$ at $m/z = 321, 323, 325, 327$. Fragment ions representative of the contaminant release agent PDMS are observed, these peaks occur at $m/z$ values of 73, 147, 221 and 281, corresponding to the ions $[(\text{CH}_3)_3\text{Si}]^+$, $[\text{Si}_2\text{O}(\text{CH}_3)_3]^+$, $[\text{Si}_3\text{O}_2(\text{CH}_3)_7]^+$ and $[\text{Si}_4\text{O}_4(\text{CH}_3)_7]^+$, respectively. In all spectra recorded from this sample (aluminium foil + deposited silver grid) a significant number of higher mass ions were also observed.

Figure 8.05. Positive ToF-SIMS spectrum recorded from a sample of aluminium foil coated with a deposited silver grid.

An imaging ToF-SIMS analysis was undertaken in the positive ion mode, so as to detect aluminium ions, $^{27}\text{[Al]}^+$, and silver ions, $^{107}\text{[Ag]}^+$ and $^{109}\text{[Ag]}^+$. A map of ions representing various species seen in the spectral analysis, such as the polymer PDMS and a high mass ion was also undertaken. Table 8.03 lists the ions selected for this analysis. The experimental conditions during this imaging analysis were primary beam energy of 18 kV, a pulse frequency of 5 kHz and a pulse width of 25 ns, magnification was at 200.
Chapter Eight: The Development of ToF-SIMS for the Analysis of FRP Composites

Table 8.03. *Positive ions selected for a ToF-SIMS image from an aluminium sample coated with a silver grid.*

<table>
<thead>
<tr>
<th>Material selected</th>
<th>Ion</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>[Al]^+</td>
<td>27</td>
</tr>
<tr>
<td>Silver</td>
<td>^{107}[Ag]^+</td>
<td>107</td>
</tr>
<tr>
<td>Silver</td>
<td>^{109}[Ag]^+</td>
<td>109</td>
</tr>
<tr>
<td>PDMS</td>
<td>((CH₃)₃Si)^+</td>
<td>73</td>
</tr>
<tr>
<td>PDMS</td>
<td>[Si₂O(CH₃)₅]^+</td>
<td>147</td>
</tr>
<tr>
<td>Unknown</td>
<td>Unknown</td>
<td>464</td>
</tr>
<tr>
<td>Unknown</td>
<td>Unknown</td>
<td>800 - 1000</td>
</tr>
</tbody>
</table>

Figure 8.06 shows secondary ion images obtained by selecting the silver ions, ^{107}[Ag]^+ and ^{109}[Ag]^+, or the aluminium ion ^{27}[Al]^+. The image of the silver ions shows that a grid type pattern of silver has been deposited successfully upon the sample's surface and the image of the aluminium ions shows a pattern opposite to that of the silver. Aluminium ions were detected through the deposited silver, although with extremely low intensity, this indicates that the deposited silver layer is relatively thick, with respect to the depth analysis of ToF-SIMS. Secondary ion images of representatives of the contaminant PDMS and of other higher mass ions are also shown in Figure 8.06. Both ion maps show that the contaminant ions are situated upon the sample's surface in a pattern corresponding to that of the silver.

The contamination ions seem to be associated with the deposition process as they are not present in the spectra from pure aluminium foil and they are situated within the lines of silver. The origin of the contamination is not known, it may be a consequence of inadequate preparation methods of the grating and/or the silver. It may be associated with the silver itself, or it may be contained within the ToF-SIMS preparation chamber and migrate towards the sample due to the heat of the deposition process. It must be noted that the contact of hot silver ions onto the surface of a sample (epoxy or other material) could possibly alter its surface chemistry, although this should not present a problem as the substrate specific ions are sputtered from areas adjacent to the silver grid.
Studies using ToF-SIMS were undertaken in order to assess the ability of the deposited silver grid to compensate for charge accumulation during the analysis of a thick (~5 mm) sample of cured DGEBA epoxy. SIMS spectra from uncured samples of DGEBA resin have been characterised previously in studies by Treverton et al, using both FAB-SIMS [88] and ToF-SIMS [89]. A peak assignment of the DGEBA monomer for positive and negative fragment ions is shown in Tables 8.04 and 8.05, respectively.

A silver grid pattern was deposited onto the surface of a thick (~5 mm) sample of cured DGEBA epoxy, using the technique previously described. During the analysis of the coated sample there was no significant reduction in secondary ion yield, associated with sample charging. A positive ion spectrum typical of the spectra recorded from the cured
DGEBA sample, with the deposited silver grid, is shown in Figure 8.07. Peaks corresponding to positive fragment ions representative of the DGEBA epoxy are observed within the spectrum at m/z values of 269, 253, 191, 135, 91, 77 and 57. These peaks correlate with those documented by Treverton et al [88 89] and to the fragmentation of the DGEBA epoxy monomer as presented in Table 8.04. In addition to the epoxy representative peaks there are a number of intense peaks within the spectrum that correspond to the silver ions $^{107}\text{Ag}^+$, $^{109}\text{Ag}^+$ and to multiple configurations of the silver ions, 2Ag and 3Ag. There is also evidence of the contaminant PDMS, indicated by intense peaks at m/z = 73, 147, 221 and 281, as well as a number of unidentified higher mass peaks.

**Table 8.04.** Positive ion fragmentation of DGEBA.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion Structure</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>[CH$_2$OH]$^+$</td>
<td>HO—CH$_2^+$</td>
</tr>
<tr>
<td>57</td>
<td>[C$_3$H$_5$O]$^+$</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>[C$_6$H$_5$]$^+$</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>[C$_7$H$_7$]$^+$</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>[C$<em>9$H$</em>{11}$O]$^+$</td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>[C$<em>{12}$H$</em>{13}$O$_2$]$^+$</td>
<td></td>
</tr>
<tr>
<td>253</td>
<td>[C$<em>{17}$H$</em>{17}$O$_2$]$^+$</td>
<td></td>
</tr>
<tr>
<td>269</td>
<td>[C$<em>{17}$H$</em>{17}$O$_3$]$^+$</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>[C$<em>{20}$H$</em>{21}$O$_4$]$^+$</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>[C$<em>{21}$H$</em>{24}$O$_4$]$^+$</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.05. Negative ion fragmentation of DGEBA.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>[C₃H₅O]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>93</td>
<td>[C₆H₅O]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>117</td>
<td>[C₈H₅O]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>133</td>
<td>[C₉H₉O]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>211</td>
<td>[C₁₄H₁₁O₂]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>283</td>
<td>[C₁₈H₁₉O₃]⁻</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

Figure 8.07. Positive ToF-SIMS spectrum recorded from a thick sample of cured DGEBA epoxy resin coated with a deposited silver grid.
8.1.3.3. Discussion

The ability of deposited silver grid to compensate for the charge accumulation was found to be satisfactory during the ToF-SIMS analysis of a thick cured thermosetting epoxy polymer sample. The number of unidentified high mass ion peaks indicates that silver cationisation of some sputtered species probably took place. However, because there were a number of contaminants associated with the silver deposition process the interpretation of spectra was extremely difficult. Some species representative of the sample could not be distinguished from species associated with the deposition process. The use of silver grid deposition in order to aid the ToF-SIMS analysis of a sample that readily charge accumulates, such as a polymer, has potential; however, unless a perfectly clean silver grid can be deposited, the method is not deemed satisfactory.

8.1.4. Microtoming

8.1.4.1. Methodology

A novel sample preparation method was developed using a histological microtome. Large blocks of cured bulk polymer were shaved using a glass knife to yield very thin (~10 µm) slices of material, Figure 8.08.

![Figure 8.08. Schematic showing the microtoming process.](image-url)
The microtomed sections were mounted in spring-loaded stubs, sandwiched between a niobium backing and cover plate. The niobium cover plates had a 10 mm diameter circular hole cut in them through which the analysis could take place. This sandwich configuration was used so as to keep the sectioned sample in place during analysis and also to provide a good electrical contact between the sample and the stub.

Initial experiments were conducted on a sample of cured DGEBA epoxy resin. 10 µm thick slices were microtomed from a thick plaque of cured resin and mounted in spring-loaded stubs as described above.

### 8.1.4.2. Results

Both positive and negative spectra were acquired using a primary beam energy of 20 kV, a pulse frequency of 5 kHz and a pulse width of 25 ns, magnification was at 1000. Spectra typical of those recorded in both the positive and negative ion modes are shown in Figures 8.09 and 8.10, respectively.

![Figure 8.09. Positive ToF-SIMS spectrum from a microtomed slice of DGEBA epoxy resin.](image_url)
The spectra acquired, in both positive and negative modes, correlate extremely well with those presented by Treverton et al [88, 89]. During acquisition, the secondary ion count rate did not diminish, indicating that the sample surface was not accumulating charge. The absence of such charging problems meant that the secondary ion yield and hence the quality of the resultant spectrum remained high.

The method of microtoming bulk polymers for ToF-SIMS analysis is a relatively clean method of sample preparation. It is noted that the spectra are free from ions representative of handling contaminants such as PDMS, which are commonly seen in spectra from externally prepared samples. There is also an absence in the positive ion spectra of any contamination from the glass cutting blade, such as peaks correlating to the ions $^{24}\text{Na}^+$ and $^{27}\text{Si}^+$. 

8.1.4.3. Discussion

Figure 8.10. Negative ToF-SIMS spectrum from a microtomed slice of DGEBA epoxy resin.
Microtoming has the advantage that the outermost layers of the sample may be removed and discarded, this means that not only are handling contaminants removed but it also enables a fingerprint characterisation of the bulk polymer to take place. An example of the contamination on the surface of cured polymer sample is shown in Figure 8.11. This spectrum was acquired from the outermost microtomed slice of a sample of cured F927 epoxy resin using a TRIFT II ToF-SIMS instrument.

![Figure 8.11. Positive ToF-SIMS spectrum from a microtomed outermost layer of F927 epoxy resin sample.](image)

Intense ion peaks observed within the spectrum all correspond to the Wiley Static SIMS Library [87] documented spectrum, which is characteristic of polytetrafluoroethylene (PTFE). There are no significant peaks observed that are thought to correspond to fragment ions representative of the epoxy resin, an explanation for this is believed to lie in the bulk resin sample fabrication process. During fabrication, F927 bulk resin was cast into moulds. The moulds were coated with a PTFE spray, so as to facilitate the release of the resin after cure. The ToF-SIMS analysis of the outermost surface of the resin reveals that the cured resin samples are coated with a layer of PTFE. This not only demonstrates the surface specificity of ToF-SIMS but also the importance of microtoming away the outermost layers of each sample, so as to remove any fabrication contaminants, ensuring that the resulting spectrum characterises the bulk material of study.
8.2. IN-SITU FRACTURE STAGE DEVELOPMENT

8.2.1. Introduction

Studies on the SIMS analysis of FRP fracture surfaces have been discussed previously, Section 7.6.2. In these studies [84, 85], the failure mechanism was characterised by the identification of marker ions believed to be characteristic of the fibres and of the matrix polymer. Both papers [84, 85] document the difficulty in choosing ions representative of fibre and matrix material and indeed use different ions to do so. The difficulties in analysing ToF-SIMS spectra from fracture surfaces are increased when using mechanical test coupons tested ex-situ using conventional test methods. There are many possible contaminants within the atmosphere of fracture in a mechanical test facility, not only from the lubrication of testing machinery but also the fracture debris of previously broken coupons. Mechanical test coupons also require sectioning after failure to allow entry into the spectrometer; this involves handling of the sample, which can increase further the likelihood of surface contamination. In order to minimise contamination effects, it is logical to develop a fracture stage that allows samples to be broken in-situ within the spectrometer. In-situ fracture stages within ToF-SIMS instruments have been utilised previously [68], as discussed in Section 7.6.2. This stage brought about fracture by impacting the test coupon. The geometry of the fracture stage and that of the in-situ coupons did not conform to any conventional mechanical testing standards. Hence in the present work a new fracture stage has been developed in order that failure may be induced within test samples not only in-situ within the spectrometer but also in a controlled manner that reflects standard conventional mechanical testing protocols and the fracture mechanics testing as described in Chapters 4, 5 and 6.

