

**NON-WOVEN, RECYCLED CARBON FIBRE
COMPOSITES: DEVELOPMENT OF TEST METHODS
AND ASSESSMENT OF PROCESS PARAMETERS**

BY

KARTHIK KRISHNA KUMAR

School of Engineering, Computing and Mathematics
Oxford Brookes University

*A thesis submitted in partial fulfilment of the requirement of Oxford Brookes University for
the degree of Doctor of Philosophy*

JANUARY 2020

Abstract

The embodied energy of carbon fibre is as high as that of aluminium yet the disposal of composite waste presents a challenge for the circular economy. The sustainable use of carbon fibre could be achieved with its reuse in recycled carbon fibre composites. However, their reinforcement architecture is quite different from that of virgin carbon fibre composites. Recycled carbon fibres are generally discontinuous, chopped, fluffy, and entangled requiring further processing. However, their transformation into non-woven textile fabrics and then to cured laminates, has recently become an efficient, cost-effective technique that makes the whole carbon fibre recycling process viable.

The development of new materials is generally followed by rigorous material qualification practices to validate their use in intended applications. It is essential therefore to develop reliable datasets to understand their capabilities and mechanical behaviour. Much of the standardised macro-scale test methods for composite characterisation were developed for continuous, fibre-reinforced composite systems and their applicability to non-woven, recycled carbon fibre composites is a gap in knowledge that needs to be addressed. This research identified and adapted experimental test methods that can objectively quantify key material properties for design purposes. On identification of suitable test protocols, a comprehensive experimental programme encompassing tension, shear, fatigue and environmental durability of particular recycled carbon fibre/epoxy composites was undertaken. The project also assessed the effect of fundamental recycling process variables on moulded composite static and fatigue behaviour.

It was found that the reinforcement architecture played a significant role in the mechanical behaviour of recycled carbon fibre composites. Test procedures were adapted or modified with significance given to test geometry, load path and failure characteristics. A specification defining appropriate testing protocols was found to be necessary to generate design allowables for the non-woven recycled carbon fibre/epoxy composites. The overriding outcome of this research was a thorough understanding of the influence of recycling processing parameters on the composite laminate performance. It was found that recycled, non-woven carbon fibre/epoxy composites have good fatigue endurance and environmental durability. The overall outcome of this research provides a rigorous basis for selection approaches of sustainable materials for various potential structural applications in the transportation industry.

Acknowledgements

I would like to thank Frazer Barnes and Mathilde Poulet for their endless support and discussions throughout the course of this research. I am particularly grateful to my director of studies, Prof. Allan Hutchinson, for his counsel, guidance and encouragement in every facet of this research and beyond. I am indebted to my supervisors, Dr. Pat Winfield for her academic support and Prof. James Broughton for the support, discussion and time taken to proof read this thesis.

This studentship was part-funded by ELG Carbon Fibre Ltd. and by Oxford Brookes University under the Brookes 150 Legacy Scholarship agreement (January 2017 – January 2020). This work would not have been possible without the financial support and materials provided by ELG Carbon Fibre Ltd. I would also like to offer my special thanks to the School of Engineering, Computing and Mathematics, Oxford Brookes University for supporting me through conferences and presentations.

I acknowledge the help provided by Michael Hartman and Dr. Nick Hooper in the laboratories, and Ian Spacksman in the workshop. The assistance provided by David Heath, Richard Offer, Will Mahoney from Oxford Brookes University and Camille Seurat from ELG Carbon Fibre Ltd., at different stages of my research is greatly appreciated.

Finally, and most importantly, I wish to thank my parents for their encouragement and support.

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Chapter 1: Introduction

1.1 Background

1.1.1 Carbon Fibre Market Size

The global demand for carbon fibre (CF) production had been increasing at 11.45% per annum and was estimated to be about 78.5 thousand tonnes as per the Composites Market Report in 2018. The estimated annual production capacity of CF worldwide was 149.3 thousand tonnes in the same year and production is expected to increase in the coming years. The overcapacity in production with respect to the demand is associated with unexpected downtime, machine efficiency and rejected materials. About 82.7% of the entire carbon fibre production is processed into carbon fibre reinforced plastic (CFRP) where the fibres are embedded into a thermoset or thermoplastic matrix [1].

CFRP is an attractive option for material selection, particularly in the transportation sector where light-weighting is the key to reduce energy consumption and improve fuel efficiency due to composites' superior strength to weight ratio. In 2017, the global demand for CFRP was determined to be 114 thousand tonnes turning over approximately US\$ 14.73 billion. The average annual growth in the worldwide turnover with CFRP since 2013 is approximately 11.88% and the high growth in its demand can be seen in Figure 1.1 [1]:

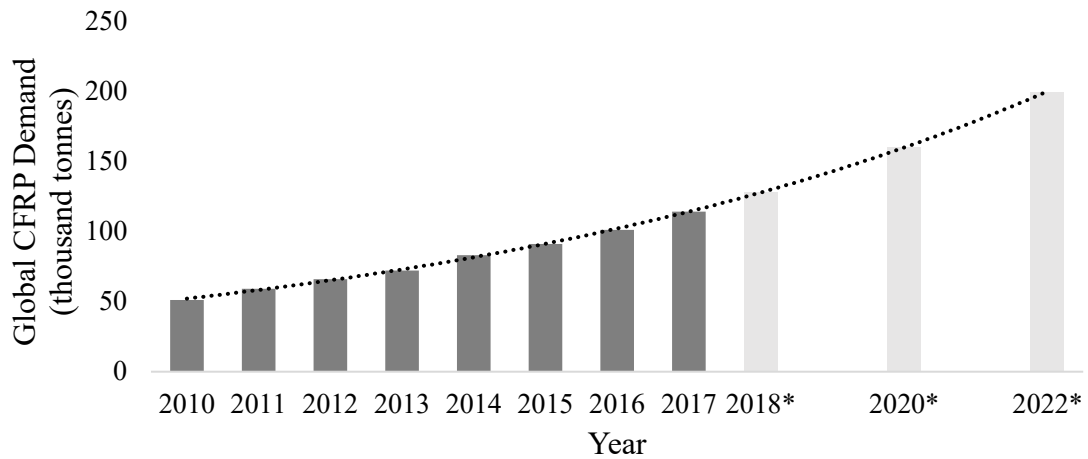


Figure 1.1: Global CFRP Demand in thousands of tonnes [1]

The light weighting advantages of carbon composites have been exploited by various industries especially the aerospace and the automotive sectors where the usage of carbon fibre products are on a steady rise. The estimated demand for carbon composites in 2018 based on the application is depicted in Figure 1.2:

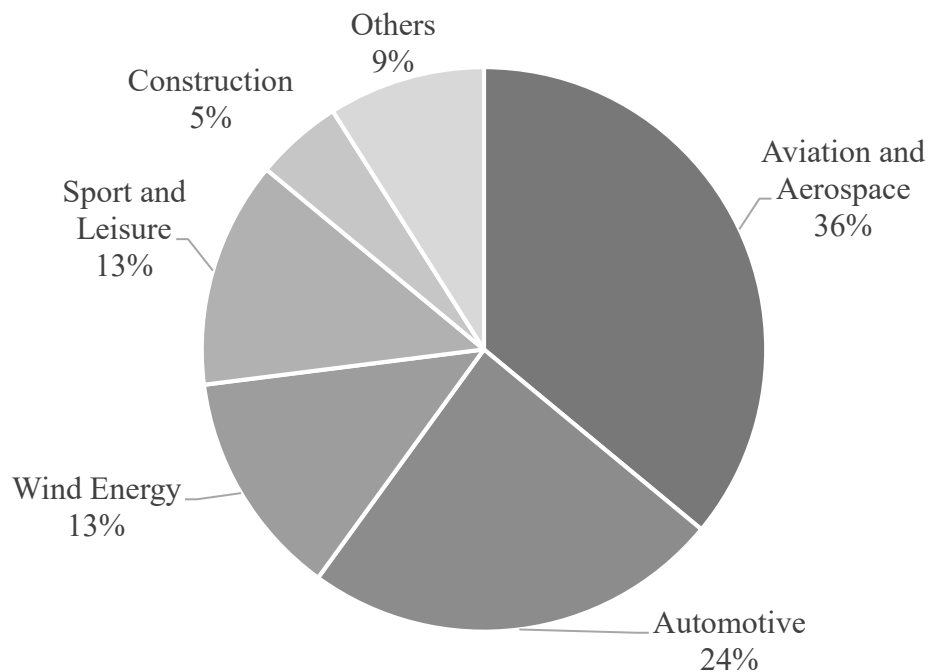


Figure 1.2: Global carbon composites demand based on application [1]

1.1.2 Sustainability and need for recycling

Carbon fibre composites have a larger impact on sustainability studies and attract more attention than glass fibre composites because the cost related to the production of carbon fibre composites is significantly more. The average price of glass fibre per kg is £1.55 and that of virgin carbon fibre (vCF) is in the range of £20-50 [2, 3]. The raw material for the production of carbon fibres is generally polyacrylonitrile (PAN) precursor. This, which are long strings of organic polymers, are made from non-renewable resources such as crude oil or natural gas [4]. Carbon fibres thus require high cost raw materials and expensive intermediate steps for its production that needs about 280MJ/kg energy, 9-10 times that of glass fibre and 5-6 times of steel [5]. Additionally, the cost of manufacturing CF components can be 20 times that of steel and 10 times that of aluminium [6]. Carbon fibres are high value materials that have a large amount of embodied energy, whose production emits 29.45 tonnes of greenhouse gases per year, that need to be reused or recycled in a circular economy for economic and environmental benefits [7].

The demand for carbon fibre composites is increasing exponentially as seen in Figure 1.1, and so will the associated waste products. 30 - 40% of all CFRP waste comes from manufacturing waste including out of date prepregs, off cuts and trim waste [8, 9]. The demand for CFRP may also increase faster than the supply. The end of life waste for CFRP is still small, but there would be no shortage of the same in the near future with the increased use of composites in the aerospace and automotive sectors. For example, there are between 19 to 29 tonnes of CFRP in airframes currently such as Airbus's A350, A380, Boeing's B787, B777-X and Bombardier's C-series [10, 11]. An estimated 3000 tonnes of CF composite waste is being generated every year and by 2030, approximately 6000-8000 commercial planes are expected to reach their end of life [12]. Much of the aerospace sector waste has been disposed as landfill which poses various environmental, economic and legal concerns [13]. It also represents a waste of a

valuable materials resource. Landfill is the least preferred waste management solution and the cost of disposing CF composite waste is approximately £170/tonne [14].

The increasing energy prices and stringent fuel economy standards impose a lot of pressure to achieve light weighting in the transportation sectors. The usage of CFRP in automobiles have been brought into the spotlight with BMW's i3 model featuring a carbon fibre car body that enabled them to reduce weight by 300 kg. [15]. The legislation imposed on the carbon dioxide emissions, which are being lowered from 130 g/km in 2015 to 95 g/km by 2021 and is targeted to 59 g/km by 2030 for new cars, further adds the urgency to achieve light weighting in vehicles and hence the demand for carbon fibre composites has been on the rise [16]. The shorter service life of automotive vehicles mean that its end of life CFRP waste will join the waste stream in significant amounts. The EU End of Life Vehicles (ELV) directive requires that at least 85% of the materials used by weight be reused or recycled to restrict landfill waste and incineration [6, 17]. Hence the use of CFRP in vehicles requires that carbon fibre be recycled.

1.2 Recycling technologies and reprocessing methods

The feasibility of recycling composites depends on whether the process can be commercially viable and whether the products have the mechanical performance suitable for its reuse in industrial applications. A number of recycling techniques are depicted in Figure 1.3.

Mechanical recycling is one of the ways to recycle composites by grinding them into reduced sizes by milling or shredding and distinguish the products as resin rich or fibre rich by sieving techniques. These can be used as fillers or as reinforcement in the new generation composite material. Although this has been applied more to glass fibre composites, the process is not commercially viable due to the availability of low cost fillers such as aluminium silicate and the poor mechanical properties of the new composite product [11, 13, 18]. The high embodied

energy and cost of CFRP demands processes where its fibres can be reclaimed from waste composite materials. This can be achieved by thermal or chemical processes.

The chemical means of recycling composites, known as solvolysis, reclaims carbon fibre by breaking the resin chains using water or solvents in reactors, with or without catalysts. The solvents used can be water or alcohols such as methanol, ethanol, propanol and acetone. The fibres can be extracted from its composite form at various temperatures and pressures depending on the kind of matrix and the solvent used in the process. Unsaturated polymers can be degraded at temperatures below 300°C with water whereas epoxy and polyether ether ketone (PEEK) resins require supercritical water. Solvolysis can be achieved at lower pressures and temperatures with the presence of alkaline catalysts like sodium hydroxide or acidic catalysts like nitric and sulphuric acids [18].

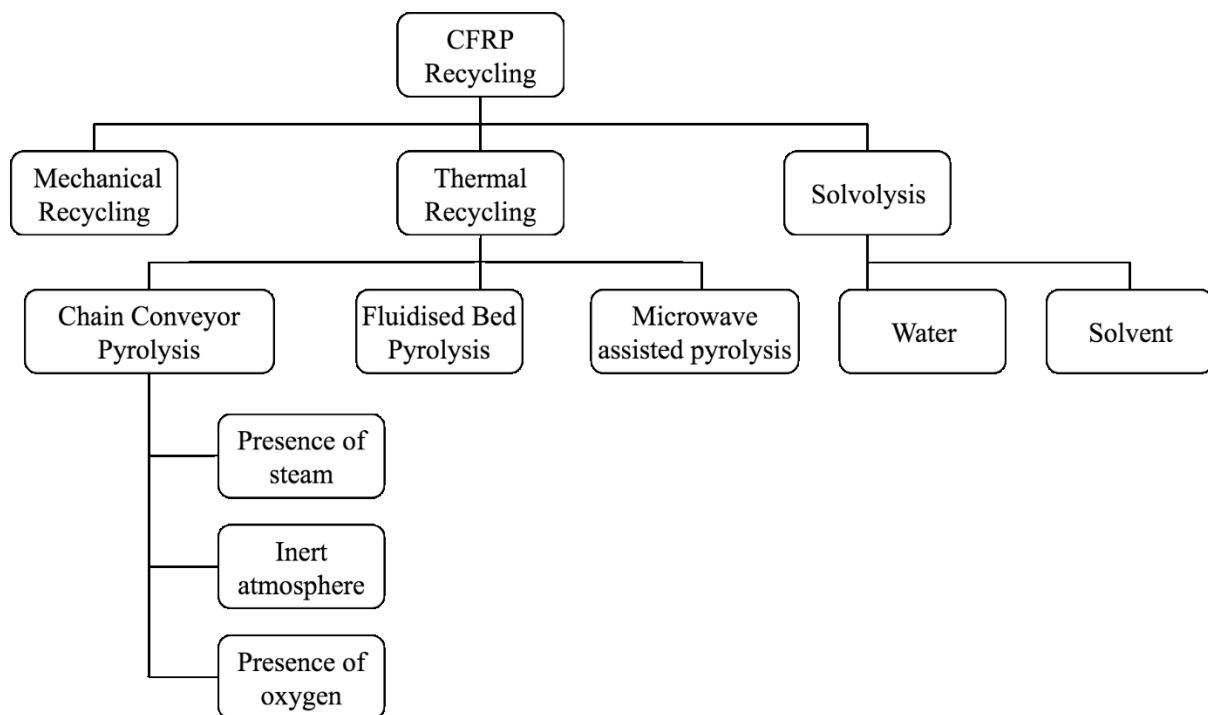


Figure 1.3: Composite recycling techniques

The thermal recycling methods known as pyrolysis decompose CFRP by subjecting it to high temperatures. Chain conveyor pyrolysis used by ELG Carbon Fibre Ltd. allows the recovery

of carbon fibres by carrying shredded CFRP waste to a furnace by means of a conveyor belt whilst undergoing pyrolysis. Pyrolysis allows the recovery of carbon fibres by volatilising the matrix into gaseous products and char in a controlled atmosphere maintained between 200°C and 650°C, depending on the resin and type of waste. It has been shown that the single recycled fibre tensile strength is never less than 85% of the virgin carbon fibre but this depends on the grade of fibre, pyrolytic temperatures, environment – inert or otherwise, and variability in the feedstock [18, 19]. Other alternative techniques include pyrolysis in the presence of steam, known as steam thermolysis for thermoplastic and thermoset composites, where up to 90% degradation in fibre strength was reported [20, 21]. In one such apparatus, CFRP waste was heated to 550°C at 10°C/min in a SiC furnace initially under a steam flow of 2 ml/min for 30 minutes followed by an oxygen rich (21% O₂) air flow at a rate of 200 ml/min for 30-75 minutes. The rCF recovered was reported to have a smooth fibre surface with minimal deposition of char and lower CO₂ emissions than that of conventional processes [22].