Modification of the entry-lock of a VG Scientific ToF-SIMS spectrometer, combined with specially designed stubs and a linear drive, has enabled a fracture stage to be engineered such that fracture surfaces may be generated under different modes of loading. The fracture stage has been designed so that it works in a similar way to a quasi-static tensile test machine, in which one crosshead remains fixed while the other moves at a controlled displacement. An entry-lock has been used with two vertically aligned ports. Figure 8.12 shows a photograph of the modified entry lock. Construction
of the fracture stage within an entry-lock means that samples can be 'set-up' by hand. Fracture surfaces may then be generated under atmospheric conditions or under vacuum (UHV conditions) or even under vacuum and then exposed to atmosphere. The entry-lock may also be interchanged between different spectrometers that use the ESCALAB MK II stub geometry, such as other ToF-SIMS instruments or XPS or Auger spectrometers within the laboratory. Each sample stage is fixed in place between the top port, a bolted flange (the fixed cross-head) and the bottom port, a linear drive (the displacement cross-head). For both stages, the fracture process and subsequent manipulation and analysis of the fracture surfaces can all be performed without the need to break vacuum. Opening of the gate valve between the entry-lock and the preparation chamber on the instrument allows the system to be evacuated using the diffusion pump; fracture may then take place under pressures of ca. $1 \times 10^8$ mbar. Both fracture surfaces of the failed coupons can be presented for analysis following mechanical testing.

![Figure 8.12](image.png)  
*Figure 8.12.* Photograph showing the modified ToF-SIMS entry-lock.
8.2.2. Mode I In-situ Fracture Stage

In-situ mode I fracture coupons are based on conventional mode I compact tension samples and conform to the ASTM standard [17]. Samples are mounted in modified ESCALAB MK II-type stubs. Each coupon is fixed between two stubs one inverted upon the other, Figure 8.13.

Figure 8.13. Photograph showing the mode I in-situ test stub.

Load is applied to the coupon via the movement of the stub, which is locked to the bottom linear drive. The stub is locked in place using an extended prong of a rotating wobble stick. Once the coupon has been fractured the wobble stick releases the bottom stub, which is then free to be manipulated through the spectrometer for analysis. The fracture stage assembly is shown in schematically in Figure 8.14. Photographs of the fracture stage assembly are shown in Figure 8.15, both ex-situ and incorporated within the entry-lock chamber.
8.2.3. Mode II In-situ Fracture Stage.

In-situ mode II fracture coupons are miniature $10^\circ$ off-axis samples with oblique end tabs, figure 8.16. Although the $10^\circ$ off-axis coupon does not fracture under a pure mode
II loading the stress state is dominated by shear and with the use of oblique end tabs the stress state has been shown to be homogeneous, as discussed previously, Section 4.3.3. Samples are mounted between two stubs, one inverted upon the other. The stubs are designed so as to provide dual mounting positions, figure 8.16.

Figure 8.16. Photographs showing the mode II miniature 10° off-axis coupons and the mode II in-situ sample mounting assembly.

The first position of the stub allows a tensile load to be applied along a vertical axis, fracture then occurs within the sample along the fibre direction (10° to the direction of applied load). The sample may then be rotated to the second mounting position so that the fracture surface is perpendicular to the vertical axis, thus allowing a 'normal' analysis orientation. During loading the top stub is locked in place mechanically to the top flange of the entry lock, whereas the bottom stub is locked to the linear drive by means of an extended prong on a rotating wobble stick. The fracture stage assembly is shown in schematically in Figure 8.17. Figure 8.18 shows photographs of the fracture stage assembly, both ex-situ and incorporated within the entry-lock chamber.
8.2.4. Morphology of in-situ Generated Fracture Surfaces

The in-situ generated fracture surfaces were examined using a scanning electron microscope. The aim of this investigation was to determine the material parameters associated with the fracture surfaces generated by the in-situ fracture stage. The results are documented in Section 3.6.1.

Figure 8.17. Schematic representation of the mode II in-situ fracture stage assembly.

Figure 8.18. Photographs showing the mode II in-situ fracture stage assembly.

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8.2.4. Morphology of In-situ Generated Fracture Surfaces

The in-situ generated fracture surfaces were examined using an electron microscope. The aim of this investigation was to establish whether the fracture surfaces generated by the two in-situ fracture stages differed and whether they conformed to the documented fracture surface patterns for mode I and mode II loadings, as discussed in Section 7.6.1.

Figure 8.19 shows two photomicrographs for comparison, one is typical of those recorded from the fracture surface of an HTA/F927 compact tension coupon and the other typical of those recorded from an HTA/F927 mode I in-situ fractured coupon. Both the mode I generated fracture surfaces are seen to have fibres coated with resin; matrix fracture appears to have occurred by cleavage, resulting in patterns such as river markings, chevron markings and branched crack structures. These fracture surface patterns correspond to those documented in fractography studies of mode I failed FRPs, as discussed previously Section 7.6.1. There is little difference between the fracture surface patterns of the in-situ failed sample and the mechanically tested coupon.

Figure 8.20 shows a comparison between photomicrographs typical of the fracture surfaces of both HTA/F927 10° off axis mechanical test coupons and HTA/F927 predominantly mode II in-situ test coupons. Both fracture surfaces show hackled and lacerated features of the epoxy. These features are consistent with other fractography studies, as discussed previously Section 7.6.1. There is no visual difference between the fracture surface from the in-situ failed sample and that of the ex-situ mechanical test coupon.

The contrasting in-situ sample fracture patterns are consistent with surfaces generated by different failure modes, as compared to ex-situ mechanical test coupons and as documented in [78]. The in-situ fracture stages have therefore induced failure by two different modes, a tensile mode I and a shear-dominated mode II – this is consistent with the failure of mechanical test coupons.
Chapter Eight: The Development of ToF-SIMS for the Analysis of FRP Composites

8.2.5. Spectroscopic Analysis

Initial ToF-SIMS analyses were undertaken of in-situ generated fracture surfaces in order to assess the quality of the resultant spectrum. Coupons of HTA/F922 were
fractured in-situ under different conditions using the mode I loading assembly. Coupons were fractured either in room atmosphere, facilitated by leaving the entry-lock door open, or under vacuum, at pressures of ca. $1 \times 10^{-8}$ mbar, which was achieved by opening the entry-lock to the preparation chamber and allowing the diffusion pump to evacuate the fracture stage chamber.

Positive ion spectra typical of the spectra recorded from the fracture surfaces generated under the two different atmospheric conditions (vacuum and room pressure) are shown in Figures 8.21 and 8.22. Spectra are compared only on a qualitative basis at this point; no comment is made about the specific ions present or their representation. A more detailed analysis of the ToF-SIMS spectra will be made in the following chapter (Chapter 9).

It can be seen from Figures 8.21 and 8.22 that there is little qualitative difference between the two spectra; the ion patterns are very similar. There is, however, a distinct difference in the secondary ion yield. Spectra acquired from fracture surfaces generated under vacuum, typically had far higher secondary ion yields than those obtained where the coupon was fractured under atmospheric pressure. This resulted in a higher resolution of peaks and an improved signal-to-noise ratio, making spectra easier to interpret and making very weak features analytically useful. Possible reasons suggested for the difference in quality of spectra are that fracture surfaces produced in atmospheric conditions are more susceptible to moisture and general hydrocarbon absorption. Absorbed species on the fracture surface could impede the emission of secondary ions as well as adding to the background noise associated with the spectrum.

All subsequent in-situ fracturing of coupons was conducted under vacuum pressures of $1 \times 10^{-8}$ mbar or below.
Chapter Eight: The Development of ToF-SIMS for the Analysis of FRP Composites

8.3 CONCLUDING REMARKS

Several novel methods have been developed that aid the ToF-SIMS analysis of cured FRP composite materials. The microtoming sample preparation method is particularly useful because it is a quick and simple procedure that results in high quality samples for analysis. This method has therefore been adopted in the characterization of composite materials as described in the following chapters.

Figure 8.21. A typical positive ToF-SIMS spectrum recorded from an in-situ fractured mode I coupon, fractured under vacuum.

Figure 8.22. A typical positive ToF-SIMS spectrum recorded from an in-situ fractured mode I coupon, fractured in atmospheric conditions.
8.3. CONCLUDING REMARKS

Experimental methods have been developed that aid the ToF-SIMS analysis of cured thermosetting polymeric materials. The microtoming sample preparation method is considered to be the most appropriate because it is a quick and simple procedure that minimises contamination. SIMS spectra recorded from microtomed slices of cured material are of high quality and are easily reproducible. This method has therefore been applied in the characterisation of composite matrix materials as described in the following chapter.

It is concluded that the in-situ fracture stage is capable of loading samples to failure under two different modes, as intended, i.e. a pure tensile mode I and a shear dominated mode II. The in-situ generated fracture surfaces offer advantages over externally produced fracture surfaces because they are free from external contaminants and under SIMS analysis are conducive to a high secondary ion yield, which aids characterisation. The characterisation of fracture surfaces by ToF-SIMS, as presented in the following chapter, has utilised in-situ generated fracture surfaces.
Chapter Nine

ToF-SIMS Characterisation of FRP Systems and Fracture Surfaces

9.1. INTRODUCTION

The experimental procedures developed within the previous chapter have been used to characterise composite material systems and their fracture surfaces.

The present chapter is divided into three major sections. The first two sections are concerned with aspects of the HTA/F927 and the HTA/F922 material systems, respectively. They both begin with a fingerprint analysis of the bulk epoxy matrix material before progressing on to characterise composite fracture surfaces. Modification of both material systems by either environmental ageing or variation of fibre pre-treatment has taken place in order to promote differences within the fracture surface chemistries. The final section of this chapter is a study into the degree of cure of a typical epoxy matrix material. Within this section an analytical method of processing ToF-SIMS data has been investigated.

ToF-SIMS analyses of the different materials were performed under various primary ion beam conditions. Alterations were made also to the pulse frequency and width and the magnification. These parameters all alter the area of analysis. The instrument variations were kept within a region, however, such that no spectra were recorded from analyses where the ion dose exceeded the static limit of $10^{13}$ ions/cm$^2$, (unless stated). An advantage often listed of SIMS over other surface analysis techniques, such as XPS, is its ability to detect hydrogen. However, in order to prevent the detector becoming saturated during the course of the analysis, as a matter of routine the hydrogen ions are
not collected. This is achieved by setting a veto within the software prior to analysis, the reason being that the sensitivity to heavier ions that arrive at the detector at a later time is enhanced. Therefore, although the detection of elemental hydrogen is possible with the equipment used, it is not employed in any of the spectra involved in this study.

9.2. HTA/F927 COMPOSITE SYSTEM

9.2.1. F927 Epoxy Resin

A finger print characterisation was recorded from a sample of cured F927 epoxy resin. The analysis sample was a microtomed slice of material, approximately 10 µm thick, cut from a thick (~4 mm) cured resin plaque; the procedure is documented within Section 8.1.4. Figure 9.01 shows a positive ion ToF-SIMS spectrum typical of the spectra recorded from a slice of F927 material. The spectrum shown was acquired from an area 100 µm by 100 µm.

![Positive ToF-SIMS spectrum recorded from a microtomed slice of F927 epoxy resin.](image)

**Figure 9.01.** Positive ToF-SIMS spectrum recorded from a microtomed slice of F927 epoxy resin.
The exact constituents of F927 epoxy are unknown; therefore precise identification and assignment of all the peaks within the spectrum to fragment ions is not possible. In the lower mass range (m/z < 60) the spectrum shows a similar pattern of intense peaks as observed in the epoxy DGEBA positive ion spectrum (Figure 8.07) and as was noted in the analysis of the epoxy F922, Section 9.3.1. The lower mass secondary ion peaks are believed to be characteristic of aliphatic hydrocarbon fragments ([C\(_{n}\)H\(_{2n+1}\)]\(^{+}\), [C\(_{n}\)H\(_{2n-1}\)]\(^{+}\), [C\(_{n}\)H\(_{2n-3}\)]\(^{+}\)); this observation concurs also with other ToF-SIMS studies of epoxy materials [85, 89]. At higher m/z values intense peaks are observed within the spectrum at m/z = 165, 115 and 91; these peaks are believed to be representative of the aromatic species, [C\(_{13}\)H\(_{9}\)]\(^{+}\), [C\(_{9}\)H\(_{7}\)]\(^{+}\) and [C\(_{7}\)H\(_{7}\)]\(^{+}\), respectively. These aromatic fragment ions are not unique to the F927 secondary ion mass spectrum; again a similar pattern of ion peaks was identified in the epoxy DGEBA positive ion spectrum (Figure 8.07) and during the characterisation of F922 epoxy resin, Section 9.3.1, as well as within the literature [85, 89].

Ion peaks unique to the F927 epoxy spectrum are observed at m/z values of 277, 197, 181, 152, 128 and 121. Although no fragment ion structure is proposed for these peaks, the peaks are believed to be representative of F927 and hence provide a fingerprint characterisation of the resin.

A negative ion ToF-SIMS spectrum typical of the spectra obtained from microtomed samples of F927 epoxy resin is shown in Figure 9.02.

![Figure 9.02](image-url)  
**Figure 9.02** Negative ToF-SIMS spectrum from a microtomed slice of F927 epoxy resin.
The limited amount of information contained with Figure 9.02 means that the ion peak pattern is not believed to be unique to the F927 epoxy material. Ion peaks present occur at very low masses; there is a dominant peak at \( m/z = 16 \), representative of the \([\text{O}]^-\) ion, as well as peaks representative of very low mass hydrocarbon fragments, such as \([\text{C}_2\text{H}_2]^–\), \([\text{C}_2\text{H}]^–\), and \([\text{CH}]^–\). Peaks representative of the chloride ions \( ^{35}\text{Cl}^- \) and \( ^{37}\text{Cl}^- \) are observed at \( m/z = 35 \) and 37.

9.2.2. HTA/F927 Composite Fracture Surface Analysis

9.2.2.1. Investigation into the Effects of Loading Mode

9.2.2.1.1. Sample Preparation

Unidirectional cured laminates of HTA/F927 were sectioned into in-situ test coupons and fractured within the spectrometer under either a pure tensile mode I loading (following Section 8.2.2) or shear dominated mode II loading (following Section 8.2.3). Coupons were fractured in vacuum under pressures of ca. \( 1\times10^{-8} \) mbar and presented for analysis without exposure to the atmosphere. Post ToF-SIMS analysis, coupons were removed from the spectrometer and mounted onto stubs for examination by electron microscope (SEM Hitachi S-3200N). In the following discussion the fractography data is considered before the chemical analysis of the fracture surface.

9.2.2.1.2. Fracture Surface Morphology

Electron photomicrographs representative of a mode I in-situ failed fracture surface and a shear dominated predominantly mode II failed fracture surface are shown in Figures 9.03 and 9.04, respectively. The mode I in-situ generated fracture surface is very planar in nature; failure appears to have occurred by matrix cleavage, resulting in a number of failure patterns as described in Section 7.6.1. Single fibres or fibre clusters seen protruding from the fracture surface are all coated with a layer of matrix residue, no bare or ‘clean’ fibres are observed.
Figure 9.03. Typical electron photomicrographs showing an HTA/F927 in-situ generated fracture surface from a mode I loading.

Figure 9.04. Typical electron photomicrographs showing an HTA/F927 in-situ generated fracture surface from a predominantly mode II loading.
The predominantly mode II in-situ generated fracture surface is dominated by hackles and lacerations in the bulk epoxy. These patterns are caused by in-plane shear and are consistent with previous electron fractography studies, as documented in Section 7.6.1. Fibres at the fracture surface have areas of matrix material still adhering to them, however, there are also areas along the fibre length that are very smooth in appearance and appear to be free from matrix material. This observation is also consistent with previous fractography studies, Hashemi et al [52] and Garg [78] both suggest that as the degree of mode II fracture increases there is an increasing extent of apparent interfacial failure between the matrix and fibres.

9.2.2.1.3. ToF-SIMS Analysis of the Fracture Surface

Figures 9.05 and 9.06 show positive ion ToF-SIMS spectra that are typical of the spectra recorded from mode I and predominantly mode II in-situ generated HTA/F927 fracture surfaces, respectively.

![ToF-SIMS spectrum](image)

**Figure 9.05.** Positive ToF-SIMS spectrum from an HTA/F927 coupon fracture in-situ under a mode I loading.
ToF-SIMS spectra from the HTA/F927 fracture surfaces are all very similar in appearance, regardless of the mode of fracture. No distinction could be made between the spectra even after a multitude of analyses, acquired under different experimental conditions and with different raster areas. This absence of any difference in surface chemistry between the two fracture modes is contrary to the visual appearance of the fracture surfaces. The fracture surface spectra are also extremely similar in appearance to those recorded from the bulk epoxy resin. Positive ion peaks are observed in both fracture spectra at m/z values of 181, 165, 152, 128, 121, 115 and 91, all of which correspond to peaks in the spectrum fingerprinting the matrix epoxy, Figure 9.01. The relative ratio of peaks present is also identical to that of the bulk epoxy spectrum. At low m/z values ion peaks are characteristic of aliphatic hydrocarbon fragments, $[\text{C}_n\text{H}_{2n+1}]^+$, $[\text{C}_n\text{H}_{2n-1}]^+$ and $[\text{C}_n\text{H}_{2n-3}]^+$, again corresponding to peaks as seen in the matrix material spectrum.

Further studies of the in-situ generated fracture surfaces were conducted using a state-of-the-art ToF-SIMS instrument, the Physical Electronics Trift II. This instrument is
capable of simultaneous spectra and image acquisition and so was utilised in order to verify that spectra were being acquired from areas of the fracture surface that were visually different.

Coupons were fractured in vacuum at the University of Surrey using the in-situ fracture stage; they were then removed and wrapped in aluminium foil, which has been shown to be relatively free from contamination. Samples were sent by post to the Physical Electronics laboratory in the USA, where they were analysed by Dr. A. Belu.

Figure 9.07 shows secondary ion images from mode I and predominantly mode II failed fracture surfaces. Two negative secondary ion images are shown for each loading mode: a total ion image and an [O]$^-$ ion image.

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**Figure 9.07.** Secondary ion images from mode I and predominantly mode II failed HTA/F927 fracture surfaces.
The secondary ion images shown in Figure 9.07 reflect the fracture surface morphologies as seen in the SEM analysis, confirming results. The mode I generated fracture surface appears relatively smooth and planar with no obvious distinguishing features, whereas the mode II generated fracture surface shows evidence of lacerations and shear hackles. Within the [O]− ion image, recorded from the predominantly mode II failed fracture surface, long filamentary features are visible, these features are separated by areas with transverse markings. Respectively, these characteristics are believed to represent fibres at the fracture surface and matrix shear hackles. Using simultaneous acquisition, spectra can be generated from these areas and compared. Figure 9.08 indicates the areas chosen for spectroscopic analysis.

![Area A Region on Fibre](Image)

![Area B Region on Matrix](Image)

**Figure 9.08.** Secondary [O]− ion image from a mode II generated fracture surface with areas used for spectroscopic analysis highlighted.

Figures 9.09 and 9.10 show negative ToF-SIMS spectra recorded from areas A and B, respectively, as indicated in Figure 9.08. There is little difference between the actual peaks present within the spectra shown in Figures 9.09 and 9.10. Peaks are characteristic of low mass hydrocarbon ions such as [C2H]+, [C2]−, and [CH]+, or of [O]− and [OH]+. There is also some evidence of the chloride ions 35[Cl]− and 37[Cl]− observed as peaks at m/z = 35 and 37.
The only consistent difference between spectra recorded from area A, that believed to be a fibre rich region, and spectra recorded from area B, that believed to be a matrix rich region, was the intensity of the secondary ion yield. Carbon fibres are conductive, whereas the matrix epoxy is an insulator. Spectra recorded from the fibre rich area would appear to be from a thin matrix overlayer adhering to the fibres. Secondary ion yield has been shown to greatly increase from thin layers of insulating material when placed over a conducting medium. This aspect was exploited in developing the microtoming technique as used to analyse bulk resin samples.

An example of the variation in ion-induced yield is shown in Figure 9.11, this is an ion-induced electron image from a predominantly mode II in-situ generated fracture surface. Two line scan analyses were performed across the area shown in the image. One was perpendicular to the fibre orientation and the other parallel to the fibres direction, as
indicted by the blue and red lines, respectively. The line scan analyses measured the intensity of the ion-induced electron yield from the surface. It may be seen from Figure 9.11 that the yield of ion-induced secondary electrons reflects the secondary ion yield as observed in the ToF-SIMS analysis; the intensity is far higher from any area that appears to be fibre rich.

![Image of ion-induced electron image from a shear dominated fracture surface and colour coded line scans showing the intensity of electron yield across the surface.](image)

**Figure 9.11.** An ion induced electron image from a shear dominated fracture surface and colour coded line scans showing the intensity of electron yield across the surface.

### 9.2.2.1.4. Discussion

The similarity between fracture surface spectra (Figures 9.05 and 9.06) and spectra representing the bulk epoxy matrix (Figure 9.01) indicates that for both modes of intralaminar fracture, failure is through the matrix material. For the mode I loading
situation a fracture plane through the matrix material is consistent with SEM results. All fibres observed at the fracture surface were seen to have a layer of matrix material still adhering to them. The SEM analysis of the shear dominated fracture surface, however, showed smooth areas on the fibres surface that were believed to be indicative of an interfacial failure. Preliminary ToF-SIMS results suggest that, contrary to the visual appearance, there is still an overlayer of matrix material adhering to the fibres.

The secondary ToF-SIMS investigation, conducted on a new generation instrument, enabled spectra to be recorded from chosen areas within the fracture surface. However, although spectra were obtained from areas that were visually different, the secondary ion spectra remained the same. The similarity of the ion fragmentation pattern confirms the previous result that there is no significant difference in the surface chemistry on the fracture surface generated by a shear dominated loading. Areas on fibres at the fracture surface, thought to be interfacial failure, yield the same SIMS spectra as areas thought representative of matrix shear hackles. This indicates that failure occurs within the matrix resin, but close to the fibre/matrix interface.