A variant of pyrolysis is the fluidised bed pyrolysis where CFRP scrap, shredded to approximately 25 mm, is sent into a silica bed on a mesh in a fluidised bed reactor. The matrix in the reactor is disintegrated by oxidation at temperatures over 500°C with the help of an air stream passing through the bed. The lighter carbon fibres are transported out of the reactor for further oxidation and processing by the air stream and separated in a cyclone while heavier impurities and metallic components settle down on the bed. Hence this process is suitable for contaminated end of life waste. The recycled fibres show a drop of about 18% in tensile strength, possibly due to increased agitation [3, 13, 23-25]. Microwave assisted pyrolysis heats the core of the CFRP waste on a bed of quartz sand in a nitrogen filled, inert atmosphere. The matrix is disintegrated into gases and oils and clean carbon fibres are retrieved. The recycled fibres show a drop of about 20% in its tensile strength [26]. Fluidised bed pyrolysis has been

developed to a pilot scale and microwave assisted pyrolysis has not been successfully commercialised [11].

1.3 rCF reinforcement architecture

Carbon fibres made from polyacrylonitrile (PAN) precursors go through a three step process: (1) stabilization, (2) carbonization, and (3) graphitization. During the stabilization stage, stretched PAN fibres are held in tension and oxidized in air at about 200 to 220°C. Next, the fibres are subjected to a carbonizing heat treatment at temperatures over 1000°C in which the PAN-based fibres become transformed into carbon fibres through the elimination of O, H, and N from the precursor. Finally, an optional graphitization treatment increases the fibres' modulus of elasticity by increasing the preferred orientation of the graphite like crystallites within each fibre [27]. Based on the mechanical properties of carbon fibres, they can be Ultra high Elastic Modulus (UHM), High Elastic Modulus (HM), Intermediate Elastic Modulus (IM), Standard Elastic Modulus (HT) and Low Elastic Modulus (LM). A graphical representation of this classification is shown in Figure 1.4.

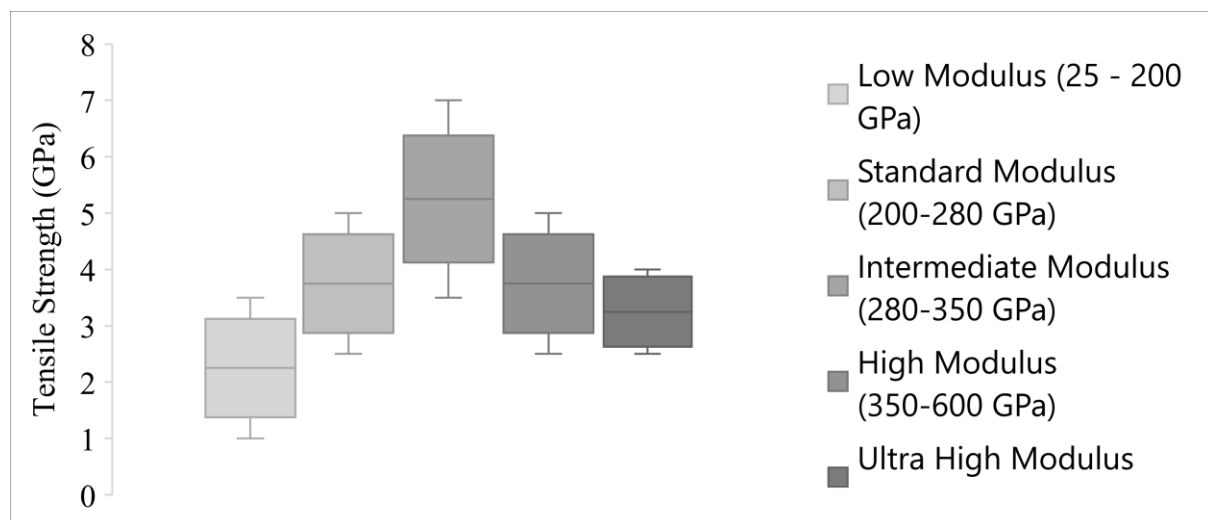


Figure 1.4: Classification of carbon fibres [28]

The key factors which influence the properties of a CF composite are the type of carbon fibre and resin, fibre volume fraction (V_f) reinforcement architecture, fibre-matrix adhesion, fibre

layup design and processing quality of the composite. CF composites are generally made of continuous bundles of carbon fibres laid unidirectionally that despite its high strength to weight ratio, show marked anisotropy due to the nature of the fibres. This directional dependence is reduced with alternative reinforcement architectures such as woven or braided textile fabrics that use continuous fibres [29].

The form of the composite after recycling depends on the scrap and the composite waste fed into the system. Although it is possible to retain the form of a continuous textile fabric after pyrolysis, much of the scrap being processed is in a variety of physical forms and they may need to be shredded before being fed into the furnace. Classification and preparation of the feedstock materials is vital to ensure consistent quality in the rCF composite and this is carried out by sorting the waste by the grade of fibres (i.e., Intermediate modulus or Standard Modulus) and the physical form of CFRP waste [30, 31]. The product of pyrolysis of CFRP is a tangled, fluffy mass of carbon fibre with variable fibre lengths, as shown in Figure 1.5, and is the intermediate form of rCF composites. Their direct introduction into composite structures would result in a poorly manufactured laminate that would be highly variable in its mechanical properties with increased defects. Considering the nature of pyrolysed carbon fibres, it would be an expensive and challenging task to retrieve the unidirectional architecture back and as a result, they need to be reprocessed by alternative means.

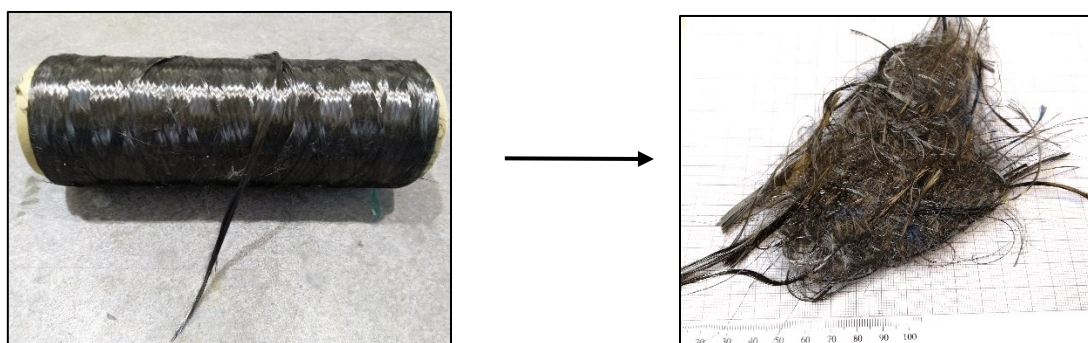


Figure 1.5: Form of carbon fibres before and after pyrolysis [7]

The last two decades have seen the development of a number of technologies to recover carbon fibres from CFRP waste, but with limited focus on reprocessing the recovered fibres into a newer composite form at an economically feasible rate. A viable method to handle the intermingled pyrolysed fibres is to process it into a textile fabric by means of a carding mill as schematically represented in Figure 1.6. To reduce the variability in the end composite product, the pyrolysed fibres are chopped into approximately 80 mm in length and rCF tows are split into smaller bundles to form random discontinuous fibres. The discontinuous rCF fibres are assembled as random fibre webs by a carding machine that are geometrically arranged in layers. The multi-layered web structure is mechanically bonded together by a needle-punching process in which barbed needles pull fibres from the lower layers. A porous, dry-laid, non-woven textile mat is thus formed. The non-woven mats are generally anisotropic as more rCF fibres are oriented in the direction perpendicular to the machine direction for the material system used here. The thickness of the mat depends on the areal weight of the fabric, which can vary from 10 g/m^2 to 1000 g/m^2 . Despite the porous nature of non-woven mats, they are known to offer enhanced crosswise strength and are less susceptible to delamination due to the z-reinforced fibres [32]. The punching density alters the non-woven fabric structure as it was found that fibre entanglement, fibre damage and random distribution of the fibres (or material isotropy) increased with increasing punching densities which thereby impacted material mechanical properties [33]. These non-woven mats are then converted into laminate form as shown in Figure 1.7.

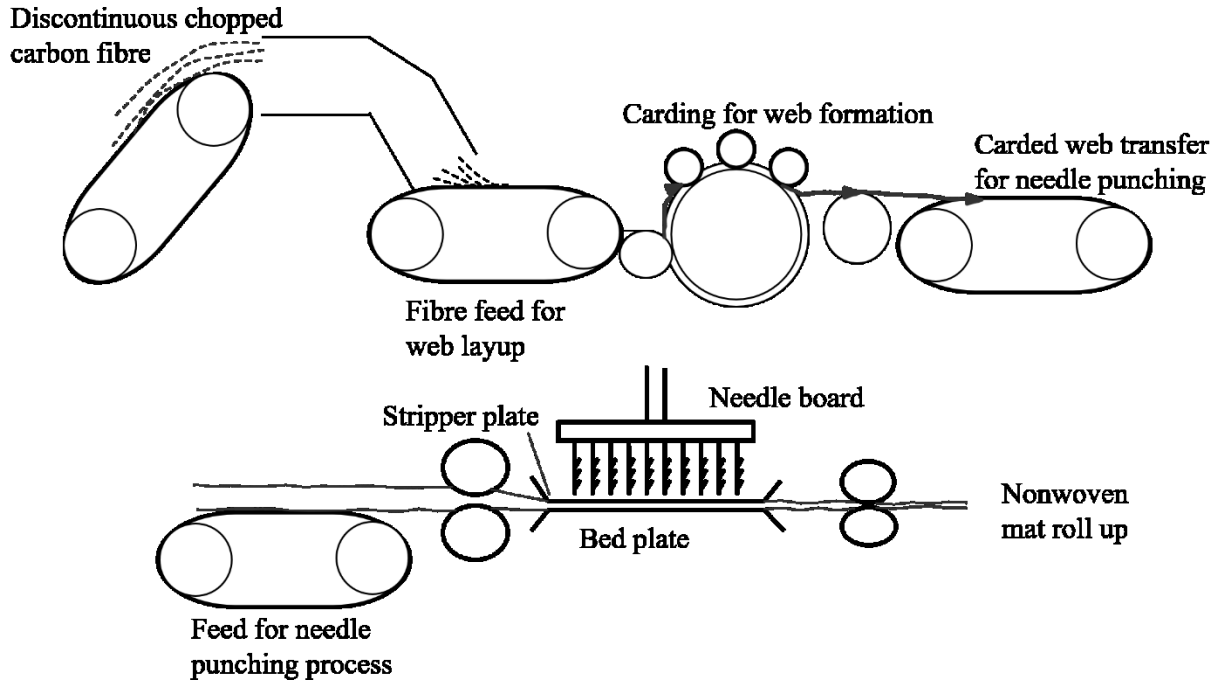


Figure 1.6: Schematic representation of carding and the needle punching process [32]

The rCF non-woven mats are remoulded into a composite form by compression moulding techniques such as Liquid Compression Moulding (LCM), Sheet Moulded Compounding (SMC) and Autoclave curing processes. The details for these processes are explained in Chapter 4. The thermoplastic form of rCF composites can be manufactured by intermingling the non-woven rCF mats with polymer strands in the carding mill. The orientation of an rCF laminate, when laid in the same direction, is defined in terms of warp and weft as shown in Figure 1.8. When the non-woven plies are laid in an $[0/90]_n$ configuration, the laminate is termed as a cross-ply.

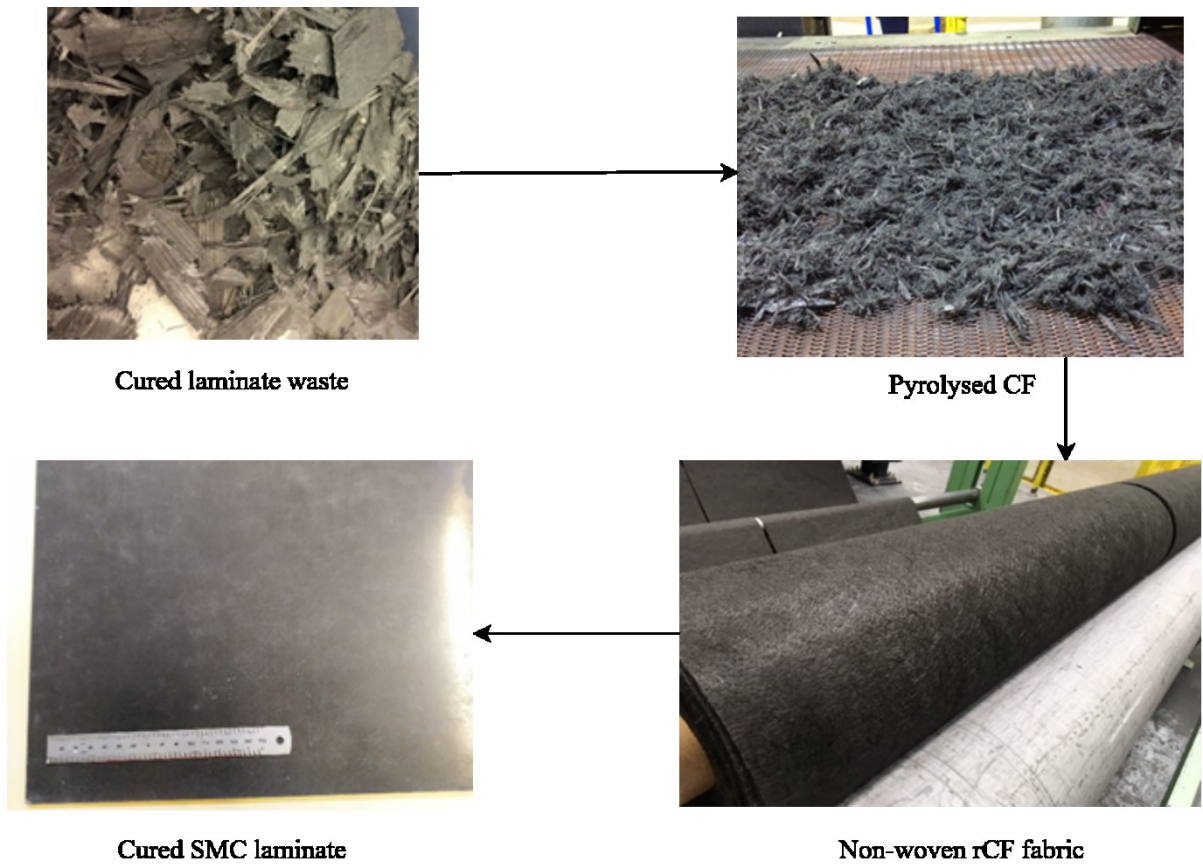


Figure 1.7: Conversion of pyrolysed fibres into needle-punched non-woven mat and remoulded into composite form by SMC [34]

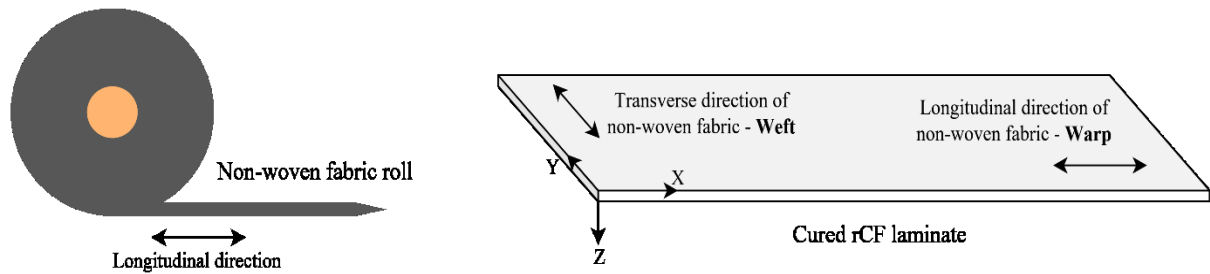


Figure 1.8: Schematic representation defining the terminology of rCF laminate directions used in this research

1.4 Markets for recycled carbon fibre

The challenge with recycling has always been controlling the production cost of rCF and availability of sufficient feedstock to ensure continuous production. The interest from aerospace industries in closing the CFRP loop by supplying cured and uncured composite waste for recycling ensures the supply chain security. Boeing states that this enables them to achieve their goal in reducing the amount of landfill waste by 20 percent by 2025 and create an economically viable solution for CFRP [35]. Its development can penetrate into new markets and is in direct competition with vCF and metals such as aluminium which form a good target in the automotive industry [24]. Although the form of the composite is different from that of vCF composites, the cheaper cost of manufacture and the light-weighting that rCF offers in comparison to traditional materials, makes it an attractive and valuable option for a variety of markets. The use of rCF materials is competitive as the mechanical properties fall within producers targets for vCF and the use of rCF can offer a 30-40% cost saving in comparison with vCF [36]. The nature of the non-woven fabrics enhances its drapeability for the manufacture of complex geometries which would otherwise be difficult with vCF composites.

Non-woven rCF composites have already been used in non-structural applications in the sports and leisure sectors such as hockey sticks and tennis rackets, in the medicine sector, in the automotive sector, electronics products such as tablets and laptops etc. where mechanical performance is not a primary concern or where a reduced stiffness is actually more desirable. It was estimated that rCF products can meet 75% of the automotive sector needs and be used in 90% of electronic applications [37]. Their usage in structural applications may be developed with a better understanding of their long-term characteristics and durability. rCF composites have been planned to be integrated in a composite bogey frame in rail vehicles to optimize the vertical and transverse stiffness, reduce overall bogey weight by 40% and reduce operational

costs by 20% in train fuel consumption and track maintenance costs by decreasing the lateral forces on the railway tracks by 40% [38].

The barriers to growth of the rCF market have been understanding the mechanical behaviour and characteristics of the non-woven rCF materials, the unavailability of design data for rCF products and the demonstration of economic, technical and environmental performance of rCF products [37].

1.5 Motivation for the project

The rCF industry is relatively new and the introduction of a new form of composite can pose challenges to designers who would need to rethink the applications that fit these products. A comprehensive understanding of rCF composites is essential to their usage in various industrial applications. The commercialisation of non-woven rCF composites would ensure partial closure of the CFRP loop that answers various sustainability and environmental issues.

The end product of the pyrolytic recycling process is a laminate reinforced with discontinuous, non-woven, randomly dispersed carbon fibres where the majority of the fibres are preferentially aligned perpendicular to the carding machine direction. The remanufacturing of non-woven rCF composites from pyrolysis faces several challenges in the form of variability that translate to uncertainties on the mechanical performance of the rCF composite. The variability in rCF composites mechanical performance can arise in the form of:

- a) variance in the loss of strength of carbon fibres by pyrolysis
- b) deposition of impurities and char on the surface that impacts the fibre-matrix adhesion
- c) history and source of the pyrolysis feedstock
- d) nature of the reinforcement architecture
- e) variations in the areal weight of the non-woven mat and V_f in the cured laminate
- f) the needle-punching process that could potentially damage the fibres

- g) manufacturing defects such as voids, variations in thickness in the laminate, differential porosity of the non-woven mat.
- h) The alignment of fibres in plane i.e. flatness, such that fibres sustain loads through tension and compression due to their 3-D orientation

These factors are compounded by different laminate remoulding techniques, resin systems, influence of sizing, fabric areal weight, density of the needle punching process, thickness of the barbed needles and type of fibre.

The nature of the porous non-woven mats limits the V_f of the rCF composite to less than 35%, beyond which compaction becomes difficult due to the needle-punching process. Their reinforcement architecture is quite dissimilar from vCF composites which have long, continuous fibres in the form of unidirectional and woven composites. The identification of suitable applications and assessment of manufacturing process parameters for non-woven rCF composites requires the generation of a consistent, reliable dataset. The unconventional reinforcement architecture in rCF composites, may demand a different interpretation of standard tests, or even modification of standard test protocols to appropriately characterise them.

The major concerns regarding the discontinuous, non-woven rCF composite product for the manufacturers (ELG Carbon Fibre Ltd.) were in relation to their mechanical strength, fatigue sensitivity and environmental susceptibility, and hence, the project focussed on these aspects. Other mechanical performance factors that are valuable for design, such as holed strength and impact resistance, are recommended for future work.

1.6 Aims and objectives

The overall aim of the research was *to develop a suite of test protocols to generate reliable design data for rCF composites* that would be realised by the following set objectives:

- a) Review carbon fibre recycling techniques, composite re-manufacturing processes and the effects of its unique reinforcement architecture in relation to mechanical response.
- b) Evaluate the limitations of test methods defined for conventional composite forms and adapt test protocols if necessary, to suit discontinuous, needle-punched, non-woven, rCF composites.
- c) Undertake a comprehensive study to analyse the static and fatigue behaviour of non-woven epoxy based rCF composites and develop a holistic framework for composite materials selection.
- d) Evaluate mechanical characteristics laminates produced from rCF fibre materials, relating properties to processing routes and variables and analyse the composite systems' damage phenomena.
- e) Establishing the reliability and limits of variability of mechanical performance data of recycled, discontinuous, non-woven composites.
- f) Investigate behaviour of rCF composites in various environmental media and test the durability of the material.

1.7 Outline of thesis

The opening chapter gives a background to recycling CF and reprocessing them into discontinuous, needle-punched, non-woven rCF composites. It also outlines the aims and objectives set for the research work undertaken here. Chapter 2 introduces to the reader the recent advances to pyrolysis and challenges to processing recovered CF. It proceeds to critically review the test methodologies used for the material qualification of unconventional fibre reinforced composite systems. This chapter also includes a brief literature review on the fatigue and durability of composite materials. The chapter concludes by identifying the gap in knowledge in the material qualification of rCF composites.

Chapter 3 devises an appropriate research strategy to fulfil the aims and objectives stated, informed by the literature review and discussions with ELG Carbon Fibre Ltd. Chapter 4 defines the materials that were used in this research. It explains the different test methods to characterise a particular material property. It also defines the test procedures for the fatigue and environmental durability of rCF composites used in this research.

Chapters 5 – 8 analyse the influence of recycling processing parameters on the physical and mechanical behaviour of the end product. Chapters 5 and 6 evaluate the described test methods on rCF composites and develops appropriate test procedures for them. Chapter 7 analyses their fatigue behaviour and Chapter 8 assesses their durability to select environmental media.

The results of this research should aid material processing selection in the manufacture of rCF composites that are summarised in Chapter 9. It also presents the material qualification work developed in this project. Chapter 10 contains the recommendations for future work in rCF composites.

Chapter 2: Literature Review

This chapter reviews the pyrolysis process used to recover the carbon fibres used in this research and related composite remanufacturing techniques. It reviews the static test methods deployed to characterise composite structures and the general durability and fatigue behaviour of composite laminates. The chapter concludes by summarising the gap in knowledge for non-woven rCF composites.

2.1 The Pyrolysis Process

The pyrolysis feedstock, i.e., the carbon fibre waste, has to be segregated based on the type of waste (out of date rolls, prepreg wastes such as off-cuts, cured laminates and end of life wastes) and their reinforcing fibre grade (SM/IM/HM - see Fig. 1.4), so as to reduce the variability imparted on rCF composites. The cured laminate wastes are shredded into smaller sizes to ensure complete combustion of the matrix in the furnace. The matrix and sizing on the CF are decomposed into gaseous products in the furnace whereas pyrolysed, fluffy fibres remain in the chain conveyor belt.

Previous studies have been influential in developing an optimal pyrolysis process that would minimize fibre damage, ensure complete burning of char, analysis of the rCF surface quality, fibre length optimization and characterisation of rCF at the fibre level [19, 23, 39-46]. The tensile strength, tensile modulus and interfacial shear strength with epoxy resin of pyrolysed fibres showed no significant difference from their virgin precursors (-1.9%, -4.4% and +4.3% respectively) according to a preliminary study [47].

Another study indicated no significant loss in the tensile moduli and a 10-15% reduction in the tensile strength of carbon fibres pyrolysed at 500°C followed by oxidation in air to remove residual char. The drops in the fibre tensile strength were attributed to the accumulation of defects and damage sustained by the pyrolysed fibres due to the oxidation effect. It was also

found that pyrolysed fibres have a reduced lateral crystallite size from 6 nm to 5 nm in diameter after pyrolysis and this was reasoned as the loss of its tensile strength. The interfacial strength of rCF with epoxy showed a 22% drop whereas it showed no reduction with PP matrix indicating that the mechanical locking effect of rCF had not changed. This suggests PP is a poor choice of resin for rCF. The drop in the interfacial strength with epoxy resin was attributed to the reduction in the surface oxygen functionalities of the pyrolysed fibres [46].

The fibres were found to be severely damaged at temperatures beyond 700°C. Pyrolysis in the absence of oxygen could leave behind char and impurities on the CF surface, as shown in Figure 2.1 (1'), which would be detrimental to good fibre-matrix adhesion [48].

The optimised pyrolysis process now has a furnace with more than one temperature zone, the primary heating zone for supporting the decomposition and combustion of the resin and a secondary heating zone to maintain the material at a temperature higher than that in the primary zone to remove char. The atmosphere in the furnace comprises of air and generated fumes, which are removed in a controlled manner such that the furnace can support the combustion of the resin in the primary heating zone. The secondary heating zone allows the combustion of char from the carbon fibre, which is undesirable as it may affect the characteristics of the rCF. The oxygen content in the primary heating zone is controlled to 5% or less by sensors to minimize the oxidation of the carbon fibres. Critically, the oxygen is not completely removed as it is needed to support the combustion of the resin and prevent increased accumulation of char, and is regulated by the controlled ventilation of combustion gases. The oxygen content is increased to approximately 10% by volume in the second heating zone to further aid the removal of char and pyrolytic residues, and to partially oxidize the surface of the recycled carbon fibres. The fumes removed are directed to external burners and waste gases are released after further treatment. The duration of the combustion process, as controlled by the belt speeds, may depend on the nature of the feedstock. The recycled carbon fibres can have grooves,

scratches and depressions on their surface as opposed to the virgin carbon fibres which have a relatively smooth surface. The partial oxidation in the recycled carbon fibres result in a rougher and hydrophilic functionalised surface which has been reported to have improved wettability and adhesion with various resin polymers, even more so than conventional carbon fibres [48, 49].

The presence of two pyrolysis zones, where the temperature and oxygen levels are controlled to 430-445°C and 2% by volume respectively in the primary zone, and are subsequently increased in the secondary zone lead to the partial oxidation of the recovered CF surface. This has been reported to increase wettability and improve the incorporation of rCF in epoxy resin systems. Table 2.1 shows the influence of the temperature and oxygen levels in the secondary pyrolysis zone on the wettability of the CF surface. A lower contact angle implies a more hydrophilic fibre surface. Unsized vCFs generally have contact angles around 75°. The partial oxidation resulted in a rougher fibre surface with increased oxygenated functional groups such as hydroxyl (C-OH), carbonyl (C=O) and carboxyl (-O-C=O) compared with those found on vCF, thereby increasing the surface energy and helping improved wettability with epoxy resin [48, 50]. The oxygen levels nevertheless need to be controlled as surface defects were observed in a highly oxidative environment that had a negative effect on the tensile strength and crystallite size of the pyrolysed carbon fibres. It was also found that in an inert atmosphere, the thermal effects of pyrolysis results in a decrease of surface oxygen concentration thereby affecting the interfacial shear strength with epoxy resins [46].

S.No.	Temperature range in Secondary Pyrolysis Zone (°C)	Oxygen levels in Secondary Pyrolysis Zone (by volume)	Contact angle in water by Wilhelmy Method (°)
1.	515 - 650	10%	69.8
2.	450 - 480	2%	84.4
3.	590 - 610	2%	77.8

Table 2.1: Contact angle of pyrolysed CF based on the temperature and oxygen levels in the secondary pyrolysis zone [48]

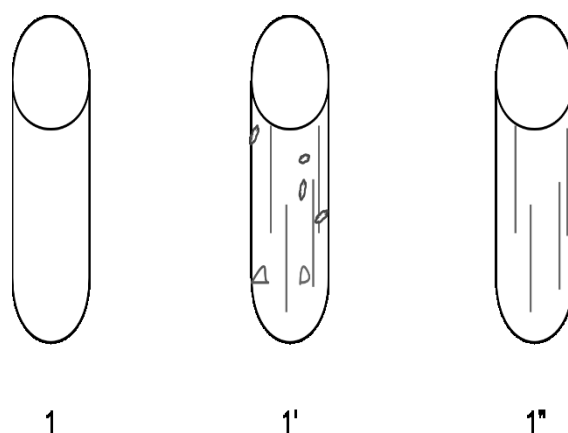


Figure 2.1: Schematic illustrations of smooth vCF surface (1); CF surface after inert pyrolysis (1') and; CF surface after modified pyrolysis (1'') [48]

Latest single fibre filament tests of pyrolysed fibres from the optimised pyrolysis process from ELG Carbon Fibre Ltd. show up to 95% and 93% retention in tensile strength and modulus of the pyrolysed fibres as summarised in Table 2.2 and an interfacial shear strength of 75 MPa with epoxy resin [51].

<u>Fibre type</u>	Tensile Strength (MPa)		Tensile Modulus (GPa)	
	vCF	rCF	vCF	rCF
<i>Intermediate Modulus</i>	4265	4080	275	257
<i>Standard Modulus</i>	3185	3016	238	229

Table 2.2: Single Fibre Filament tests on CF before and after pyrolysis [51]

2.2 Recovery and reuse of CF

Pyrolysed carbon fibres are thus able to retain much of their strength and stiffness. However, the recovery of CF by pyrolysis result in fluffy, entangled fibres which are difficult to handle. As stated in the Section 1.3, the reinforcement form of rCF composite is very different from the precursor composite and much of the recent research on rCF was focussed at the fibrous microscopic level. The marked difference in the physical form of vCF and rCF has become the biggest barrier in a ‘closed CFRP life cycle’ that prevents the reuse of CF waste in the same structural units from which it was discarded [9, 18]. The maximum potential of carbon fibres can be exploited only when the fibres are realigned and preferably continuous, thereby achieving fibre volume fractions close to 0.5.