9.2.2.2. Fracture Surface Modification Through Environmental Degradation

9.2.2.2.1. Introduction

In an attempt to promote a change in the characteristics of the fracture surface, an environmental degradation study was conducted. Moisture absorption can cause a wide variety of mechanical and thermophysical property changes in polymeric matrix composites materials [9]. Principally, water absorption tends to promote interfacial debonding between the fibre and matrix, impairing stiffness and strength, particularly under shear and transverse loading [8]. No mechanical test data were generated from this environmental study; it has been used solely as a means to promote an alternative fracture surface for the ToF-SIMS investigation.
9.2.2.2. Sample Preparation

Pre-prepared in-situ composite coupons were placed within an airtight container and held under hot/wet conditions, 85 % relative humidity and 50 °C, for 3 months. The samples were weighed periodically to measure the uptake of moisture. Figure 9.12 shows a graph of the moisture uptake over the 3-month ageing period.

![Graph showing the moisture uptake, as weight gained, of HTA/F927 mode I in-situ composite coupons.](image)

Coupons were removed from the ageing tank and fractured within the spectrometer under either a pure tensile mode I loading (following Section 8.2.2) or shear dominated mode II loading (following Section 8.2.3). Fractures took place in vacuum under pressures of 1x10^-8 mbar; fracture surfaces were presented for analysis without exposure to the atmosphere. Post ToF-SIMS analysis, coupons were removed and mounted onto stubs for SEM analysis.

9.2.2.2.3. Fracture Surface Morphology

In order to ascertain whether the environmental ageing period had brought about different fracture morphologies a fractography study was made using electron
microscopy. Figures 9.13 and 9.14 show typical electron photomicrographs from the fracture surfaces of aged mode I and predominantly mode II composite coupons, respectively.

![Electron photomicrographs](image)

**Figure 9.13.** Typical electron photomicrographs showing the morphology of aged mode I generated HTA/F927 fracture surfaces.

SEM analyses of the aged coupons fracture surfaces shows a different surface morphology to that of the un-aged coupons (Figure 9.03), for a mode I loading. There is a significant amount of, what appears to be, fibre matrix separation at the fracture surface. The number of resin rich areas is reduced and there is a large increase in
"clean" fibres free of any matrix residue. Similar changes in intralaminar mode I failed CFRP fracture surfaces after high moisture absorption have been documented by Garg in [78].

Figure 9.14. Typical electron photomicrographs showing the fracture surface morphology from aged HTA/F927 coupons, fractured under a predominantly mode II loading.

The morphology of failure surface produced from aged coupons, fractured under a predominantly mode II loading, does not differ significantly to that of the un-aged coupons (Figure 9.04). Matrix features such as hackles and laceration are still evident.
Fibres at the fracture surface can be seen with matrix material still adhering to them, although clean fibres are also evident in places. Garg [78] reports that intralaminar mode II fracture surface morphologies were relatively unaffected after coupons had experience moderate moisture exposure. The lack of noticeable changes in fracture morphology is also reported for the interlaminar mode II situation, as analysed using wet specimens (moisture content 1.6 %, exposure 70 °C / H₂O) [78].

9.2.2.2.4. ToF-SIMS Analysis of the Fracture Surface

Figures 9.15 and 9.16 show positive ion ToF-SIMS spectra recorded from an aged coupon, fractured in-situ under a mode I loading. The spectra presented are typical of both types of characteristic spectra recorded from this fracture surface. All analyses were acquired from an area of approximately 5 µm by 5 µm.

The first spectra variant (Figure 9.15) has an intense peak at m/z = 23, corresponding to the inorganic ion [Na]⁺. The only other intense peaks within the spectrum are due to low mass organic ions such as [C]⁺, [C₂H₃]⁺ and [C₃H₃]⁺.
The second spectra variant (Figure 9.16), recorded from the same fracture surface, also has an intense peak corresponding to the inorganic ion [Na]^+, however, peaks are also present at much higher m/z values. These peaks have previously been identified as being characteristic of the matrix material F927 epoxy. Ion peaks within the spectrum that conform to those observed previously, occur at m/z = 181, 165, 152, 128, 121, 115 and 91.

![Figure 9.16. Positive ToF-SIMS spectra from an aged coupon fractured in-situ under a mode I loading.](image)

Figures 9.17 and 9.18 show positive ion ToF-SIMS spectra recorded from an aged coupon, fractured in-situ under a predominantly mode II loading. The two spectra are typical of all the spectra recorded from this fracture surface, although the example spectrum shown in Figure 9.18 was recorded with far higher frequency than that presented in Figure 9.17. Analyses were acquired from an area of approximately 5 µm by 5 µm.
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Figure 9.17. Positive ToF-SIMS spectrum from an aged coupon fractured in-situ under a mode II loading.

Figure 9.18. Positive ToF-SIMS spectra from an aged coupon fractured in-situ under a mode II loading.
The spectrum shown in Figure 9.17 is very similar in appearance to one of the types of spectra recorded from the aged mode I fracture surface, Figure 9.15. Likewise the spectrum shown in Figure 9.18 is similar to the other type of spectra recorded from the aged mode I fracture surface, Figure 9.16. The $[\text{Na}]^+$ ion peak is present in both spectra, along with peaks at low mass values, which are believed indicative of aliphatic hydrocarbon fragments ($[\text{C}_n\text{H}_{2n+1}]^+$, $[\text{C}_n\text{H}_{2n-1}]^+$, $[\text{C}_n\text{H}_{2n-3}]^+$). Figure 9.18, however, also contains intense peaks characteristic of aromatic species ($m/z = 165, 115$ and $91$, corresponding to the ions $[\text{C}_{13}\text{H}_9]^+$, $[\text{C}_9\text{H}_7]^+$ and $[\text{C}_7\text{H}_7]^+$, respectively), as well as additional unidentified peaks that correspond to the epoxy matrix fingerprint ($m/z = 181, 152, 128$ and $121$).

9.2.2.2.5. Discussion

SEM analysis of both the aged coupon fracture surfaces has revealed areas on fibres apparently free from matrix material. Areas of bare fibres were significantly more evident in the mode I generated fracture surface than in the predominantly mode II generated fracture surface.

ToF-SIMS analysis has resulted in two different types of spectra being recorded from both the fracture surfaces. The first type of spectra contained an array of intense peaks at low $m/z$ values, indicative of simple hydrocarbon ions, and little other information at higher $m/z$ values. These spectra are believed to be characteristic of interfacially failed regions on the fracture surface, and are thought to represent bare fibres. Similar spectra are presented by Vickers [68] from a ToF-SIMS analysis of tows of HTA carbon fibres. The observation of spectra containing predominantly low mass ion fragments is said to be a result of the carbon fibre's structure. In order to yield fragment ions possessing more than six carbon atoms, a large number of aromatic C-C bonds would have to be broken without causing further damage to the fragment concerned, the probability of this occurring is thought to be very low. The low ionisation efficiency of such large organic fragments is also said to compound the low probability of emission of such ions.

The second spectra type, recorded from the aged coupons, are similar in appearance to spectra characterising the bulk matrix epoxy and to spectra recorded from un-aged
coupon fracture surfaces. These spectra are thought to represent areas of failure either within the bulk matrix material or of the matrix side of interfacial failure.

9.2.2.3. Concluding Remarks

ToF-SIMS spectra recorded from HTA/F927 composite coupons, with an optimised interface, indicate that there is no difference in failure loci chemistry, regardless of the mode of fracture. Although SEM observations suggested that there were possible regions of interfacial failure within the mode II generated fracture surface, ToF-SIMS results show that fracture always occurred through the bulk matrix medium of the composite. Analysis on fibres present at the fracture surface indicated a thin overlayer coating of matrix material. For this material system (without modification) there is no evidence of any interfacial failure between the fibre and the matrix, or of any change in composition near the interface leading to a characteristic interfacial failure surface.

The environmental ageing process is believed to have weakened the fibre-to-matrix bond, leading to areas of interfacial failure on both the fracture surfaces; regardless of the loading mode. This prediction of the failure locus is confirmed by SEM observations and ToF-SIMS results.

9.3. HTA/F922 COMPOSITE SYSTEM

9.3.1. F922 Epoxy Resin

A ToF-SIMS fingerprint characterisation was recorded from a sample of cured bulk F922 epoxy resin. A thick cured resin plaque (~6 mm) was microtomed to yield 10 µm slices of material for analysis; the process is described in section 8.1.3.

Figure 9.19 shows a positive ion ToF-SIMS spectrum typical of spectra recorded from a slice of F922 material. The spectrum was acquired from an area of 100 µm by 100 µm. F922 epoxy resin is known to be a simple formulation, primarily comprising of the
TGDDM epoxy monomer. Highly characteristic ions were detected at m/z values of 218, 130, 118 and 106. The corresponding ion assignments for these m/z values are shown in Table 9.01, which are possible peak assignments of the tetrafunctional epoxy monomer, TGDDM. Additional intense peaks were observed at m/z = 165 and 91 corresponding, respectively, to the aromatic ions \([C_{13}H_9]^+\) and \([C_7H_7]^+\). Peaks representative of these aromatic species were also observed in spectra from both the DGEBA epoxy resin (Figure 8.07) and the F927 epoxy resin (Figure 9.01). There are also a number of intense peaks in the lower mass range (m/z < 60) of the spectrum that are common to the previous epoxy resin studies. These common peaks are, again, due mainly to aliphatic hydrocarbon fragment ions \([C_nH_{2n+1}]^+\), \([C_nH_{2n-1}]^+\), \([C_nH_{2n-3}]^+\).

![Figure 9.19](image-url) Positive ToF-SIMS spectrum recorded from a microtomed slice of F922 epoxy resin.

An example of negative ion ToF-SIMS spectra recorded from the F922 epoxy resin is not shown because spectra did not provide any additional information that was believed to aid the characterisation of F922 epoxy. An intense peak representative of the \([O]^-\) ion dominated all spectra recorded in the negative ion mode. Additional ion peaks
were observed at m/z values of 12, 13, 17, 24 and 25, which correspond to the ions \([\text{Cl}^-]\), \([\text{CH}]\), \([\text{OH}]^-\), \([\text{C}_2]\) and \([\text{C}_2\text{H}]^-\), respectively.

### Table 9.01. Positive ion fragments of TGDDM

<table>
<thead>
<tr>
<th>m/z</th>
<th>Molecule</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>([\text{C}_3\text{H}_3\text{O}]^+)</td>
<td>CH(=\text{C})−CH(=\text{O})H</td>
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<tr>
<td>57</td>
<td>([\text{C}_3\text{H}_5\text{O}]^+)</td>
<td>(\begin{array}{c}+\text{O}\	ext{CH}_2\text{CH}−\text{CH}_2\end{array})</td>
</tr>
<tr>
<td>91</td>
<td>([\text{C}_7\text{H}_7]^+)</td>
<td>\begin{array}{c}+\text{O}\	ext{CH}\text{CH}−\text{CH}\text{CH}−\text{CH}−\text{CH}\text{CH}_2\end{array})</td>
</tr>
<tr>
<td>105</td>
<td>([\text{C}_7\text{H}_8\text{O}]^+)</td>
<td>\begin{array}{c}+\text{O}\	ext{CH}_2\text{CH}−\text{CH}_2\text{OH}\end{array})</td>
</tr>
<tr>
<td>106</td>
<td>([\text{C}_7\text{H}_8\text{N}]^+)</td>
<td>\begin{array}{c}+\text{N}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>115</td>
<td>([\text{C}_9\text{H}_7]^+)</td>
<td>\begin{array}{c}+\text{N}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>118</td>
<td>([\text{C}_9\text{H}_8\text{N}]^+)</td>
<td>\begin{array}{c}+\text{N}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>130</td>
<td>([\text{C}_9\text{H}_8\text{N}]^+)</td>
<td>\begin{array}{c}+\text{N}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>165</td>
<td>([\text{C}_{13}\text{H}_9]^+)</td>
<td>\begin{array}{c}+\text{N}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>218</td>
<td>([\text{C}<em>{13}\text{H}</em>{16}\text{O}_2\text{N}]^+)</td>
<td>\begin{array}{c}+\text{O}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>379</td>
<td>([\text{C}<em>{23}\text{H}</em>{27}\text{O}_2\text{N}_2]^+)</td>
<td>\begin{array}{c}+\text{O}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
<tr>
<td>422</td>
<td>([\text{C}<em>{23}\text{H}</em>{30}\text{O}_4\text{N}_2]^+)</td>
<td>\begin{array}{c}+\text{O}\text{H}_2\text{CH}_2\text{CD}_2\end{array})</td>
</tr>
</tbody>
</table>
9.3.2. HTA/F922 Composite Fracture Surface Analysis

9.3.2.1. Introduction

HTA/F922 cured laminates were utilised from a previous study. Unidirectional panels had been produced using epoxy sized HTA fibres that had undergone differing levels of electrochemical oxidative surface treatment, 0 %, 100 % and 200 %. A treatment level of 100 % is the industrial standard level. In a mechanical properties study, Rezaifard et al [16] have shown that the level of fibre electrochemical oxidative treatment has a marked effect on the intralaminar fracture toughness, transverse tensile strength and transverse flexure strength (TFS) of unidirectional HTA/F922 laminates. The change in transverse flexure strength as a function of the fibre surface treatment level is shown in Figure 9.04. A reduction in the surface oxidative treatment level of carbon fibres is thought to reduce the fibre to matrix bond strength and hence has a detrimental effect upon the mechanical performance of the composite.

Figure 9.20. Transverse flexure strength of HTA/F922 as a function of the surface treatment level, after [16].
Fracture surface analyses have been undertaken using the different composite variants. Coupons produced with 100 % sized fibres, the commercially available standard, have been fractured in-situ in a support investigation into the effects of loading mode on the fracture surface chemistry. Coupons produced with 0 % sized fibres and 200 % sized fibres have been utilised in an attempt to characterise the fibre to matrix interface for this material system. ToF-SIMS investigations on these two composite variants (with 0 % and 200 % sized fibres) have been conducted on fracture surfaces produced ex-situ from conventional mode I compact tension mechanical test coupons.

9.3.2.2. In-situ Fractured 100% HTA/F922

9.3.2.2.1. Sample Preparation

Coupons of HTA/F922 composite (manufactured with 100 % electrochemically surface treated fibres) were fractured in-situ under either a controlled mode I loading regime or a shear dominated predominantly mode II loading regime, using the procedure as documented in Section 8.2.2. Failure took place in vacuum under pressures of 1x10⁻⁸ mbar. Fracture surfaces were presented for analysis without exposure to the atmosphere.

9.3.2.2. ToF-SIMS Results

Figures 9.21 and 9.22 show positive ion ToF-SIMS spectra typical of the spectra obtained from the mode I generated fracture surface and the predominantly mode II, shear dominated, fracture surface, respectively. The spectra were acquired from areas approximately 10 µm by 10 µm.

All recorded spectra were qualitatively similar in appearance regardless of the primary ion beam conditions and other experimental variables such as raster area. The fracture surface generated under a pure mode I loading has the same spectroscopic characteristics as that generated from a predominantly mode II loading. No intense ion peaks are evident that allow a difference to be distinguished.
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Figure 9.21. **Positive ToF-SIMS spectrum from the fracture surface of an in-situ mode I failed HTA/F922 composite coupon.**

Figure 9.22. **Positive ToF-SIMS spectrum from the fracture surface of an in-situ mode II failed HTA/F922 composite coupon.**
Considering the higher mass range, intense peaks that are common to both spectra occur at m/z values of 218, 165, 130 and 118; these peaks have previously been identified as being characteristic of the matrix epoxy, Table 9.01. The additional peaks observed at m/z = 106, 105, 91, 57 and 55 are also thought to be representative of the epoxy, these peaks correspond to the fragment ions, \([\text{C}_7\text{H}_8\text{N}]^+\), \([\text{C}_7\text{H}_5\text{O}]^+\), \([\text{C}_7\text{H}_7]^+\), \([\text{C}_3\text{H}_5\text{O}]^+\) and \([\text{C}_3\text{H}_3\text{O}]^+\), respectively. There are, in fact, little differences in the fracture surface spectra to that of the bulk matrix material.

In the lower m/z range the spectra from both fracture surfaces are dominated by a peak at m/z = 23 indicating the presence of the sodium ion \([\text{Na}]^+\). This ion is not believed to be present as contaminant as there is no evidence of other contaminant species, such as release agents. Sodium is thought to be present on the surface of the carbon fibres. \([\text{Na}]^+\) was only detected in analyses of the composite fracture surface. Vickers \cite{68}, using ToF-SIMS, documents an increase in the presence of \([\text{Na}]^+\) with % of oxidative treatment of HTA carbon fibres, stating that the ion is believed to be adsorbed onto the fibres during the oxidative procedure, which occurs in an aqueous electrolyte.

### 9.3.2.2.3. Discussion

ToF-SIMS spectra from both the fracture surfaces reveals ions characteristic of the epoxy matrix F922, regardless of the loading mode of fracture. Although the sodium ion, \([\text{Na}]^+\), is detected, which is believed to originate from the fibres within the composite, it is not thought to indicate the presence of bare fibres at the fracture surfaces. Failure is not thought to have occurred interfacially between the fibres and the matrix. The relative sensitivity of ToF-SIMS to ions of varying ionisation potential has been shown by Vickers \cite{68}. In this study an example is given where the sodium ion \([\text{Na}]^+\) dominates a ToF-SIMS spectrum, however an XPS analysis of the same sample indicated that there was less than 1.5 % Na present on the samples surface. ToF-SIMS is highly sensitive, because of low detection limits, to mobile ions of low ionisation potential, such as \([\text{Na}]^+\). Therefore, as with the HTA/F927 composite system, failure is believed to have occurred cohesively through the matrix material of the composite irrespective of the loading mode of fracture.
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9.3.2.3. HTA/F922 Produced With 200 % Treated Carbon Fibre

9.3.2.3.1. Sample Preparation

Compact tension test coupons were produced from a laminate of HTA/F922, which had been fabricated with 200 % surface treated fibres. Samples were fractured under a pure mode I tensile loading using conventional tensile test procedures as described in Section 5.2.1. Mechanical test data were not generated for the samples, the purpose of their failure was to produce fracture surfaces for ToF-SIMS analysis. This composite variant was studied before the development of the in-situ test facility. Fractured coupons were sectioned into 1 cm long samples, in order to allow entry into the spectrometer. The sectioned coupons were fixed into modified ESCALAB MK II-type stubs and locked in place with a grub screw.

9.3.2.3.2. ToF-SIMS Results

Figure 9.23 shows a selected region from a ToF-SIMS spectrum that is typical of the spectra obtained from the 200% HTA/F922 composite fracture surface. The area of analysis was approximately 5 µm by 5µm. The spectrum shows ion peaks representative of the TGDDM matrix at m/z values of 165 and 118. Present also is a peak characteristic of the release agent contaminant PDMS, this occurs at an m/z value of 147 and corresponds to the fragment ion [Si₂O(CH₃)₃]⁺.
Figure 9.23. **Positive ToF-SIMS spectrum from a 200 % fibre treated HTA/F922 composite fracture surface.**

From the same fracture surface a single spectrum was obtained that showed distinctly different characteristics, Figure 9.24. This spectrum was obtained under the same primary beam and experimental conditions as that shown in Figure 9.23 and for the same field of view.

The peaks representative of TGDDM ion fragments (m/z = 165 and 118) are absent, however the intense peak at m/z = 147 is still present and there is an additional peak at m/z = 135. A peak at m/z = 135 could be assigned to a multitude of organic ions, however, within this project it has been observed to correspond to the fragment ion [C₉H₁₁O]⁺ representative of the epoxy DGEBA, Section 8.1.3.
9.3.2.3.2. Discussion

Prior to incorporation into the matrix, carbon fibres are sized with an epoxy so as to improve the interfacial bond; the most commonly used industrial epoxy size is DGEBA. Because the fibres in this composite system were given a 200% electrochemical surface treatment prior to being sized it is possible there existed a weak inter-phase region between the fibre-size and the matrix epoxy. A weak interfacial bond would limit the transfer of load from the matrix to the fibres and so reduce the mechanical performance of the composite, this corresponds to the drop in mechanical properties as reported in [16], shown in Figure 9.20. It is possible that the spectrum shown in Figure 9.24 has been recorded from a region of failure within the interphase between the fibre-size and matrix and hence is representative of the fibre size material, DGEBA. Spectra were, however, obtained from mechanical test coupons, because these coupons required sectioning to allow entry into the spectrometer there is some contamination associated with the fracture surface. Contamination appears to be in the form of the release agent PDMS, hence an intense peak is observed within the selected region at m/z = 147. Because known contaminants are present there is a possibility that the variations in spectra are due to other unspecified contaminants and not variations within the locus of failure of the composite. The reduction of contaminant species so as to improve the clarity of spectra from the fracture surfaces was the main driving force for the production of the in-situ fracture stage, documented earlier.

9.3.2.4. HTA/F922 Produced With 0 % Treated Carbon Fibre

9.3.2.4.1. Sample Preparation

Compact tension test coupons were produced from a laminate of HTA/F922, which had been fabricated with 0% surface treated fibres. Samples were fractured under a pure mode I tensile loading using conventional tensile test procedures as described in Section 5.2.1. Mechanical test data were not generated for the samples, the purpose of their failure was to produce fracture surfaces for ToF-SIMS analysis. This composite variant was studied before the development of the in-situ test facility. Compact tension
mechanical test coupons were sectioned, post-fracture, into 1 cm long samples so as to allow entry into the spectrometer. A lack of fibre to matrix adhesion meant that there was a significant amount of loosely bound fibres at the fracture surface. Because of the loose nature of the fracture surface, sectioned coupons were mounted in spring-loaded stubs beneath cover plates. Initial samples, loaded into the spectrometer in stubs without a cover plate, could not be analysed, because once a potential was applied to the stub, loose fibres and debris within the fracture surface caused arcing between the stub and the high voltage extraction optics.

9.3.2.4.2. ToF-SIMS Results

Two different variants of positive spectra were recorded from the compact tension coupon's fracture surface. Typical examples of both these spectra are shown in Figures 9.25 and 9.26. Each spectrum was acquired from an area approximately 5 µm by 5 µm.

![Figure 9.25. Positive ToF-SIMS spectrum from a 0% fibre treated HTA/F922 composite fracture surface.](image)
Intense peaks at low m/z values dominate the spectrum shown in Figure 9.25, there is little high mass information. Of the low m/z value peaks the most dominant occurs at m/z = 23, which is assigned to the [Na]$^+$ ion. Other inorganic ions present in the spectrum include [K]$^+$ at m/z = 39, although there is a large possibility that this peak has a contribution from the [C$_3$H$_3$]$^+$ organic ion. The remainder of the most intense peaks are seen at m/z values of 51, 29 and 27, corresponding to the ions [C$_4$H$_3$]$^+$, [CHO]$^+$ or [C$_2$H$_3$]$^+$ and [C$_2$H$_3$]$^+$, respectively.