The mechanical means of realignment such as combing, gilling and carding typically employed for the production of clothing textiles from wool or cotton could severely damage the carbon fibres. Potential techniques for alignment of discontinuous fibres including extrusion processes, filtration approaches, and the use of centrifugal forces, magnetic or electric fields and pneumatic means is generally limited to the alignment of short fibre composites. In certain cases, the degree of alignment was reported to be unsatisfactory [52, 53]. The HiPerDiF (High-Performance Discontinuous Fibre) method, a continuous hydrodynamic alignment process, directs a fibre-water suspension jet through a nozzle into a narrow gap between two parallel plates to form highly aligned tow type preforms. The mechanical performance of aligned rCF was reported to be comparative to continuous fibre composites and achieved a fibre volume fraction of 0.55 but this laboratory scale set up is, so far, limited to fibre tows of 3 mm in length. The authors concluded that the use of thermoset rCF composites were not favourable for closed loop recycling [54, 55]. The initial development of a bench-top centrifugal fibre alignment rig as per the fibre alignment process developed by the Explosives Research and Development Establishment (ERDE) used a filtration approach to form an aligned mat of 0.46 fibre volume

fraction with 3 mm long fibres. The fibres were suspended in glycerine to form a CF slurry that was fed via a convergent nozzle into a rotating drum with a mesh screen set at 1500 rpm. The aligned fibres deposited themselves in the mesh containment and a vacuum was used for extracting the glycerine [56]. Carbon Conversions had developed a 3-Development Preforms (3-DEP) process to manufacture fabrics of 0.3 fibre volume fraction that controls the placement and orientation of fibres up to 25 mm in length [57]. A uniweave process was developed at the University of Bordeaux for aligning short, discontinuous fibre tows after solvolysis and was compared with a laminate manufactured with random, fluffy recycled fibres. The overall fibre alignment, fabric areal weight, fibre volume fraction and tensile properties in the composite incorporating fluffy fibres were found to be much less than the laminates incorporating discontinuous tows [18, 58]. Another alternative to fibre realignment was developed by blending rCF of 50 mm in length with 20 mm long PP fibres into a continuous sliver, that was drafted and spun into a yarn. The yarns were then wound onto a steel frame unidirectionally and compression moulded [39].

The limitations of these realignment processes are identical in that either they require short fibres or the processes have not been scaled up in spite of the potential they offer. The development of a high volume, low cost product is essential to make rCF a successful commodity, and thus attempt to close the CFRP life cycle loop. Rapid production and conversion of fluffy discontinuous fibres into useful end products as an economically viable process can be achieved via a textile process such as transformation into non-woven fabrics by either dry laid or wet laid papermaking techniques.

rCF recovered by fluidised bed pyrolysis was manufactured into its composite structure by comingling rCF, with an average fibre length of 1.43 mm, with PA fibres by a wet papermaking process into a non-woven mat. The fabric was compression moulded resulting in a thermoplastic composite of 0.25 fibre volume fraction with randomly dispersed rCF. Its static

tensile characteristics and life cycle environmental impact of CF recycling was studied with an identically manufactured composite reinforced with vCF of 12 mm average fibre length. It was found via the respective energy model that the energy requirement of rCF production is very low relative to vCF [59]. A preliminary study on rCF composite was conducted on an out of date 2-D CF/epoxy woven prepreg fabric, subjected to pyrolysis at different temperatures and remanufactured into its thermoset composite structure by resin film infusion, preserving its woven reinforcement architecture. Pyrolysis at lower temperatures resulted in deposition of residual resin on rCF whereas at higher temperature cycles, the fibre strength was severely degraded. It was found that re-manufacturing was challenging as they were contaminated with residual resin. The mechanical performance at the fibre and composite level was reported to be very complex and depended on the pyrolysis temperature cycle and remanufacturing process [60]. The pyrolysis process at ELG Carbon Fibre Ltd. has since been optimised to reduce residual resin contamination and fibre strength degradation. Further studies on rCF composites have been studied on 0.25 V_f thermoset and 0.2 V_f thermoplastic (CF-PP hybrid) varieties of dry-laid non-wovens made of vCF of fibre lengths between 5 – 100 mm and wet-laid non-wovens made of pyrolysed rCF of fibre lengths between 10 – 30 mm. The tensile characteristics of 150 gsm dry-laid non-wovens outperformed 250 gsm wet-laid non-wovens in both the thermoset and thermoplastic varieties, and this difference was tied to the difference in areal weights of the fabrics. The authors concluded that a higher difference in strength between the warp and weft directions indicates improved orientation of the fibres [61]. Similar to the non-woven rCF textile fabrics made by ELG Carbon Fibre, CFK Valley Stade Recycling GmbH & Co. KG had developed CarboNXT recycled non-woven veils for SMC processes and had found that SMC reinforced with rCF non-woven mats had significantly better tensile and bending properties in comparison with SMC reinforced with chopped vCF. Further studies on the same

materials demonstrated that non-stitched rCF non-woven composites had better mechanical in-plane properties in tension, compression and bending than stitched composite varieties [62].

The obstacles to product development have been pinned down to the lack of appropriate specifications, misinformation regarding the availability of an industrial CF recycling process and lack of confidence in the quality of the products that could be overcome by developing further applications for the high quality rCF composites [63]. Given the different form of rCF from that of vCF composite materials, recycling of carbon fibre is not a completely closed loop process. Nevertheless, rather than disposing of carbon fibre waste, the current recycling and reprocessing technologies offer a valuable new commercial product that requires different approaches to design, testing and material selection, until a more efficient reprocessing methodology is introduced.

2.3 Review of Static Test Methods

The specification and use of rCF composites in potential engineering applications requires the development of data that can give a comprehensive description of the material system and the cost involved in qualifying new materials is substantial. Traditional materials used in structural applications are defined by well-established standards and handbooks. The major barriers to the increased adoption of composites have been the lack of awareness and applicability of standards for composites [64, 65]. The existing standards which characterise composites are limited to particular composite reinforcement systems such as unidirectional and woven architectures. This is because much of the fibre reinforcements during the early development of composites in the 1980's involved the production of long, continuous fibres which is unattainable with the current technologies available for the manufacture of rCF composites. Codes and standards were eventually developed with emphasis on continuous forms of composites which spurred their adoption in structural applications. The set of test methods that are traditionally employed to qualify a composite material by the 'building block' certification pyramid predominantly used by the aerospace industries are specific to continuous fibre composites. However, questions arise regarding their applicability for qualifying new composite material systems. Furthermore, design professionals lack confidence in the reliability and long term durability of advanced composites, which is particularly true for rCF composites owing to the absence of data and design guidelines besides the stigma involved in the use of 'recycled materials'. This forms a barrier in the adoption of new forms of composites and hinders the use of sustainable composite structures. The response of rCF on exposure to various environmental conditions is thus of significant interest.

The inherent anisotropic nature of composites, be it the conventional continuous forms or the discontinuous forms we see in rCF materials, demands an extensive amount of inter-laboratory and intra-laboratory testing to determine the design allowables of the material. Different test

protocols need to be developed to characterise this new branch of materials that can recognise its application and that adequately represent them. The need for the careful preparation of specimens for testing and different forms of reinforcements demanding altered test methods from the conventional composite forms aggravates the problem of inhomogeneity [66].

The common practices in literature for characterising the basic static mechanical properties in tension and shear are quite diverse and are subject to the nature of reinforcement in the composite. The acceptance of standardised test schemes for other reinforcement forms depended heavily on the response of the material to these loads.

2.3.1 Static In-plane Tension Tests:

The choice of standard tensile test methods in literature for various reinforcement types and structures is predominantly between the straight-sided geometry described by ASTM D3039 [67], BS EN ISO 527-5 [68] and the dogbone geometry described by ASTM D638 or BS EN ISO 527-4 [69], besides unorthodox shapes such as bowtie geometries [70], all represented in Figures A2.1 – A2.4. As seen in Table 2.3, the ambiguity in the selection of appropriate testing practice for a material similar to non-woven rCF is reciprocated at the industrial level too. Certain industries such as Airbus tend to develop independent test methods to qualify composites such as AITM-1007 for tensile properties [71].

S.No.	Reinforcement nature	Test method	Source
1.	Wet-laid non-woven CF/PP; fibre length of 6 mm	ASTM D638	[72]
2.	UD prepreg CF/epoxy	ASTM D3039	[73]
3.	Randomly oriented prepreg chips of discontinuous CF/epoxy	ASTM D3039	[74]
4.	Aligned short fibre (3 mm length) rCF/epoxy	ASTM D3039	[75]
5.	Plain weave and Eight Harness Satin woven CF/epoxy	ASTM D3039	[76]
6.	Randomly dispersed Kenaf/PP, batches of 130 mm and 20 mm fibre lengths	ASTM D638	[77]
7.	Non-woven Kenaf/epoxy, fibre length 40 mm	ASTM D3039	[78]
8.	Randomly oriented CF/PA6, fibre length 25 mm	JIS K7164 (similar to ASTM D3039)	[79]

9.	Plain Weave, continuous GF/PU and GF/Epoxy	ASTM D3039	[80]
10.	Random, discontinuous GF/PET, fibre length 50 mm	Non-standard geometry	[81]
11.	Realigned tows of rCF/epoxy	ASTM D3039	[58]
12.	Discontinuous, non-crimp fabric of CF/epoxy, fibre length 30 mm	ASTM D3039	[82]
13.	Discontinuous, non-woven Kenaf/PP and Jute fibre/PP, fibre length 60 mm	ASTM D638	[83]
14.	Random, chopped CF/ Vinyl Ester, fibre length 25 mm	ASTM D638	[84]
15.	Discontinuous aligned CF mat/epoxy, fibre length 3 mm and 12 mm	ASTM D3039	[56]
16.	Woven rCF/epoxy	ASTM D3039	[85]
17.	Random continuous rCF/epoxy, fibre length 200 mm	ASTM D3039	[86]
18.	Discontinuous, aligned and random rCF/epoxy, fibre length up to 90 mm	ISO 527-5/ ASTM D3039	[87, 88]
19.	Chopped strand CF/polyester	ASTM D638	[57]
20.	Random non-woven glass/polyester	ASTM D3039	[89]
21.	Random and aligned, wet laid non-woven rCF/epoxy, fibre length of 10 mm	ISO 527-5/ ASTM D3039	[90]
22.	Random chopped rCF/PEEK, fibre length up to 20 mm	ASTM D3039	[91]
23.	Quasi-isotropic, continuous, prepreg CF/epoxy	AITM-1007	[71]
24.	Random, discontinuous GF/epoxy, fibre length 25 mm	ASTM D3039	[92]
25.	Random short GF/epoxy	ASTM D3039 & ASTM D5379	[93]
26.	Needle punched, non-woven GF/polyester composite, fibre length 70 mm	ASTM D3039	[33]

Table 2.3: Test methods identified in the literature for similar composite reinforcements to non-woven rCF composites

The coupon geometry must be designed such that the stress will be greater in the central gauge section than in the grips where the tensile load is introduced. With the straight sided/rectangular shaped coupons there generally is a combination of compression, shear and axial tensile forces acting in the grip section of the coupon that interfere with the efficient distribution of stress into the central gauge region of the material. Load transfer can be improved with the use of end-tabs as described in the standard but this does not guarantee an even distribution of stress across the gauge section of the coupon and is particularly true for materials that are not composed of continuous reinforcement types. MIL-HDBK-17-1F Vol.1 states that tensile

specimens with dogbone geometry are generally accepted for characterising low-modulus (below 20 GPa), unreinforced materials and low-reinforcement volume materials incorporating randomly oriented fibres [94]. ASTM D638, initially developed for testing unreinforced plastics, does not adequately cover testing parameters for advanced composites due to its intended scope, but it is also used to characterise composites by researchers and sometimes in industry as seen in Table 2.3. ISO 527-4 further distinguishes the use of dogbone geometry for composites incorporating non-unidirectional mats, short or milled fibres and isotropic composites. However the classification of short fibres in composites can be vague and reinforcements with fibre lengths up to 50 mm long generally fall into this category, defined by the load transfer length from Equation 2.1 [29]. In addition, the distribution of fibres in non-woven rCF mats, although random, a greater percentage of fibres has been found to orient themselves in the weft direction, a proprietary feature of textile carding mill – hence the resulting rCF composite is not expected to be isotropic in nature.

$$\frac{l_t}{d} = \frac{\left(\frac{E_f}{E_c}\right) \sigma_c}{2\tau_y} \quad (2.1)$$

where l_t is the load transfer length from the fibre to the matrix, d is the fibre diameter, E_f and E_c are the elastic moduli of the fibre and composite respectively, σ_c is the composite failure strength and τ_y is the interfacial shear strength between the fibre and the matrix.

As described in ASTM D638, the use of a particular geometry should primarily relate to the nature of the reinforcement in the composite and its fibre volume fraction rather than setting a limit based on the estimated material stiffness at 20 GPa [69]. In the case of thermoset based composites, while several authors have used straight sided geometry for studying the tensile response of non-woven discontinuous composites, the problem rests in the premature failure of the material as evident in the scarcity of coupon failure in the central gauge section [47, 82, 86-88, 92]. For the few coupons that may indeed fail in the gauge section, the cause of failure

could be attributed to a void or a manufacturing defect at the point of failure rather than a true representation of the material strength. The presence of a tri-axial stress state at the grips may suit continuous fibre composites in transferring the load to the central gauge section but may not suit composites reinforced with short fibres.

The use of straight sided specimens in a study relating to the impact of needle punching density on the mechanical performance of an E-glass/polyester composite of fibre length around 70 mm indicated that the tensile strength in both warp and weft directions increased with increasing punching density. The result seems erroneous as the fibre damage and material isotropy increases with increasing punching densities and hence could be the influence of poor load introduction to the specimen gauge section, given that the flexural, impact, tension-tension fatigue and wear properties have all declined with punching density [33].

The low reinforcement content in such composites drives the material failure under tension to be matrix dominant rather than fibre dependent and this is particularly true with composites reinforced with short fibres, non-woven composites and recycled carbon fibre laminates. The loftiness in rCF non-woven mats, a consequence of the needle punching process, limits the maximum attainable fibre volume fraction. Higher fibre volume fractions can theoretically be attained at higher compression pressures but due to the intermingled nature of the reinforcement, the fibres could damage themselves and contribute to higher laminate variability. A constructive argument against the use of dogbone geometries could be the reduction in representative area of the material due to the smaller width and hence cross section in the coupon. This would however be reflected as an increased standard deviation of the sample. An exception to the use of dogbone coupons on rCF composites would be if the fibres were to be aligned in a particular direction and in such a case [75], straight sided rectangular coupons are more relevant to prevent splitting failures at the transition region. The use of rectangular geometry for non-woven rCF composites could tentatively be used for preliminary

estimation of the material tensile response but can by no means describe the precise strength limits of the material itself. Given that composite material qualification and standard practices are costly and time-consuming, it is imperative that the best method is employed for the right material system.

The Iosipescu test method subjecting a rectangular coupon with V notches in shear has also been used to estimate the tensile strength of a composite, provided a tensile failure mode occurs. A good correlation was observed in a study involving a thermoset glass fibre composite but the gauge length of such a specimen is under a combined tension, compression and shear loads that the result should only be an estimation useful in cases of limited availability of material sample [93, 95].