The spectrum shown in Figure 9.26 is another example of positive spectra recorded from the fracture surface. Spectra of both types were recorded in equal abundance. That shown in Figure 9.26 is similar to that shown in Figure 9.25, however, it contains additional peaks at higher m/z values. These additional peaks are present at m/z values of 165, 130, 118, 91, 77 and 57, which correspond to the fragment ions [C$_{13}$H$_9$]$^+$, [C$_9$H$_8$N]$^+$, [C$_8$H$_8$N]$^+$, [C$_7$H$_7$]$^+$ and [C$_3$H$_5$O]$^+$, respectively. The higher mass ions are all
documented in Table 9.01, as possible ion fragments originating from this composite's matrix material, TGDDM.

In the negative ion mode, again, two different variations in spectra were recorded from the compact tension coupon's fracture surface. Typical examples of both these spectra are shown in Figures 9.27 and 9.28. Each spectrum was acquired from an area approximately 5 µm by 5 µm.

![Figure 9.27](image1.png)

**Figure 9.27.** Negative ToF-SIMS spectrum from a 0% HTA/F922 composite fracture surface.

![Figure 9.28](image2.png)

**Figure 9.28.** Negative ToF-SIMS spectrum from a 0% HTA/F922 composite fracture surface.

The spectrum in Figure 9.27 is dominated by an intense peak at m/z = 26. The peak at m/z = 26 is thought to be due to the ion [CN], there may be a contribution from [C₂H₂] although it is probably minimal due to its low stability.
The spectrum in Figure 9.28 shows a number of intense peaks. These peaks are representative of simple low mass fragment ions such as [C']', [CH]', [O]' and [C2H]'. Peaks are also seen at m/z = 48 and 49 which may correspond to the ions [C4]' and [C4H]'. respectively, although there is probably a contribution from sulphur containing ions. An intense peak at the high m/z value of 93 is observed. Negative ToF-SIMS spectra very similar to that shown in Figure 9.28, which include a peak at m/z = 93 are presented by Vickers [68]. These spectra were recorded from tows of 0% oxidised HTA carbon fibres. Vickers [68] suggests the ion [C6H5O]'' is most likely to be responsibily for the peak at m/z = 93 and that it implies that there is a possibility of phenol functional groups existing on the carbon fibre's surface.

9.3.2.4.3. Discussion

Considering the positive ion ToF-SIMS spectra, one spectrum shows only low mass data whereas the other contains additional peaks at relatively higher mass values. Spectra similar to these two variations were recorded from the aged HTA/F927 composite coupons. Section 9.4.2.2.4, and were thought to be indicative of regions of interfacial failure within the fracture surface. It is thought that Figure 9.25 shows a spectrum recorded from an interfacially failed fibrous region within the fracture surface and conversely Figure 9.26 shows a spectrum from a matrix rich region within the fracture surface (interfacial or matrix-cleavage). Vickers [68] presents a ToF-SIMS spectrum recorded from a tow of 0% electrochemically treated HTA carbon fibres, which is very similar to the spectrum shown in Figure 9.25. It is stated in [68] that relatively little high mass information can be gained from the ToF-SIMS analysis of 0% electrochemically treated carbon fibres because of their highly graphitic structure. It is thought that there is a low probability that large fragment ions, that would characterise the surface with relative ease, will be emitted from this material under SIMS analysis.

The second variation of spectra (Figure 9.26) was very similar to those solely characteristic of the matrix material, and so is thought to represent matrix-rich areas within the fracture surface.
In the negative ion mode, again two different types of spectra were recorded. That shown in Figure 9.28 is similar to spectra presented by Vickers [68] on the analysis of 0 % electrochemically treated HTA carbon fibres. The other variant, Figure 9.27, shows the presence of the \([\text{CN}]^-\) ion, this particular ion has been used in a previous SIMS study of carbon fibre composite fracture surfaces by Denison et al [84] as a representative of the carbon fibres. In [84] this ion is chosen as a fibre marker as it was thought to arise from the incomplete pyrolysis of the polyacrylonitrile used in the fibre manufacturing process. The carbon fibres were from a different manufacture than the fibres used in this study. The presence of the \([\text{CN}]^-\) ion is not documented by Vickers [68], in this study it is stated that there was not a significant proportion of nitrogen containing species present on the carbon fibre surfaces. It is, however, pointed out that the low ionisation potential of the \([\text{CN}]^-\) species must be considered. It is possible that the detection, or not, of the \([\text{CN}]^-\) ion is a function of the ToF-SIMS analyses, an instrumental effect of varying beam conditions. Although both the negative ion spectra are thought to represent interfacially failed fibrous regions within the fracture surface, contributions to ion peak pattern from fragment ions representative of the matrix material can not be ruled out because of the incomplete analysis in the negative ion mode of the bulk matrix material. The matrix material is, however, a relatively simple formulation and is not believed to contribute to the \([\text{CN}]^-\) ion peak.

Because of the 0 % electrochemical fibre surface treatment, it is believed that there was significant interfacial failure of the composite laminate; this explains the poor mechanical performance [16] and the amount of loose fibres present at the fracture surface. The different ToF-SIMS spectra recorded from the fracture surface are thought to be representative of the different constituents of the composite, one showing characteristics of the carbon fibres the other characteristics of the matrix material.

\section*{9.3.2.5. Concluding Remarks}

Regardless of loading mode, failure of this commercially available carbon fibre composite system (produced with 100 % electrochemically treated fibres) is by matrix cleavage. The ToF-SIMS results indicate no evidence of any interfacial failure between
the fibre and the matrix, or of any change in composition near the interface leading to a characteristic interfacial failure surface.

Failure of the composite variant produced with 200% electrochemically treated fibres is believed to have occurred within the inter-phase region between fibre and matrix. Spectra may show peaks representative of the size material used to improve the interfacial bond, although there is possibility that these peaks are representative of post fracture contamination.

A significant amount of interfacial failure is believed to have occurred within the composite coupon produced with 0% electrochemically treated carbon fibres. Positive ToF-SIMS spectra are thought to represent fibrous areas and matrix rich areas within the fracture surface. Two different types of negative spectra have been identified, both of which show characteristics that have been documented within the literature as being representative of fibre-rich regions.

On the whole, spectra are not thought to be characteristic solely of the individual components of the composite; moreover they contain a mixture of varying proportions of fragment ions originating from the fibre and matrix material. This is because the area of analysis, approximately 5 µm by 5 µm, is only just smaller than the diameter of the carbon fibres, approximately 8 µm. The possibility that spectra were recorded from an analysis encompassing only fibre or only matrix is small.

Thus far, ToF-SIMS analyses of composite fracture surfaces have concentrated on the detection and distinction of species representative of either fibre or matrix material. Characterisation of epoxy matrix materials has occurred by identification of ions that correspond to a fragment of the un-cured epoxy parent monomer. The un-cured epoxy monomer may not truly represent the cured cross-linked matrix material. In order to aid ToF-SIMS characterisation of FRP materials a secondary investigation was undertaken by ToF-SIMS into the cross-link density of an epoxy. It was hoped that such an investigation might highlight very subtle difference between SIMS spectra as associated with the degree of cure of an epoxy matrix and that these difference could be correlated to fracture surface spectra indicative of the fibre-matrix bond.
9.4. CROSS-LINK DENSITY INVESTIGATION

9.4.1. Introduction

A more detailed investigation was conducted into one epoxy material system in order to ascertain whether subtle differences in the cross-link density could be detected by ToF-SIMS. The end goal of this study was to provide a tool with which to investigate further any differences between the ToF-SIMS spectra of the composite fracture surface. Although spectra from the composite coupons were visually very similar, regardless of failure loading mode, it was thought possible that slight differences in the secondary ion pattern and/or yield could reveal variations in the interfacial chemistry and thus characteristics of the composite failure loci.

The epoxy resin system DGEBA, as used in the manufacture of the glass fibre composite, was investigated. This resin system was chosen because it had a relatively simple formulation and all of the constituents were available in the ‘raw’ uncured form. Initial studies were made of the individual uncured components. The resin system was then mixed and degassed in the same manner as for composite production; samples were place in a fan-assisted oven at the cure temperature. Viscosity measurements were taken as the system cured in order to establish the gel formation time. Samples were removed at different time intervals during the curing process and analysed using ToF-SIMS. The gel formation time was used as a guide to indicate whether samples would be liquid, semi-solid or solid.

9.4.2. Characterisation of the Uncured Components

Constituents of the resin system are given in chapter three, but are repeated here for convenience. The bulk epoxy resin of the system was Astor-Stag Epoxide Resin 300; this is a DGEBA epoxy. An acid anhydride curing agent, NMA was used in conjunction with a tertiary amine cure accelerator, K61B. The chemical structures of each of the resin components are given in Figure 9.29.
The exact chemistry of the curing procedure is complex and will not be discussed in detail. In general, the cure of an epoxy by an acid anhydride occurs by the opening of the anhydride ring with the formation of carboxy groups, these groups then go on to open the epoxide ring. The reaction between an epoxy and an anhydride is rather sluggish therefore it is common practise to increase the rate by the addition of a catalyst, usually a tertiary amine. For this case the tertiary amine appears to react preferentially with the anhydride to generate a carboxy anion. This anion opens the epoxide ring by nucleophilic attack leaving an alkoxide ion, which then forms another carboxy anion from a second anhydride molecule and so on [90]. Figure 9.30 shows the reaction of the anhydride with the tertiary amine and the subsequent attack of the epoxide group.
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Figure 9.30. Reaction of an anhydride with an epoxy functional group via a tertiary amine cure accelerator, after [90].

It was thought that ToF-SIMS analyses of the uncured resin components would reveal characteristic signature spectra. The spectra could then be compared to that of the resin formulation at different cure intervals and the disappearance of signature ions be plotted, along with the formation of ions representative of the cured material.

Sample preparation involved wiping a clean aluminium stub across a droplet of the uncured component. Using this method a very thin layer of polymer was deposited onto the analysis stub, the thin layer meant that specimens did not accumulate charge during analysis. Positive and negative ToF-SIMS spectra typical of all the analyses recorded from the un-cured epoxy are shown in Figures 9.31 and 9.32, respectively.
The positive ion spectrum of the un-cured DGEBA resin, contains peaks at m/z = 340 and 341 corresponding to the molecular and protonated molecular ions of DGEBA, respectively. No peaks of significant intensity occur above mass 341. There is a very intense peak at m/z = 325, which corresponds to the DGEBA parent ion less one of the methyl groups. Other intense peaks that correspond to fragment ions highly characteristic of the DGEBA monomer are observed at m/z values of 269, 191, 135, 91, 77, 57 and 31. Structures for these characteristic fragment ions are given in Table 8.04. Additional peaks of high intensity occur within the positive ion spectrum at m/z values of 115, 107, 59 and 41. Treverton et al [88] also document the occurrence of these
additional secondary ions within a spectrum recorded from an un-cured DGEBA epoxy resin sample. In this study [88] the peak at m/z = 115 is assigned to the fragment ion:

![Fragment ion at m/z = 115](image.png)

The fragment ion most likely to account for the m/z = 107 peak is:

![Fragment ion at m/z = 107](image.png)

The intense peak at m/z = 59, is thought to occur because of hydrogen addition to the epoxide group and is believed to correspond to:

![Fragment ion at m/z = 59](image.png)

The remaining peaks within the spectrum occur at low m/z values and are representative of aliphatic hydrocarbon fragment ions of the type: \([\text{C}_n\text{H}_{2n+1}]^+, [\text{C}_n\text{H}_{2n-1}]^+\) and \([\text{C}_n\text{H}_{2n-3}]^+\). Simple hydrocarbon fragment ions of this type have been observed in all the SIMS analyses of epoxy materials.
The negative ion spectrum, recorded from the uncured DGEBA epoxy resin sample, has high mass peaks of significant intensity at m/z values of 283, 211, 133, 117, 93, 73 and 57. These peaks correspond to the fragment ions, \([C_{18}H_{19}O_3]^-\), \([C_{14}H_{11}O_2]^-\), \([C_9H_6O]^-\), \([C_8H_5O]^-\), \([C_6H_5O]^-\), \([C_5H_5O_2]^-\) and \([C_3H_5O]^-\), respectively. These fragment ions have been derived from the DGEBA epoxy monomer, their structures are given in Table 8.05. The lower mass range of the spectrum is dominated by the \([O]^-\) and \([OH]^-\) ions at m/z = 16 and 17, respectively. Significant contribution is also made from other simple organic ions such as \([C_2H]^-\), \([C_2]^-, [CH]^-\) and \([C]^-,\) corresponding to the peaks at m/z = 25, 24, 13 and 12, respectively.
The spectra obtained, in both positive and negative modes, conform extremely well to those presented by Treverton et al [88], from an analysis by FAB-SIMS on the same uncured epoxy resin DGEBA system, albeit from a different manufacturer.

Positive and negative ToF-SIMS spectra, typical of the analyses recorded from both the curing agent and the cure accelerator, are shown in Figures 9.33 to 9.36. The most intense peaks within each spectrum are assigned to a possible fragmentation ion. There are several peaks for which no ion fragment could be deduced, these peaks could be attributed to additions within the constituents or external contaminants. In the positive mode, intense peaks are observed that are common to both the curing agent spectra and the cure accelerator spectra. It is possible that because both analyses were undertaken on the same day that there are some memory effects associated with the analyses. Differences are noted, however, between the spectra obtained from the bulk uncured epoxy and those of the curing constituents.

**Figure 9.33.** Positive ToF-SIMS spectrum from the un-reacted curing agent NMA.
Figure 9.34. Negative ToF-SIMS spectrum from the un-reacted curing agent NMA.

Figure 9.35. Positive ToF-SIMS spectrum from the un-reacted cure accelerator K61B.
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9.4.3. Characterisation of the Curing Process

9.4.3.1. Sample Preparation

To analyse whether subtle changes in the cross-link density could be detected using ToF-SIMS, samples were required at different levels of cure. The components, resin, curing agent and cure accelerator, were measured out and mixed in the ratio 100:60:4 parts by weight, respectively. Following mixing the formulation was degassed in a vacuum oven at 40 °C. The resin mixing and degassing procedure was kept identical to that as used in the manufacture of composite coupons, Section 3.3. After degassing the resin was transferred to a fan-assisted oven, which had been pre-heated to 180 °C. Samples were taken for analysis immediately after mixing and then every 10 minutes into the curing schedule, which was 3 hours at 180 °C.

Up until the gel time, specimens were prepared in the same manner as the uncured resin components; the mixture was wiped over a clean aluminium analysis stub. Samples that
would be taken after the gel time were prepared by pouring the degassed resin mixture into conical moulds. The moulds were removed from the cure oven at particular intervals (post-gel) and dropped into a bath of liquid nitrogen. It was hoped that the rapid quench procedure would “freeze” the resin in its particular cure position. Once the resin emitted no more heat it was removed from the liquid nitrogen bath and sectioned using a microtome. Microtomed sections were taken from the very tip of the conical resin solid in order to obtain a sample that had undergone the highest cooling rate. Microtomed samples were mounted in spring-loaded stubs, sandwiched between niobium backing and cover plates.

9.4.3.2. ToF-SIMS Results

Figures 9.38 and 9.39 show positive ion spectra recorded from the epoxy resin mixture at various cure stages. Negative ion spectra are shown in Figure 9.40. Spectra are presented in the form of normalised count rate in order that direct comparison may be made. Each individual spectrum is normalised to its total secondary ion intensity. Peaks within the spectra are not marked with fragment ions, as is the convention, but by the component they are thought to originate from i.e. DGEBA, NMA or K61B. Only peaks within the first spectrum are marked for ease of comparison.

In both the positive and negative spectra, the normalised intensity of all the high mass peaks, thought to correspond to the un-cured epoxy resin and the curing components, decrease as the curing procedure advances. This is thought to relate to the consumption of the components to the cross-linking cure reaction. Some lower mass ion fragments corresponding to un-reacted components are also noted to decrease in normalised intensity, particularly the very intense peak thought to correspond to the opened epoxide ring at m/z = 59 in the positive spectrum. Other fragment ions, however, such as the positive aromatic ion [C₇H₇]+ observed at m/z = 91 increases in intensity as the cure procedure advances. A very intense peak at m/z = 143 in the negative spectrum is seen to occur after 10 minutes into the curing procedure. The intensity of this peak then drops away as the cure reaction proceeds further. It is thought this peak may be representative of the catalysed acid anhydride, the first step of the cure reaction.
Figure 9.38. Positive ToF-SIMS spectra showing the change in composition of a curing epoxy resin system, over the m/z range 0 - 150.
Figure 9.39. Positive ToF-SIMS spectra showing the change in composition of a curing epoxy resin system, over the m/z range 150 - 350.
Figure 9.40. Negative ToF-SIMS spectra showing the change in composition of a curing epoxy resin system.
Figures 9.41 and 9.42 show graphically the change in normalised intensity of selected peaks in both the positive and negative ion spectra, respectively, as a function of the cure time. The normalised peak area intensity is plotted against cure time. Fragment ion structures are given with each plot, the ions are thought representative of each peak, respectively, larger illustrations of these structures are given in Tables 8.04 and 8.05 and in Section 9.4.2.

Figure 9.41. Plots showing the change in normalised intensity of selected positive ion peaks during the cure reaction of the DGEBA / NMA / K61B epoxy resin system.
Figure 9.42. Plots showing the change in normalised intensity of selected negative ion peaks during the cure reaction of the DGEBA / NMA / K61B epoxy resin system.

9.4.3.3. Discussion

The cross-link density of the epoxy system can be monitored up to a cure time of approximately 1 hour by following the intensities of selected fragment ions characteristic of the un-reacted components. After a cure time of approximately 1 hour the ToF-SIMS spectra in both the positive and negative modes were not observed to change. In order to investigate further the possibility that any subtle changes in composite fracture surface chemistry relate to failure loci, simple visual observation of the ToF-SIMS spectra is not deemed sufficient. Commercially available composite systems undergo a lengthy cure operation, which is normally followed by an additional post-cure procedure. It was thought that because no visual difference could be noted from this simple epoxy system after a cure time of 1 hour, a third of the normal cure
time, change in the complicated composite fracture surface spectra from a coupon that had undergone a 3 hour curing procedure as well as a post-cure operation would be impossible to observe.

Simple observations of the ToF-SIMS spectra are thus insufficient to detect very subtle differences in the cross-link density of a partially cured epoxy resin. A technique is required to process the spectra in order to highlight the characteristics of the sample. Gilmore and Seah [91] have recently developed such a technique from a study of the effects of different primary ion energy densities at a surface. Application of this procedure to SIMS spectra from thermoplastic resins is thought to lead to characterisation of the components of the original molecules, before fragmentation. A preliminary investigation has been made of this technique.


9.4.4.1. Introduction

Gilmore and Seah [91] have recently developed gentle – SIMS (G-SIMS) from a study of the effects of different positive ion beam species, and their energies, on the fragmentation behaviour of secondary ions generated in static SIMS. Application of the technique involves the acquisition of two static SIMS spectra. The two spectra are generated either using different primary ion beam energies or by using two different primary ion species. Gilmore and Seah [91] found that the effects of beam energy were weak over an entire mass spectrum; however, large differences were observed in restricted mass ranges amongst fragmentation groups. The G-SIMS method unifies all of the fragmentation behaviour and then extrapolates the data back to a spectrum, which would be emitted from a surface plasma of very low temperature and thus has very little post-emission rearrangement or fragmentation. The peaks in the G-SIMS spectrum are believed to be directly characteristic of the material without rearrangement and are thought to provide direct interpretation and identification.
The method has been shown to be very successful in the interpretation of static SIMS spectra recorded from some thermoplastic materials – polycarbonate and polystyrene [91]. Intense peaks corresponding to aliphatic and aromatic hydrocarbon ions dominated original SIMS spectra recorded from polycarbonate and polystyrene samples. Many of the peaks were common to both spectra and were not thought directly related to either materials structure. In contrast, after application of the G-SIMS procedure, the majority of hydrocarbon peaks within both spectra had been significantly reduced in intensity. In addition secondary ion peaks, which were thought solely characteristic of each materials structure were greatly enhanced in intensity. The new G-SIMS spectrum is thought to be easier to interpret, with simpler identification of characteristic molecular groups than in a traditional SIMS spectrum.

The application of the G-SIMS procedure to spectra recorded from simple thermoplastic materials results in easier quantification of the original material [91]. A study has been applying the G-SIMS procedure to spectra recorded from a more complex polymeric material: a thermosetting epoxy resin. It is hoped that if a methodology can be established whereby complex SIMS spectra can be simplified for visual interpretation of the original material, new insights may be obtained from spectra recorded from composite fracture surfaces.

9.4.4.2. Sample Preparation and Data Acquisition

Samples of bulk epoxy resin were produced from the DGEBA / NMA / K61B system, following the procedure given in Section 9.4.3.1. Resin coupons were fully cured (3 hours at 180 °C). The cured blocks of epoxy were microtomed into 10 µm slices, following Section 8.1.4. The slices of material were then wrapped in clean aluminium foil and sent to TASCON (ToF Analytical Services and Consulting), Munster, Germany for analysis using an ION-TOF ToF-SIMS IV instrument. This state-of-the-art instrument was used for analysis because it is equipped with multiple primary ion sources. ToF-SIMS spectra were recorded using, [Ga]+, [Cs]+ and [SF5]+ primary ion beams at a range of beam energies, shown in Table 9.02. For each analysis the primary ion beam was rastered over an area of 100 µm by 100 µm.
Table 9.02. Primary ion beam species and analysis energies.

<table>
<thead>
<tr>
<th>Primary Ion Beam</th>
<th>Beam Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga⁺</td>
<td>25 keV</td>
</tr>
<tr>
<td>Ga⁺</td>
<td>15 keV</td>
</tr>
<tr>
<td>SF₅⁺</td>
<td>9 keV</td>
</tr>
<tr>
<td>SF₅⁺</td>
<td>5 keV</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>9 keV</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>5 keV</td>
</tr>
</tbody>
</table>

9.4.4.3. Data Analysis

The manipulation of spectroscopic data and the subsequent application of the G-SIMS process was conducted following the methodology set out by Gilmore and Seah [91]. The study of the material by three different primary ion sources each at two different energy levels generated an enormous volume of data. Spectra were reduced in size by identification of the most intense peaks, 118 for each spectrum, following [91]. The results then formed a matrix of intensities, \( I_{x,y} \), with \( x_o \) mass peaks at \( y_o \) beam energies at mass \( M_x \) for each source ion. For fragmentation analysis, spectra were normalised to yield intensities \( J_{x,y} \), by dividing by the geometric average intensity of the \( x_o \) mass peaks, Equation (9.01).

$$J_{x,y} = \frac{I_{x,y}}{\left( \prod_{x=1}^{x_o} I_{x,y} \right)^{1/x_o}} \quad (9.01)$$

An average spectrum for all of the ion beam energies, \( A_x \), was then formed from this normalised set using:

$$A_x = \frac{1}{Y_0} \sum_{y=1}^{y_0} J_{x,y} \quad (9.02)$$
A new matrix of relative intensities, $F^*_{x,y}$, was produced by dividing each normalised spectrum by $A_x$.