2.3.2 Static in-plane and out-of-plane shear:

As many industries begin to rely more on composites and bonded materials, reliable and accurate shear testing becomes a necessity [96]. The anisotropic nature of composites mean that it is important to understand the shear response including in-plane shear and out-of-plane shear. In addition to the material structural capabilities, they can be devised to assess the fibre-matrix interface and inter-ply bond quality. The random dispersion in non-woven rCF composites imply that its shear characteristics strongly depends on how the composite is loaded with respect to principal material directions, with reference to Figure 2.2. It would be more critical to compute the weaker interlaminar shear over in plane shear as the reinforcement architecture would provide additional in-plane and biaxial mechanical strength in the XY shearing planes. Many test methods have been developed to measure out-of-plane shear such as Short Beam Shear (SBS) [97, 98], Double Notch Compression [99], Double Beam Shear [69], Iosipescu shear [100], 10 or 45 degree off axis tensile test [68], two-rail shear [97], etc. However, getting reliable and repeatable data is of particular concern in the selection of test

methods for rCF composites. In the event of an interlaminar shear failure, cause for failure could be the breakdown of the fibre-matrix interface, a matrix failure, delamination between the plies or a combination of them depending on the interfacial strength between the fibre and the matrix and the shear strength of the matrix which makes interpretation of the experimental results complicated.

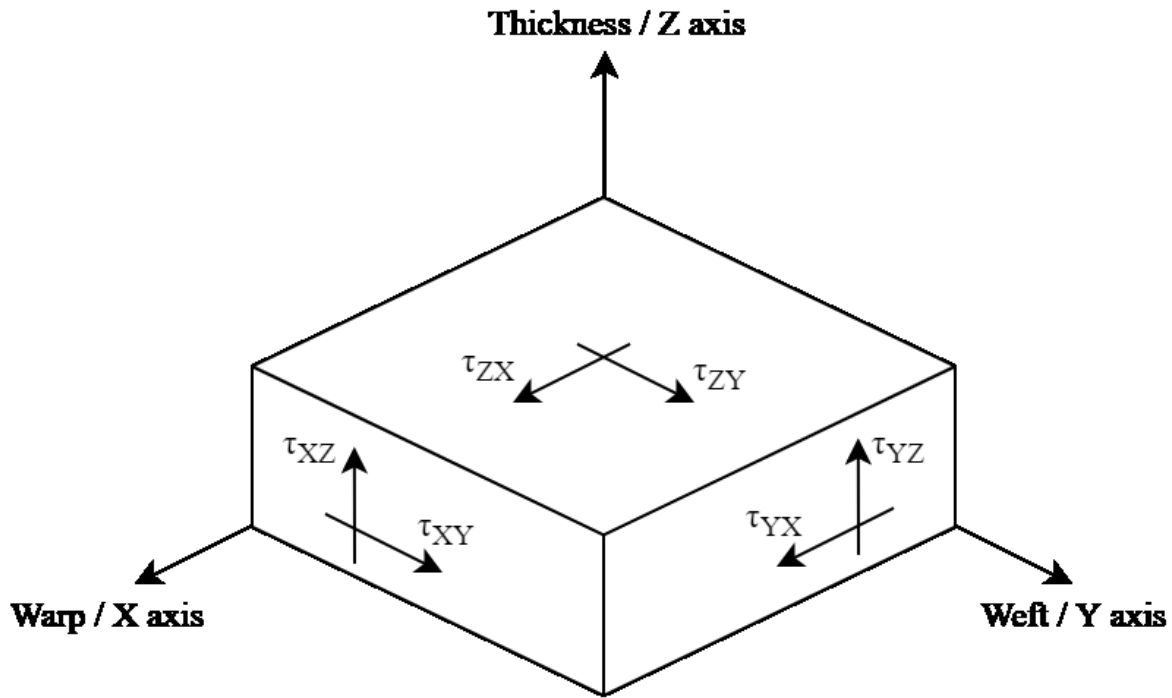


Figure 2.2: Shear plane notations in the X (warp), Y (weft), and Z (thickness) directions for rCF laminates used in this research

The difficulty with the majority of interlaminar shear test methods is the requirement to achieve a state of pure and uniform shear over the gauge region repeatedly for that specific material under examination. Judging the validity of a test at the composite level is more limited than that at the fibre level, e.g., the micro-droplet test, in that the actual locus and modes of failure have to be consistent with the standards originally established for conventional composite reinforcements. The SBS test has been a popular, widely known and quick test to determine the apparent interlaminar shear strength of a composite but shear failure is rarely achieved.

Studies on an rCF composite with non-crimp long random fibre reinforcement of 0.33 V_f reported an ILSS of 37.2 MPa by SBS. It was justified that it was typical in discontinuous composites to have lower short beam strength than continuous fibre systems due to the absence of well-defined interlaminar planes [86]. Other studies report that it may be necessary to alter the specimen geometry or the test procedure, even for continuous fibre reinforcements as had been done for the SBS test. This is possible by reducing the surface area of shear failure by introducing a longitudinal notch [101], use of a thick beam [102] and bonding the laminate between strips of metallic plates [103] to facilitate interlaminar failure. A recent variant of the short beam shear test is the double beam shear (DBS) test that was reported to produce interlaminar failure in unidirectional (UD), cross-ply and quasi-isotropic composite layups by 5 point bending, after failing to produce any delaminations by the SBS test [104].

The shear properties of a composite are often determined by the Iosipescu shear test. Pure shear failure in an Iosipescu in-plane shear test is characterised by a notch-to-notch crack and can be seen in composites with layups of continuous fibre reinforcements of $[0]_s$, $[90]_s$, or $[0/90]_s$ specifically along the 90° direction. To accommodate the composite's orthotropy, the optimal V-notch angle of an Iosipescu specimen is rescaled by Equation 2.2:

$$\tan \theta = \frac{\tan \theta_{iso}}{\sqrt[4]{E_2/E_1}} \quad (2.2)$$

where $2\theta_{iso} = 110^\circ$ and E_2 and E_1 are elastic moduli along the principal directions of the laminate being tested [105, 106]. The modified V notch angle specimens was reported to produce uniform shear stress fields for a range of CF/epoxy and GF/epoxy composites. It was concluded that the 90° notch angle works best for a highly anisotropic material tested in the weaker direction [107].

However, for random fibre reinforced composites, failure resorts to a tensile failure characterised by a crack at 45° from the notch axis [95, 108-110]. This is also true for 3D textile

composites where a 4 notch Iosipescu specimen was developed due to the lack of weak shear strength planes in the material [111]. In-plane shear failure is plausible in laminates with a higher degree of anisotropy than random fibre reinforced composites due to the influence of normal stresses in the gauge section of the specimen.

The use of Iosipescu shear for the determination of out-of-plane shear or interlaminar shear, along the XZ and YZ planes, has been seldom reported because of the difficulties involved in manufacturing a thick composite laminate and the catastrophic failure in transverse tension along notch flanks for UD specimens [112-114]. The Iosipescu shear strength of a UD laminate along the 90° direction was reported to be numerically equal to the through the thickness shear strength and hence testing in the XZ plane is rarely used in practice [100].

Along the 0° direction of a UD laminate, the common observation of failure is a sequence of horizontal cracks and splitting of fibres near the top and bottom notch roots followed by horizontal cracks between the notches in the gauge section. It was recommended to increase the angle of the V notch as per Equation 2.2 to induce horizontal delamination cracks in the gauge section between the notches but it was shown that the stresses associated with the initial horizontal splitting and the ultimate shear failure are relatively close to each other. Furthermore, the point of failure of the material to be considered as representative for the material is debatable and the shear strength of the material should be linked with the first delamination or horizontal splitting observed rather than the ultimate strength [100, 106, 107]. Although these arguments may hold for UD composites, it could be understood that for non-woven and other textile composites, achieving shear failure and the material response to shear loads depend heavily on the nature of the composite reinforcement and the plane of load introduction into the test specimen.

Another alternative to measure interlaminar shear is the double notch shear (DNS) test and it has been shown that the shear strengths from the Iosipescu shear test and DNS shear test along

the XZ plane are identical in a UD CF/epoxy composite [100]. The DNS remains a simple and reliable test method for interlaminar shear characterisation on the condition that the failure of the specimen occurs as a longitudinal notch to notch crack signifying the delamination of the laminate due to a compression load. Consistent shear failure have been reported in CFRP and GFRP based UD and cross-ply fibre systems [108, 115] and it was later recommended that the a 90 degree lay-up be used to induce pure interlaminar shear in the gauge section of the specimen [116]. However DNS has a lot of drawbacks including poor stress uniformity, high stress concentrations at the notch and dependence on the notch distance and depth that lead to the development of inclined double notch shear test [100, 117, 118].

2.4 Fatigue in Composites

A major challenge associated with rCF composites lies in establishing suitable markets and their introduction to structural applications, because their capabilities over longer periods of loading are not well established [18, 23]. Previous work with rCF composite forms has been limited to static mechanical tests. The use of vCF in a non-woven reinforcement form is rare as it serves little purpose, application and cost wise. The research here can be considered as the first step towards a more profound understanding of the tension-tension fatigue response of rCF composites. The fatigue testing methodology developed for rCF composites is in line with the general practices for composite materials, along with the principal conclusions derived from their static mechanical response.

The general consensus with recycled and short fibre composites is that they have a shorter life period, behave poorly under cyclic loads and thus could be unfit for structural applications. Many of the failures of structural components have traditionally been attributed to fatigue and hence it is critical to understand if rCF composites are suitable for long-term usage under fatigue loading conditions. Fatigue damage in composites is complex because they often undergo multiple locations of micro-damage simultaneously. Failure eventually occurs as a

combination of matrix damage, delaminations, fibre-matrix debonding, void growth, interlaminar cracks and fibre breakage [119]. The initiation and growth of micro cracks during cycling leads to a continuous material softening and apparent degradation of its elastic modulus [120]. During fatigue loading, an initial decrease in stiffness is seen due to early composite damage, followed by slow material degradation during its life period and ultimately a rapid stiffness reduction causing fracture. This concept is applied to the design of aircraft structural components where the residual strength and stiffness are considered to decrease as damage accumulates due to fatigue loading, as shown in Figure 2.3 [121-123].

Various generalised empirical fatigue theories have been proposed, based on the stiffness and residual strength degradation of composites, which are however not directly related to the damage mechanism of composites [124]. The development of damage due to tension-tension fatigue in continuous, woven and non-crimp textile composites, as explained experimentally [125], reflects the degradation of stiffness of samples during fatigue tests. The drop in stiffness in unidirectional [126-129], woven [130, 131], non-crimp [125, 131, 132], short fibre [120, 133] and discontinuous [134] carbon fibre and glass fibre composites with fatigue loading has been widely reported and often associated with continuous matrix deterioration and disintegration of the fibre-matrix interface [135]. In load-controlled fatigue tests, the changes in the amplitude of fatigue strain that result in changes in slope of fatigue hysteresis curves is an indication of stiffness change in the material. The stiffness change in composites under cyclic loading is significant because many engineering structures are stiffness critical and are designed to undergo definite deformations for optimum performance [136]. The drop in stiffness can though, be used as a non-destructive technique to monitor fatigue damage in the material [137].

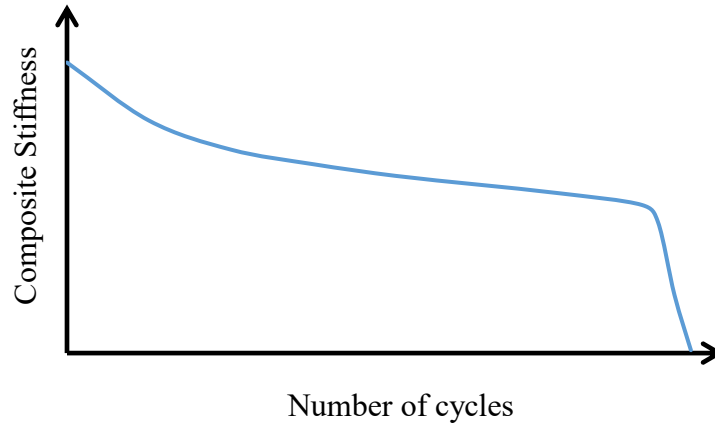


Figure 2.3: Schematic degradation of stiffness due to fatigue loading as hypothesised in literature

An experimental study on the post-fatigue tensile behaviour of a 5-harness satin weave CF composite showed that the induced fatigue damage caused a 7-8% increase in the stiffness of the specimens [138]. This was explained as the straightening of the load-carrying warp yarns in tension-tension fatigue. Studies on natural fibre/epoxy composites made of random mat reinforcement have not shown any indication of stiffness degradation [139], rather an increased stiffness was reported owing to the partial alignment of micro fibrils towards the fatigue loading direction [140, 141].

Fatigue damage mechanisms are dependent on the type of loading and the amplitude of fatigue loads. The failure mechanisms involved in low-cycle fatigue are similar to static failure mechanisms and typical fatigue damage mechanisms occur in high cycle fatigue [142]. The fatigue load response of textile composites depends on the architecture of their reinforcement together with the type and volume fraction of its constituents, environmental conditions and loading conditions [143].

2.5 Hygrothermal durability of composites

The exposure of composites to moisture and environmental fluids may also influence mechanical properties and is linked to the plasticisation of the matrix and degradation of the fibre-matrix interface. Generally, the matrix dependent properties of unidirectional vCF/epoxy composites such as transverse tensile strength or interlaminar shear strength are known to decline due to moisture uptake. The impact of moisture on rCF composites is of particular interest due to the lower V_f , reinforcement nature and potential influence of the pyrolysed CF's to fluids. Although CFs are generally impermeable to moisture, the increase of hydroxyl, phenolic and amine groups on rCF surfaces after pyrolysis point to an increase of hydrogen bonding sites to the matrix for water molecules in the composite structure. The composite composition, grade of the matrix polymer, type and proportion of filler, presence of defects and voids and the state of cure and processing conditions are important considerations in assessing the moisture uptake of the material [144].

Moisture absorption in composites is a time and temperature dependent process and generally occurs by diffusion in a Fickian manner, where the moisture uptake reaches an asymptotic value or a saturation point. The bulk diffusion of water molecules in the matrix occupying the free volume voids and the capillary transport into the gaps between the fibre-matrix bondlines or the individual plies in a laminate are the first modes of water ingress in polymer composites [145]. Further, the water molecules either form single hydrogen bonds with the hydrophilic matrix polymer chains by breaking the van der Waals forces between the polymer chains resulting in plasticisation or multiple hydrogen bonds bridging polymer chains that leads to a pseudo or secondary cross linking [146-148]. The single hydrogen bonding is the dominant mode of sorption that causes reduction in physical properties and glass transition temperature. The multiple hydrogen bonding is harder to remove by desorption. A fluctuation of elastic modulus could possibly be expected due to the interplay of these two effects [149]. At this

stage, matrix swelling takes place causing through-the-thickness stresses that may or may not lead to micro-cracking or delaminations [150, 151]. Besides the dimensional and mechanical property changes caused due to swelling, absorbed water can cause degradation of the composite by discolouring or blistering at its surface [145]. The damage mode of thermoset composite materials, which generally have brittle matrices, could change from matrix dominated to fibre-matrix interfacial failures after accelerated aging processes [152]. Furthermore, the fibre-matrix interface is a crucial region as moisture induced into this interface, possibly aided by the differences in the thermal expansion coefficients between the fibre and the matrix, can cause irreversible damage and further micro-crack propagation, all of which is detrimental to the material strength [151, 153].