The $F^*_{x,y}$ values have been plotted between $m/z = 20$ and 110 for each primary ion beam source at both of the utilised energy levels, only the fragment ions identified as either $[\text{C}_x\text{H}_y]^+$ or $[\text{C}_x\text{H}_y\text{O}_z]^+$ are shown, Figures 9.43, 9.44 and 9.45.

The general trend within the fragmentation plots is one of a series of parallel groups of points. The largest fragment in each group is preceded by ions with the subsequent loss of one hydrogen atom. The G-SIMS process considers that the largest fragment of each group is closely related to the polymer backbone whilst those with hydrogen loss are indicative of damaged fragments and are thought to contribute little extra information in the original spectrum. This cascade pattern corresponds to results obtained by Gilmore and Seah [91] on work with thermoplastic materials.

![Figure 9.43](image)

*Figure 9.43. Fragmentation plots, recorded with a [Ga]$^+$ primary ion source.*
**Figure 9.44.** Fragmentation plots, recorded with a \([\text{Cs}]^+\) primary ion source.

**Figure 9.45.** Fragmentation plots, recorded with an \([\text{SF}_3]^+\) primary ion source.
9.4.4.4. The G-SIMS Procedure and Results

The first step of the G-SIMS procedure is to ratio the normalised spectra recorded using a low energy primary ion species to the spectra obtained using a high energy primary ion species. This ratio gives a factor $F_x$. $F_x$ to the power of $a$ ($a$ is a constant that is not critical, but a magnitude of 13 is stated by Gilmore and Seah as being the most useful), multiplied by $M_x$, which is the mass of the emitted fragment (incorporated to enhance the natural fall in emission with mass) gives the factor $G_{0,x}$, Expression (9.03).

$$G_{0,x} = M_x . F_x^a$$  \hspace{1cm} (9.03)

The intensities of the G-SIMS spectrum, $I_{0,x}$, are then given by the multiplication of an existing normalised spectrum, $N_x$, by the factor $G_{0,x}$, Expression (9.04).

$$I_{0,x} = G_{0,x} . N_x$$  \hspace{1cm} (9.04)

Figures 9.46, 9.47 and 9.48 show the static SIMS spectrum and the $G_0$-SIMS spectrum for each of the different primary ion sources.

Figure 9.46. Positive ion spectra of epoxy resin (a) static SIMS acquired with 15 keV [Ga]$^+$, (b) $G_0$-SIMS.
Figure 9.47. Positive ion spectra of epoxy resin (a) static SIMS acquired with 5 keV \([\text{SF}_5]^+\), (b) \(G_0\)-SIMS.

Figure 9.48. Positive ion spectra of epoxy resin (a) static SIMS acquired with 5 keV \([\text{Cs}]^+\), (b) \(G_0\)-SIMS.

The \(G_0\)-SIMS spectrum, calculated from spectra recorded using a \([\text{Ga}]^+\) primary ion beam, is totally dominated by an intense peak at \(m/z = 110\). All other spectral
information has been suppressed. The other G₀-SIMS spectra, calculated from [Cs]⁺ and [SF₅]⁺ primary ion beams, contain far more information, although the suppression and amplification of peaks within both spectra differs. The most intense peaks within the [SF₅]⁺ G₀-SIMS spectrum occur at m/z values of 121, 93, 82 and 69, peaks at these m/z values do not correspond to those determined previously as characteristic of the components of the epoxy resin system (DGEBA/NMA/K61B). The [SF₅]⁺ G₀-SIMS spectrum has intense peaks at m/z = 202, 189, 178, 165, 152, 128, 115, 103, 91, 77, and 39. Some of these peaks are thought to correspond to the original components of the uncured resin.

9.4.4.5. Discussion

The differences in appearance of the G-SIMS spectra to each other and to the normal SIMS spectra may possibly be attributed to the material type. The epoxy resin system is a heavily cross-linked thermosetting polymer and therefore may not be characterised by simple molecules. Investigations up to this point have attempted to characterise the cured epoxy material by identification of the un-cured resin components and their possible fragmentations. The cured material is a highly complex three-dimensional network, it is possible that the G₀-SIMS procedure is amplifying peaks characteristic of this structure, however this does not account for the variations in G₀-SIMS spectra across the different primary ion source range. Application of the G-SIMS technique was not extended to composite fracture surface spectra. Although the G-SIMS process has been carried out in accordance with [91] it was thought that at present there is insufficient knowledge and practise of the technique for its successful application to complex thermosetting materials. Further investigations of the G-SIMS process to other material systems were not conducted because the available ToF-SIMS instruments (VG Scientific based systems) were not equipped with multiple primary ion sources.

9.4.5. Concluding Remarks

In ToF-SIMS fractography studies identification of species representative of either fibre or matrix material may be used to establish the existence (or absence) of interfacially
failed regions within the FRP fracture surface. Considering epoxy matrix FRPs, identification of the matrix material is by fragmentation ions characteristic of the un-cured parent monomer. Whilst this is sufficient to recognize the presence of the matrix material it does not lead to any addition information about its chemical structure or as-fractured condition. It was conceived that possible subtle differences in the epoxy materials fragmentation ions were undistinguishable in the complex spectra that arose from FRP fracture surfaces. Therefore the investigation into the cross-link density of DGEBA, a typical epoxy FRP matrix material, was conducted. This investigation has established that secondary ion mass spectra generated from samples at different levels of cure cannot be visually differentiated after a cure time of approximately 1 hour, this period of time corresponds approximately to the gel time of the material. The cross-link density investigation relied upon identifying peaks that corresponded to fragmentation ions that were characteristic of the un-cured materials components. In analysing ToF-SIMS data the identification of materials, to date, has relied upon correlating peaks within a secondary ion mass spectrum to characteristic fragmentation ions that can be derived from the parent materials chemical backbone. Correlating peaks within a secondary ion mass spectrum to characteristic fragmentation ions is not straightforward; the process becomes increasingly complicated at higher masses because the number of possible fragmentation ions is greater. The practice of peak assignment relies upon pattern recognition, a skill that is developed with increasing experience. Library spectra are available, however, these are only broadly comparable because of different instrumentation effects. Spectra manipulation following the recently developed G-SIMS procedure, has been shown to improve the ease of characterisation of some thermoplastic materials by increasing the intensity of only ions that are truly representative of the analysis material. Successful application of the technique to other materials, such as a cured thermosetting polymer, where current identification relies upon the un-cured chemical structure would be of significant advantage and may possibly highlight differences between the cross-link densities of the material. A preliminary investigation applying the G-SIMS procedure to complex spectra generated from a thermosetting epoxy sample has revealed inconclusive results. Further work and understanding is required before the technique may be successfully applied to thermosetting polymeric materials, and hence to FRP epoxy matrix materials.
Chapter Ten

Concluding Remarks and Future Work

10.1. CONCLUDING REMARKS

In this study, the intralaminar fracture of fibre reinforced polymer composite materials has been evaluated through the measurement of mechanical properties and the ToF-SIMS analysis of fracture surfaces.

Intralaminar strength-based material properties of the HTA/F922 CFRP composite system have been measured experimentally using un-cracked obliquely tabbed off-axis tensile coupons. The results show that there are significant interactions between the transverse normal and shear components of stress at failure. Further off-axis strength data taken from the literature for a GFRP composite system also shows significant interaction between the transverse and shear components of stress at failure.

Intralaminar fracture mechanics properties have been measured experimentally using cracked obliquely tabbed off-axis tensile coupons and compact tension specimens. By varying the fibre angle in off-axis tensile coupons fracture loadings have been generated with different mode I to mode II ratios. Compact tension specimens have been used to generate failure under a pure mode I tensile loading.

Fracture mechanics results generated from cracked coupons have been used to plot failure envelopes in both G and K space for the GFRP and the HTA/F927 CFRP composite systems. The failure envelope of the GFRP material system is dominated by the mode I fracture mechanics component of loading. Failure envelopes following a
similar trend have been identified within the literature, notably for delamination fracture; this type of failure envelope is thought characteristic of brittle FRP composite material systems. In contrast to the GFRP system the failure envelope of the HTA/F927 CFRP material system shows some interaction between mode I and mode II fracture mechanics components. Other failure envelopes exhibiting a similar interaction between the mode I and mode II fracture mechanics components have been identified within the literature for delamination fracture, these failure envelopes are thought characteristic of tough FRP composite material systems.

A methodology has been established for sample preparation for ToF-SIMS analysis of cured thermosetting polymeric materials. The method of microtoming is a quick and simple procedure that results very thin slices of material. The sectioned samples do not accumulate charge as readily as thick plaques, this results in a higher yield of secondary ions improving the quality of spectra and simplifying interpretation. The ease of sample analysis is of particular importance for use with older ToF-SIMS spectrometers. Because samples may be obtained from the bulk of the material they are free from handling contamination, which makes spectra interpretation simpler and more reliable.

An in-situ fracture stage has been designed and constructed for use within the ultra high vacuum confines of the ToF-SIMS spectrometer. This stage is able to fracture coupons under different modes of loading; a tensile mode I and a shear dominated mode II. From the in-situ generated fracture surfaces it is possible to record good quality SIMS spectra. Fracture surfaces may be presented for analysis with or without exposure to atmosphere.

ToF-SIMS analysis of failure surfaces reveals that fracture, irrespective of loading mode, of dry composite coupons with an optimised interface, is characterised by cohesive failure through the matrix material. Although the fracture surface morphology can be seen to vary with loading mode, the chemistry of the fracture surface, as analysed from ToF-SIMS spectra interpretation, remains constant. Alterations to the fibre pre-treatment level have resulted in fracture surface ToF-SIMS spectra being recorded that have different characteristics to that from the standard composite fracture surface. The spectra suggest that composites produced with 0 % oxidised fibres failed interfacially between the fibre and the matrix. ToF-SIMS analyses of failure surfaces from environmentally aged composite coupons also show some different characteristics to
those recorded from dry composite coupons. The results from composite coupons fractured after a period of environmental ageing are also believed to indicate areas of interfacial failure within the fracture surface.

10.2. FUTURE WORK

The following pieces of work proceed naturally from the results presented in this thesis:

Having established that variations in the fracture surface chemistry between dry composite coupons with optimised interfaces and environmentally aged composite coupons can be detected by ToF-SIMS analysis, it would be of interest to quantify the environmental ageing process. It may be possible to correlate a change in the mechanical performance of the composite to the changing fracture surface characteristics. This method could be used to observe whether or not a reduction in the mechanical performance of the material can be predicted from ToF-SIMS fracture surface analysis prior to any changes observed in more conventional methods of fracture surface analysis such as SEM observations. It would, perhaps, also be of interest to determine the effects of the environmental ageing process on the failure envelope, to establish whether the mode I and mode II fracture mechanics components are affected to the same degree.

Further development of the in-situ fracture stage is possible, the most obvious addition would be a motor drive to facilitate tests at a variety of different, controlled, strain rates. The fracture stage may also be utilised in the study of failure of a variety of other materials and could easily be modified to accommodate different coupon geometries. It, perhaps, also has potential for generating fracture surfaces of adhesively bonded joints.

Further analysis of the G-SIMS procedure is required before the technique can be successfully applied to spectra generated from complex thermosetting polymer materials and FRP fracture surfaces. There would appear to be a requirement for a processing technique that simplifies ToF-SIMS spectra, making identification of the original material through visual interpretation more accurate. G-SIMS is a technique that has
been shown to simplify and enhance secondary ion mass spectra generated from simple thermoplastic materials and therefore warrants further study in order to ascertain whether its application can be extended to other material systems.
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