Assessing the global environmental durability of composites at a laboratory scale can be challenging as the standard test methods measuring the degradation examines a single mechanism in isolation. In addition, the accelerated tests for one particular mechanism concerns the most damaging environment at this scale and may not correspond directly to the real world environments where the composite is exposed to additional weathering conditions such as ultraviolet or high energy radiations, erosion due to sand and rain, acids and alkalis and biological effects [145]. The large variability associated in such a hypothetical test subjected to multiple degrading environments would make it difficult to judge the reasoning behind the actual damage of the material. Hence it would be ideal to evaluate the impact of one such mechanism, i.e., hygrothermal durability as an accelerated test, that may be critical to the potential application phase of rCF composites. However, a well-made and well-designed composite structure is extremely durable. CF/epoxy composite laminates are adversely affected to moisture especially when they are overloaded and subjected to strains higher than expected.

2.6 Summary

2.6.1 Applications for rCF composites

The adoption of composites in engineering applications is driven by the need to achieve light weighting and energy efficient systems. The typical composite properties commercially available are listed in Table 2.4. The selection of composite materials for a particular application may either be performance driven or cost driven. The use of UD CF have been able to increase the factor of safety and achieve light weighting simultaneously in strength and stiffness driven applications. However its widespread selection has been limited as CF composites are generally expensive and comes at the steep price of neglecting sustainability and environmental impacts.

S.No.	Composite System	Density (g/cm ³)	Tensile Strength (MPa)		Tensile Modulus (GPa)	
			σ_l	σ_t	E_l	E_t
1.	UD vCF/epoxy (AS/H3501; $V_f \sim 0.66$) [29]	1.6	1447	51.7	138	8.96
2.	Woven vCF/epoxy (T300/Fiberlite 934; $V_f \sim 0.6$) [29]	1.5	499	458	74	74
3.	UD E-glass/epoxy; $V_f \sim 0.45$	1.8	1062	31	38.6	8.27
4.	Chopped 25 mm fibre length, SMC, CF/Epoxy (Lytex® 4149); $V_f \sim 0.55$ [154]	1.48	217		34.5	
5.	Chopped 12.7 mm fibre length, SMC, Fibreglass/Epoxy (Lytex® 9063 BK-E); $V_f \sim 0.63$ [155]	1.82	193		18	
6.	Non-woven rCF/epoxy, SMC, <i>as advertised</i> ; $V_f \sim 0.3$ [156]	1.37	254.1	388.6	21.7	35.9

Table 2.4: Mechanical properties of commercially available composites

The introduction of rCF composites into the market does not completely close the CFRP life cycle given the current technological limitations in drawing out continuous recycled fibres after pyrolysis. Nevertheless, they support the continued efforts in the conversion of would-be landfill waste into valuable products, reducing environmental impact and their use could aid in

the efficient management of fuel and overall costs. The end product of recycling CF composites is rather a new composite form different from the virgin CF structure. The assessment of the rCF composites in their applicability to structural components thus becomes important.

The end application of rCF composites would certainly be defined by the ease of manufacture, performance, weight-saving and cost criteria set for a particular product, and requires analysing the benefits of using rCF over conventional materials in the form of either evolutionary redesign or original design from a new concept [157, 158]. The high cost of vCF composites allows their use only in the top end sectors. The key enabler of using CF composites in automotive applications would be the lower supply cost that rCF composites offer. While the aerospace industries dissociate themselves from discontinuous CF mats in critical structures because of their lower mechanical efficiency and variability/uncertainty of mechanical performance, the automotive industry, although extensive users of composites, are less willing to pay the cost for vCF mats. The supply of lower cost fibres recovered from waste products could assist in the transition to lighter and more fuel efficient automobiles [6, 150, 159]. A life cycle assessment of compression moulded non-woven rCF composites in comparison with vCF composites concluded that rCF can replace conventional metallic components in automotive applications whilst achieving significant weight and cost savings [3]. Furthermore, it was determined by Airbus that rCF non-woven composites could meet the basic composite laminate requirements for aircraft interior sidewalls and could potentially replace continuous glass fibre offering significant advantages in cost, weight and surface finish [160]. BMW have suggested the use of SMC rCF as reinforcement C-pillars, roof bow and trunk partition walls [161]. Further applications of rCF composites can be realised by the development of reliable data. Identifying the strength and deformation limits of the material to provide a comprehensive description of the material system will hence offer a feasible alternative material choice to a design engineer.

2.6.2 Assessment of mechanical behaviour

The list of standards and testing protocols available to material production industries, to evaluate new composite material systems, may not be appropriate considering that they were developed for traditional continuous, unidirectional fibre reinforcement systems, which were themselves gradually modified and adapted from gauging the performance of metals. The performance of advanced composite structures is analysed by heavily relying on existing codes and standards that inhibits the uptake of new composite forms across many sectors for existing or new applications despite the benefits that the materials offer [162]. The difficulty with composites as always lies in their anisotropy and inherent heterogeneous nature whose complexity increases in textile based composites as in the case of rCF composites.

The continuous emergence of new materials that do not respond to loads in the same manner as the earlier developed ones makes it difficult to generate a database and standardized test scheme for the composite family [163]. Furthermore, numerous standard test methods are available for the determination of the same material characteristic but with regards to composites, they have been developed with unidirectional continuous forms of composites in mind. Even the newer alternatives proposed, for example the BS ISO 19927:2018 for interlaminar shear strength determination, have been developed for UD/continuous reinforced composites [164]. These test methods have generally been used in research and industry for the evaluation of new composites, but given their differing material response, they may be inapplicable, resulting in a less reliable dataset. The BSI standards have recognized this drawback for certain composite systems such as natural fibre composites, multi-axial ply composites, textile glass reinforced plastics, sheet moulding compound based composites, etc. and have developed dedicated standard test procedures, for example, BS EN 15534-1:2014 [165], BS EN 13706-2:2002 [166], BS EN 14598-2:2005 [167], BS EN 14527-2:2000 [168], BS ISO 8605:2001 [169], BS EN 13473-2:2001 [170].

The critical technological challenge currently with rCF composites is the inability to replicate the reinforcement structure of the virgin composite system. The processing of the rCF mats into composite plaques by laminate remoulding techniques also play a vital role in the mechanical load response. The random distribution of the discontinuous fibres raises much variability issues. Material variability, long term performance and environmental durability are all factors that could influence material selection. It is therefore prudent to analyse the data and the nature of failure of rCF composites.

It became apparent, both from reviews of literature and in detailed discussions with ELG Carbon Fibre Ltd., that establishing reliable and consistent test protocols for rCF composites is an urgent requirement. The development of appropriate test methods and the necessity of a dedicated set of test protocols for discontinuous, non-woven rCF reinforced composite was identified as a gap in knowledge that has to be addressed. Furthermore, there was a necessity to assess and understand the long-term mechanical behaviour of rCF composites.

Chapter 3: Project Strategy

3.1 Hypothesis

The development of a new composite system in the form of discontinuous, non-woven rCF/epoxy leads to the necessity to generate design allowable data that is representative of this particular commercial product. This data needs to be evaluated and analysed with respect to its use in existing and potential new applications.

The research hypothesis is to assess whether recycled carbon fibre composites require the development of a specific set of standard testing protocols that are different to those traditionally employed for evaluating the performance of virgin carbon fibre composites.

3.2 Research Strategy

Chapter 2 highlights the use of numerous test methods and the rather vague selection practices of macro-scale tests for the characterisation of advanced composite materials. The UK Standards activity highlights the need to harmonise and validate the established test methods for new composite systems. It may therefore be necessary to adapt standard testing practices to suit rCF materials that would enable the generation of suitable design data. This must be assessed at an early stage.

The overall aim of the research is to develop a suite of test protocols to generate reliable design data for rCF composites. The study focusses on analysing the effectiveness of established test procedures to judge the performance of rCF materials at the coupon level. Modifications to the standard testing practices will be proposed if necessary and the implications of the material response will be discussed. A catalogue of effective macro-scale testing methods for the development of preliminary design data of this class of composites will be developed accordingly. A key objective of the research is to assess the fatigue and durability of rCF composites. The variability in test data expected with randomly reinforced rCF composites will

be examined with rigorous statistical data analyses. Figure 3.1 depicts the overall research strategy.

The project explores the practical applications of rCF composites adhering to the ‘building block’ approach to certification of new materials adopted by the aerospace industry, including long-term durability and hygrothermal effects. This study also sheds light on the capability of rCF composites in fatigue critical applications and the material response to cyclic loads with live specimen monitoring, non-destructive and destructive techniques.

In addition, the project assesses the consequences of pyrolysis at the composite level by studying the influence of the reinforcement architecture on discontinuous, non-woven vCF along with rCF composite systems. The effect of surface roughening at the coupon level is also evaluated.

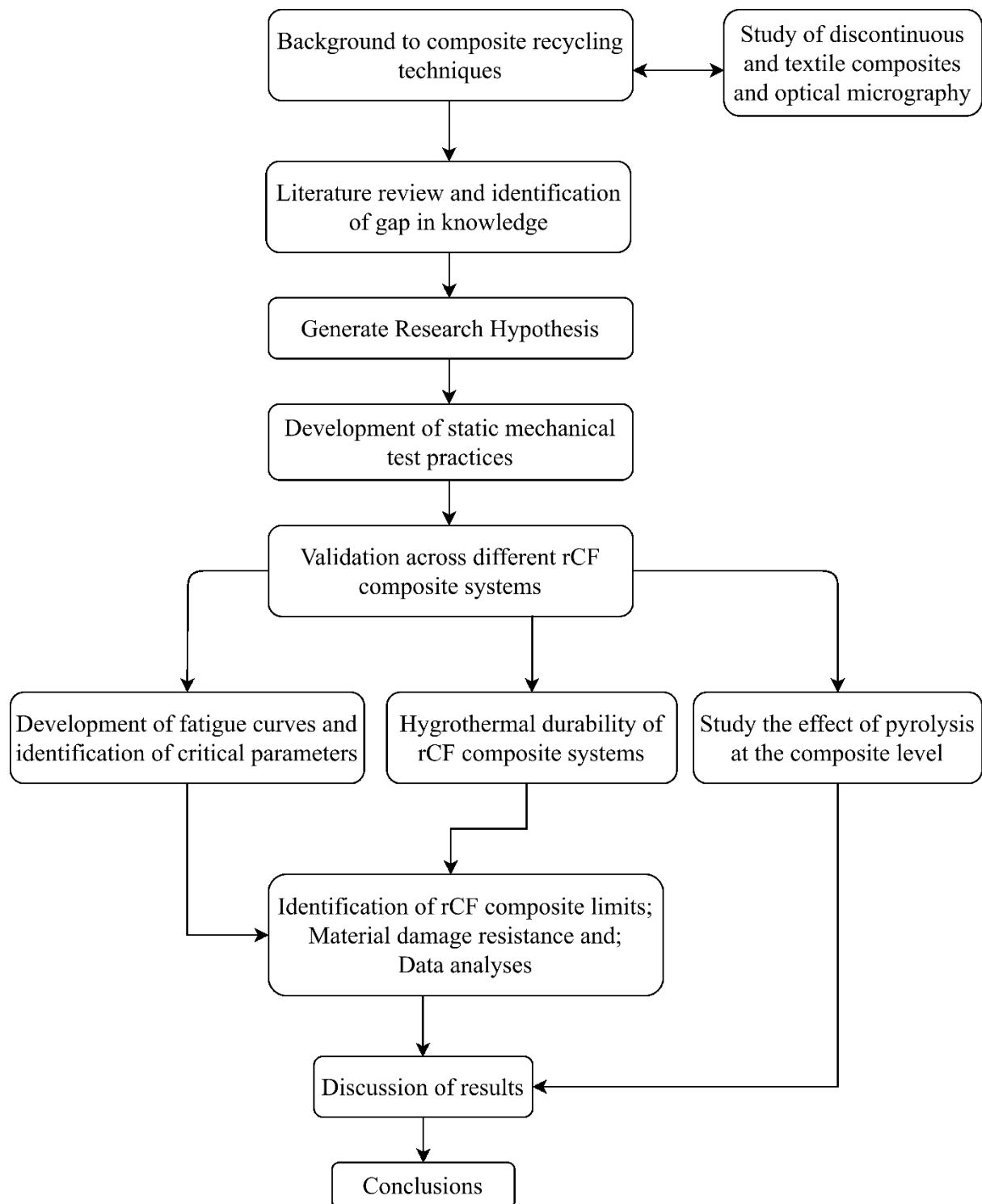


Figure 3.1: Flowchart of research strategy

3.3 Outcomes of Research

The research is expected to provide insight into the:

- i. development of test protocols that adequately represent rCF composites, reducing variabilities that arise due to testing practices
- ii. durability of rCF composite systems in accelerated environments
- iii. steps to study the fatigue response of rCF materials and fatigue failure mechanisms
- iv. qualitative prediction of composite life service
- v. effect of recycling parameters and processing on static and cyclic mechanical behaviour.

3.4 Original contribution to knowledge

In addition to the development of appropriate means of measurement of tensile properties of rCF composites, the research identifies an experimental set up that enables interlaminar shear failure in a multi-dimensional reinforced laminate. The cyclic and durability characteristics of rCF composites represents a new contribution to the literature that identifies the performance limits of the material, aiding in material selection. A fatigue theory is hypothesized that is unique to composites reinforced with discontinuous, non-woven architectures. The influence of recycling at the composite level is analysed, enabling a better understanding of any composite degradation after pyrolysis.

Chapter 4: Materials, Methods and Data Analysis

4.1 Materials

The different rCF composite systems used in this research can be primarily classified based on:

- a) fibre type
- b) resin system and laminate processing methodology.

4.1.1 Fibre Type

The fibres used in rCF non-woven mats have their designated fibre codes from ELG Carbon Fibre Ltd. and are defined in Table 4.1. The strength of recovered carbon fibres themselves evaluated by single fibre fragmentation tests provide estimates of the fibre tensile modulus and tensile strength, as collected in Table 2.2. The recycled fibres used in this research were either standard modulus (SM), of up to 270 GPa stiffness and tensile strengths between 4 and 5 GPa, or intermediate modulus (IM) fibres of stiffness between 270 and 330 GPa and tensile strengths between 5 and 6 GPa [30].

<i>Designated Fibre Code</i>	<i>Fibre Source</i>
<i>SM45D</i>	Repurposed/reused standard modulus fibres; not pyrolysed and; sizing still intact
<i>IM56D</i>	Repurposed/reused intermediate modulus fibres; not pyrolysed and; sizing still intact
<i>IM56R</i>	Pyrolysed fibres from out-of-date rolls, uncured wastes and; sizing removed
<i>IM56L</i>	Pyrolysed fibres recovered from cured laminate wastes; sizing removed

Table 4.1: Fibres used in rCF non-woven mats

4.1.2 Laminate Reprocessing

The laminates were all provided by ELG Carbon Fibre Ltd. Typical dimensions of a laminate plaque were (450 x 450 x 3) mm³. The pyrolysed or repurposed fibres are converted into CARBISO™ M mats which are non-woven carbon fibre fabrics as described in Section 1.3.

The needle punching density for the non-woven mats was set at 30 punches per cm². The non-woven fabrics were cured into rectangular plaques with epoxy resin. The epoxy resin formulations are defined by the process used to cure the laminates. The fibre types used were based on the availability of composite waste type during the course of the research. The cured laminates thus used for characterisation in this research are classified in Table 4.2. The directionality of the laminate was defined earlier in Figure 1.8.

<i>Laminate Curing Methodology</i>	Fibre Type	Epoxy Resin System	Filler/Additive
<i>Liquid Compression Moulding (LCM)</i>	SM45D, IM56R	Hexion™ EPIKOTE™ Resin TRAC 06170 + EPIKURE™ Curing Agent TRAC 06170	HELOXY™ Additive TRAC 06805 Release Agent (1 - 2 pbw)
<i>Sheet Moulding Compounding (SMC)</i>	SM45D, IM56R, IM56L, IM56D	Hexion™ EPIKOTE™ Resin TRAC 06605 + EPIKURE™ Curing Agent TRAC 06608	HELOXY™ Additive TRAC 06805 Release Agent (2 - 4 pbw)
<i>Autoclave</i>	SM45D	Epoxy resin system (Confidential)	Fire Retardant Filler

Table 4.2: rCF laminates based on remoulding techniques

LCM cured rCF laminates used Hexion™ EPIKOTE™ Resin TRAC 06170 (100 parts by weight (pbw)) with EPIKURE™ Curing Agent TRAC 06170 (16 pbw). The resin system is of low viscosity (11 mPa.s at 120°C), benefits from a short curing cycle of 2 ½ minutes at 120°C and is one that is typically used for the manufacture of structural automotive parts. The cured, unreinforced resin system has a tensile strength of 74 MPa and stiffness of 2.57 GPa [171]. The mould release agent was applied to the top and bottom plates of the mould. The rCF fabrics were cut to appropriate dimensions (generally 480mm x 480 mm), laid up, weighed and left on a flat mould of a hot press. The resin was heated to 80°C in an oven and the curing agent to 30°C to reduce their viscosities. The resin to fabric ratio was generally taken as 75:25 by weight. The corresponding weight of the resin taken was mixed well with 16% of the curing

agent. The epoxy resin system was poured over the topmost layer of non-woven rCF fabrics and pressed at 750 Psi and 120°C.

SMC cured rCF laminates used Hexion™ EPIKOTE™ Resin TRAC 06605 (100 pbw) with EPIKURE™ Curing Agent TRAC 06608 (23 pbw). The resin system has a viscosity of 7 Pa.s at 23°C and is suitable for the production of high performance SMC materials reinforced with chopped fibres [172]. Sheets of an intermediate rCF ‘prepregs’ were manufactured by rolling the epoxy resin system on the top and bottom surfaces of the non-woven fabrics on a dedicated SMC line. Release agent was applied to the top and bottom surfaces of the flat mould plates. The rCF prepregs were then cut to appropriate dimensions, hand-laid and pressed at 150°C, 2000 Psi for 10 minutes.

Autoclave cured rCF laminates used an epoxy resin system with a fire retardant filler, suitable for rail, marine and civil applications. The cured, unreinforced resin system has a tensile strength of 44 MPa and stiffness of 5.2 GPa. Similar to the process used for SMC cured laminates, non-woven fabric were pre-impregnated with the resin. The prepregs were then laid up and cured at 120°C for 45 minutes at a pressure of 85 Psi in an autoclave.

The non-woven mats in any of the above processes could be laid in the same orientation (0 degrees) or in a ‘cross-ply’ orientation (0/90 plies). All of the autoclave cured laminates used in this research were made of 4 plies of 200 gsm mats, were of 2 (+/- 0.2) mm thick and had a V_f of approximately 0.21. For LCM and SMC laminate systems, these parameters (i.e. number of plies, areal weight, V_f , laminate thickness, etc.) will be mentioned where used.

4.2 rCF Composite Microstructure and Attributes

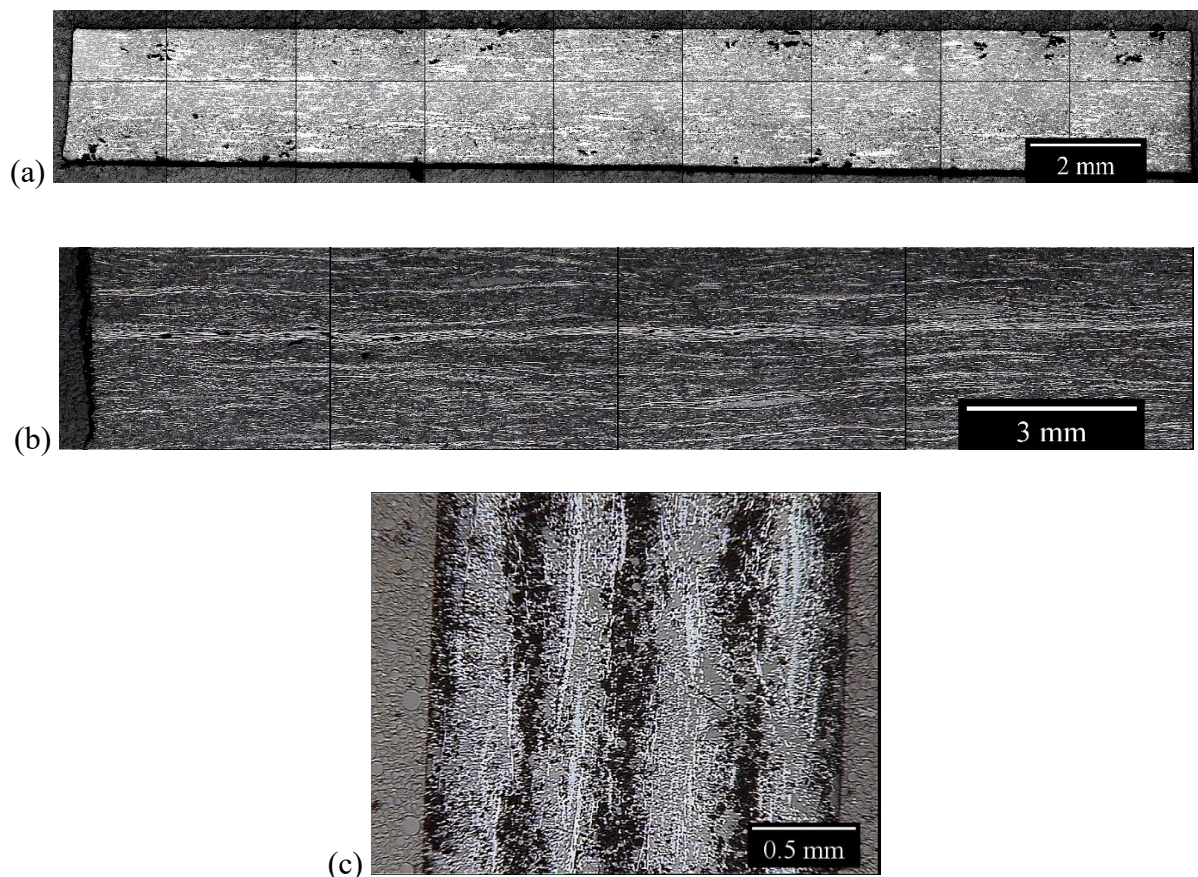
This section discusses in brief the rCF composite microstructure used in this research and their differences from conventional vCF composites. The composite structure and distribution of the fibres in the cured laminates was studied with the help of image analysis by optical microscopic

techniques. Optical microscopy is also useful in determining the volume fraction, void content and thus, in judging the quality of the manufacturing process.

rCF specimens from the composite plaque were encapsulated in a cold mounting medium such as acrylic resin that has fast curing properties at room temperature and has limited shrinkage [173]. The purpose was to attain a well-polished cross-sectional surface to distinguish the constituents of the composite laminate on an optical microscope. Two part acrylic resin with the trade name Variset from MetPrep was used that has a cure time of 15 minutes at room temperature [174]. The specimens were cleaned and dried before encapsulation to ensure good bonding of the acrylic resin. The encapsulation of the samples was followed by initially grinding them with 320p grit size SiC paper to obtain a planar surface. The samples were then polished with 9 μm diamond abrasive on Planocloth H surface paper and followed by 0.3 μm alumina abrasive on Planocloth surface cloths. The surface was cleaned thoroughly with distilled water and air dried after each stage. It was important to avoid any scratches falling on the viewing surfaces as they would be seen as voids in micrographs. These polishing steps leave a mirror-like finish onto the viewing surface of the sample.

Micrographs of the cross-sections of the laminates were taken from an optical microscope, Olympus BX51 in bright field illumination mode and the images were captured using a JVC colour video camera. Generally, voids were distinguishable at low magnifications and the fibres were visible at higher magnifications. The principle of operation is reflected light microscopy where light reflected off the flat, polished surface is captured by the camera. Voids, micro cracks or indentations are seen in darker shades as light deflects off the sample at different angles. The micrographs were analysed using ImageJ software [175], which digitizes the micrograph into a binary image, creating a contrast between the constituents and counts the fibre ends or voids as an area fraction depending on the image magnification. Figure 4.1 (a) – (c) depicts the cross-sectional views of LCM, SMC and autoclave cured rCF composites as

opposed to the cross-sectional view of a typical 0/90 vCF composite, manufactured by vacuum bagging UD preregs in-house. The darker spots within the cross-sectional views are identified as voids within the laminate and Figure 4.1 (c) shows the presence of ply separations in autoclave cured laminates. Figure 4.2 shows the typical microstructure of compression cured rCF composites at higher magnification that highlights the lower fibre packing efficiency and depicts regions of fibre rich locations in rCF composites. The random fibre distribution in rCF composites is evident from Figures 4.1 - 4.2 and much of the ‘aligned’ fibres in sections of the laminate are part of tows of carbon fibre that were not dispersed during the carding process. As a result, there could be regions of fibre-rich areas and resin-rich areas within the laminate.



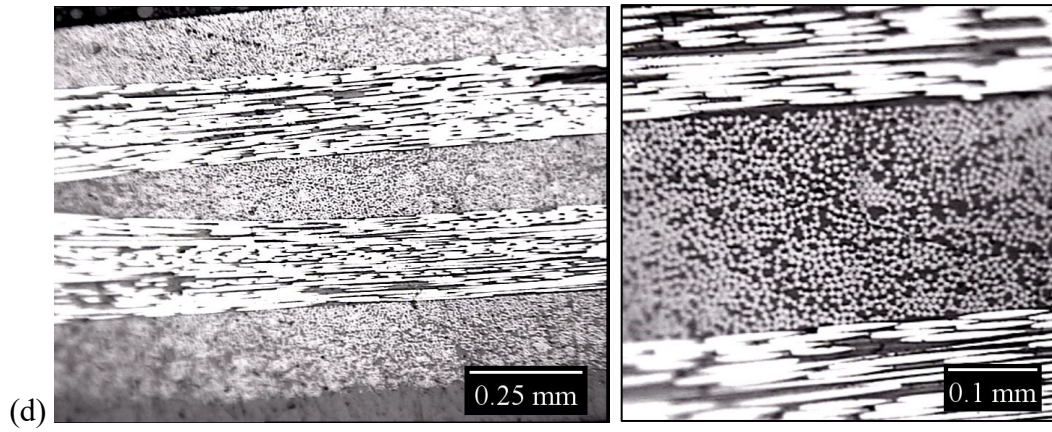


Figure 4.1: Cross sectional views of (a) LCM laminate, (b) SMC laminate, (c) Autoclave cured laminate and (d) Typical 0/90 vCF laminate

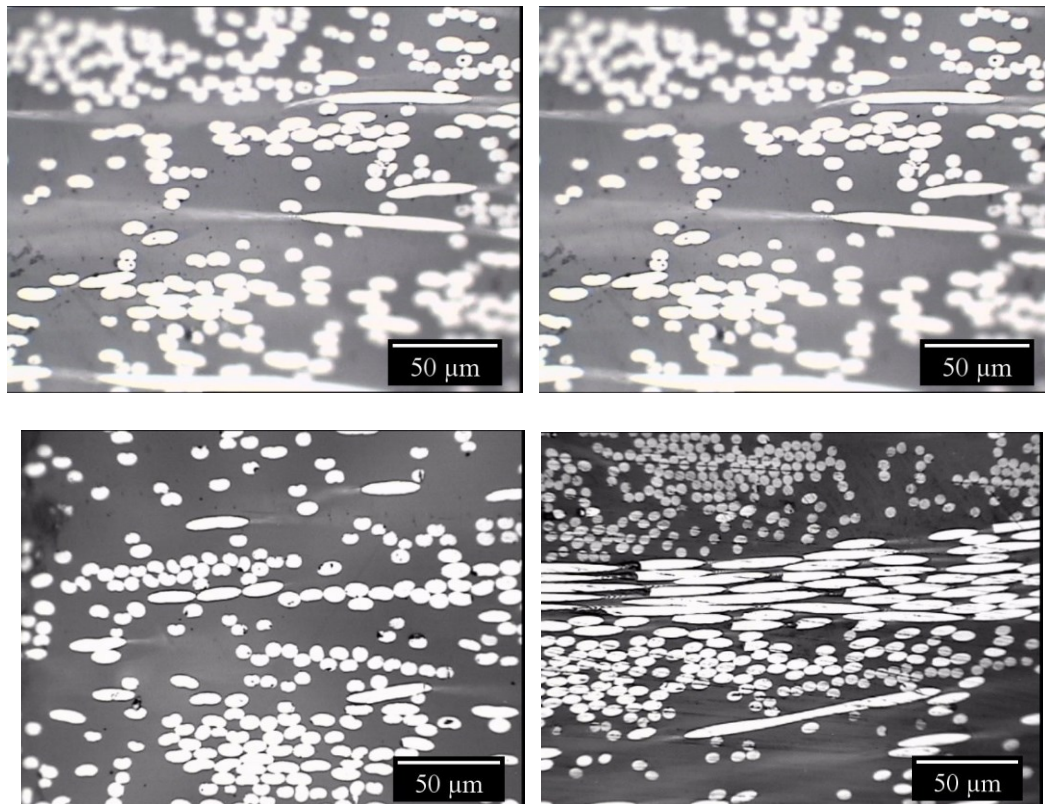


Figure 4.2: Typical cross-sectional view of compression moulded rCF composite at higher magnification

4.3 Static Mechanical Tests

This section describes the static test methods used to characterise polymer reinforced composites and various adaptations as used in the literature. Their validity was assessed based on the specimen design and nature of failure, data collected, constituent element proportions, besides accounting for the laminate manufacturing and processing issues. All specimens were conditioned at 23°C and 50% RH for at least 24 hours prior to any mechanical tests.

4.3.1 Tensile Tests

Tensile properties give a general indication of the strength and stiffness of a composite material. A gradually increasing tensile load is applied, until failure to a prismatic coupon that is clamped between tensile wedge grips with serrations. Parameters that may influence the test results are coupon geometry and preparation techniques, composite conditioning and test environment, test speed, machine calibration, coupon alignment between the grips and strain measurement instruments [67].

Tensile tests were carried out on a calibrated 100 kN load cell on an Instron 5582 operated via dedicated Bluehill software. The coupons were clamped by coarse diamond serrated wedge grips. Strain measurements were taken with an Instron knife-edge extensometer of 25 mm gauge length, attached to the masked surface of the rCF specimen to minimise slippage. The extensometer was left on the specimen until failure. Loading and unloading the specimen a few times before the start of the test further helps clamp the knife edges firmly onto the specimen as a minor slip may translate to large errors in elastic moduli calculations [176]. The tensile modulus was calculated between the strain intervals of 0.05% to 0.25%. The strain rate during all uniaxial tension tests was maintained at 2 mm/min. All tensile based tests were carried out at laboratory temperature and humidity conditions. As discussed in Section 2.3.1 and Table 2.3, rectangular and dogbone shaped coupons are commonly reported in the literature.

The international tensile test standards across conventional composites and plastics are quite similar with regard to the testing parameters, with the exception of the coupon geometry. Composites with unidirectionally reinforced fibres are generally tested with rectangular shaped coupons as per standards such as ISO 527-5 and ASTM D3039 [67, 68], which also state that they are applicable for discontinuous fibre composites. The rectangular prismatic specimens used initially in this research were cut from the rCF panels with a diamond coated disc as recommended for carbon fibre composites. In certain cases, end-tabs were bonded to the coupons with epoxy adhesives. The tabs were made of E-glass fibre-reinforced composite, aluminium or were prepared from rCF composites themselves, having low bevel angles ($7 - 10^\circ$) as recommended in ASTM D3039. An acceptable failure from the standard was classified as one that fails within the gauge length of the coupon, 2 centimetres away from the grips.

The use of dogbone-shaped coupons has become popular in recent literature involving short fibre composites, non-woven composites, textile composites and natural fibre composites [72, 77, 83]. The change in the width from the load-introduction region at the grips to the gauge section must be gradual and a shoulder radius has to be machined with high precision to prevent the introduction of stress concentrations. The coupons here were prepared using a three fluted end mill bit tool made out of tungsten carbide in conjunction with a mild steel dogbone template manufactured in house. In certain cases, coupons were manufactured by waterjet cutting. The type-1 geometry from ASTM D638-14 [69] was used. An acceptable failure, classified by the author, was one that fails within the 50 mm gauge length of the coupon geometry.

4.3.2 Shear Tests

4.3.2.1 In-plane Shear

The applicability of Iosipescu shear test method as specified by ASTM D5379 for in-plane shear was verified with rCF composites [177]. The standard mentions its suitability for discontinuous, short, random fibre composites to characterise shear properties. The experimental set up as shown in Figure 4.3, uses a prismatic specimen of dimensions $(80 \times 20 \times t) \text{ mm}^3$ with symmetric 90° -V notches through the height which are loaded asymmetrically in compression to maximise shear between the notches.

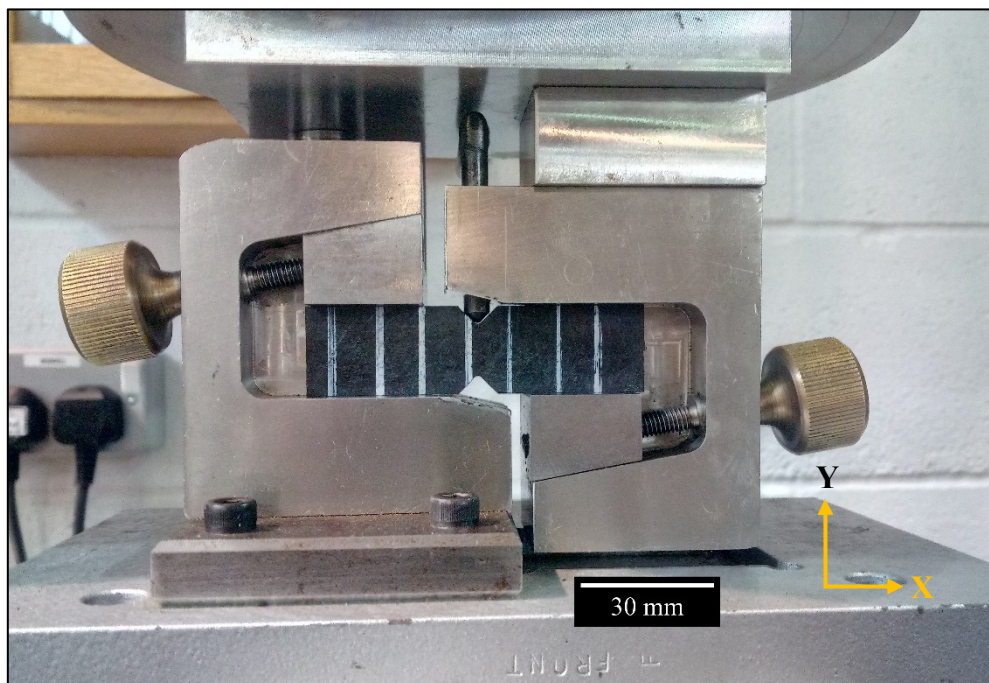


Figure 4.3: Iosipescu experimental set-up

Specimens were manufactured from the cured rCF laminate plaques by water jet cutting. The specimen rests on the back face of the set-up to reduce specimen twisting, with the notch aligned at the centre between the two grips. The ASTM D5379 recommends bonding of E-glass fibre end tabs to both faces of the specimen if its thickness is less than 2.5 mm, to reduce the possibilities of crushing failures and specimen twisting and thus a few samples were end-tabbed. The relative movement of the moving upper grip to the fixed lower grip induces a shear

strain between the notches along the direction of compression. A notch-to-notch crack was characterised as an acceptable failure mode. The upper grip movement was facilitated by the crosshead of a 50kN Testometric test machine at a speed of 1 mm/min. The ratio of the maximum force at failure to the cross sectional area between the notches was taken as the shear strength of the material.

This method, however, does not guarantee a shear failure in all composite material systems. For brittle materials such as epoxy composite systems, a failure at 45° to the notch axis indicates a tensile failure and was reported to be numerically equal to the material tensile strength [95]. Furthermore, alternate V-notch angles were tested in this study, considering the orthotropy of rCF composites. The V-notch angles were calculated from Equation 2.2 derived in the literature [106, 107]. The resulting V notch angle was approximately 105° for non-woven, rCF laminates alongside trials with V notch angles of 60°, 120° and 135°.

4.3.2.2 Out-of-plane Shear

The measurement of out-of-plane shear in discontinuous composite materials is challenging due to the difficulty of subjecting the material to a state of pure shear through the laminate thickness and achieving acceptable failure modes. Four different out-of-plane shear test methods for characterising composite materials as discussed in Section 2.3.2, were investigated for rCF composites here. All of the tests were run on a Testometric M500-50CT Universal Test machine at room temperature conditions and a crosshead displacement speed set at 1 mm/min. A sample size of at least six specimens were considered for each of the tests.

Short Beam Shear (SBS)

The SBS test method by three point bending, as described by ASTM D2344 [97] and ISO 14130 [98], has been used to determine the interlaminar shear strength (ILSS) in the XZ plane of the composite laminate by the use of a short beam specimen with a small span to thickness

ratio. Specimens of dimensions shown in Figure 4.4(a) and Table 4.3 were subjected to three point bending, with the objective of maximizing shear in the central region of the specimen.

The apparent interlaminar shear stress was calculated from beam theory using Equation 4.1:

$$\tau = (3F)/(4bh) \quad (4.1) [97]$$

where F is the failure load in N, b and h are the width and thickness of the test specimen in millimetres and τ is the shear strength in MPa. The ASTM D2344 and ISO 14130 differ slightly with specimen geometry and experimental set up as summarised in Table 4.3. It is required that the specimens fail by an interlaminar crack in the mid-plane of the beam for an acceptable result.

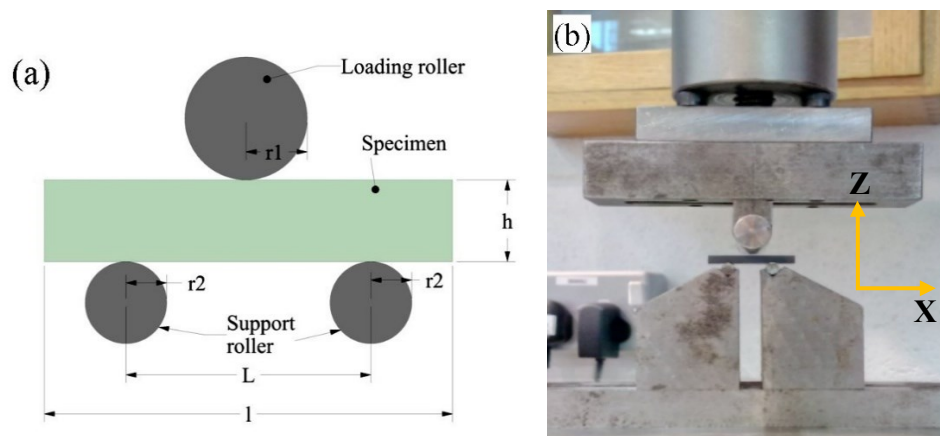


Figure 4.4: (a) Schematic of Short Beam Shear specimen and (b) test apparatus

Parameter	ASTM D2344	ISO 14130
$r1$	3 mm	5 mm
$r2$	1.5 mm	2 mm
L/h	4	5

Table 4.3: Fixture dimensions of Short Beam Shear Test

Modifications to the short beam specimen, as discussed in section 2.3.2, were also investigated with rCF composites as per recommendations from literature. The first adaptation introduced

a notch of 1 mm depth along the length of the short beam specimen, thus reducing the cross-sectional area forming an 'I-beam' specimen. The second adaptation involved bonding two flat aluminium plates of 2 mm thickness and of similar length and width to the standard specimen on its top and bottom faces, forming a sandwich beam specimen. A third adaptation was to manufacture a laminate with 54 plies of non-woven fabrics which was accomplished by co-bonding three cured laminates of 6 mm thickness with epoxy adhesive. As the geometry is similar to the standard SBS test, only a single specimen of dimensions (110.4 x 37.8 x 18.4) mm³ was manufactured and subjected to a 3-point bending load.

Double Notch Shear (DNS)

The DNS test method was used to estimate the through-the-thickness shear strength of thermoset and randomly dispersed fibre reinforced composites as specified by ASTM D3846 – 08 [178, 179]. An axial compressive load was applied onto the edge of a double notched specimen of length 79.5 mm, thickness 2 mm and width of 12.7 mm that was firmly held in a supporting jig to prevent buckling of the test specimen as shown in Figure 4.5 (b). Autoclave cured laminates were used for this test as it was expected that they were likely to exhibit inter-ply failures. The experimental apparatus was manufactured in house. The notches were machined to half the thickness of the specimen and were centrally located on opposite faces of the specimen, spaced at a distance of 6.4 mm with a diamond coated saw. The shear failure as per the DNS test was characterised by a crack along the shearing plane between the staggered notches of the specimen. The shear strength of the material in the ZX (or ZY) plane is defined as the ratio of the maximum load carried by the specimen until rupture during the test to that of the shear area between the notches.

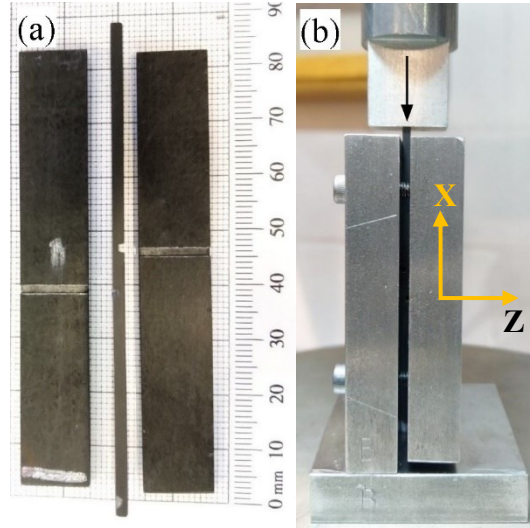


Figure 4.5: (a) Double Notch Shear Specimen and (b) Test Apparatus

Double Beam Shear (DBS)

The DBS method was used to determine the interlaminar shear of composite laminates in the XZ (or YZ) plane of the composite laminate as specified in BS ISO 19927:2018 [164]. A short beam specimen was subjected to a 5 point bending load as shown in Figure 4.6(a) with the use of cylindrical rollers that have a contact diameter of 6 mm. Sample dimensions of (15t x 5t x t) mm³ were used for autoclave, LCM and SMC cured laminates. The beam was supported by three equidistant rollers based on the thickness of the beam used and loaded by two other rollers until specimen failure or sudden drop in load. The shear failure was defined by delaminations or interlaminar failure on the mid-plane region of the specimen. The shear strength, derived from the classical beam theory, was determined from Equation 4.2.

$$\tau = (33F)/(64bh) \quad (4.2) [164]$$

where F is the critical failure load in N, b and h are the width and thickness of the test specimen in millimetres and τ is the shear strength in MPa.

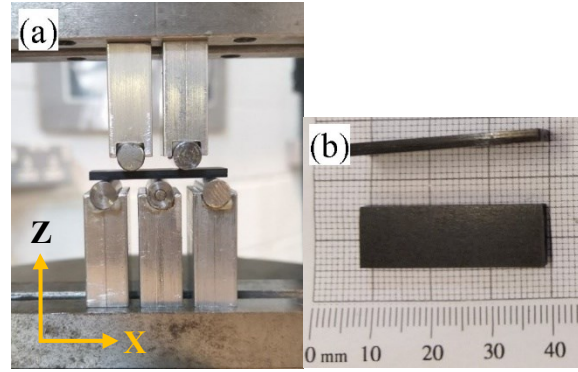


Figure 4.6: (a) Double Beam Shear Test Apparatus and (b) Specimen Geometry

Iosipescu Shear for interlaminar shear

The out-of-plane shear or interlaminar shear in the ZX (or ZY) plane was determined by remanufacturing the central gauge section of the standard Iosipescu specimen by bonding three 6 mm thick cured laminates together with epoxy. The 90°-V notch was cut using an end mill tool. The length of the Iosipescu specimens were achieved by symmetrically bonding 6 mm thick rectangular laminate blocks oriented in the XY plane to the prepared gauge section (Figure 4.7).

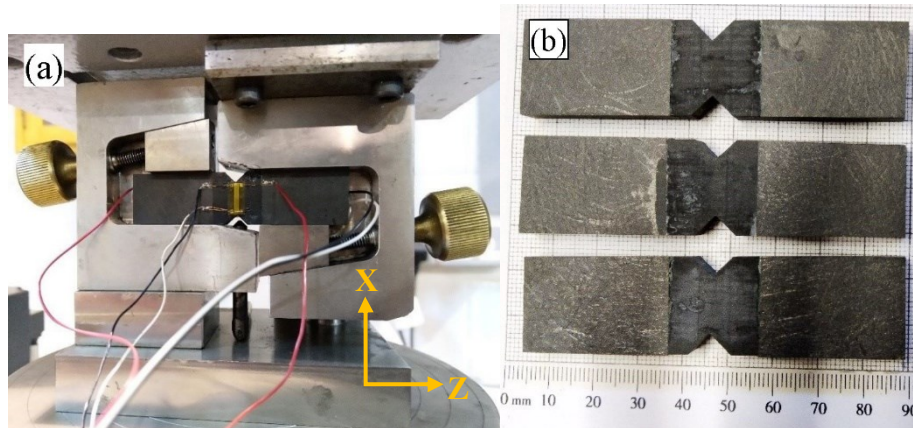


Figure 4.7: (a) Iosipescu Shear test apparatus and (b) remanufactured ZX/ZY plane Iosipescu specimens

The out-of-plane shear in the XZ (or YZ) plane was determined by bonding 6 mm thick cured laminates together until the required width of the Iosipescu geometry was achieved and the V notches were cut out by an end mill tool (Figure 4.8). The V notches were cut at 90° for one

set of specimens and at 135° for another set. In the XZ (or YZ) plane, the shear strength was determined from the strength at the first occurrence of delamination or splitting in the specimen. The selection of a 6 mm thick laminate for out-of-plane shear facilitates the V notch to be cut within one laminate and prevent its penetration or the root end of the V notch at the bond lines between the laminates. It was confirmed in all cases that the generation of the V notch did not produce any micro-cracks in the specimen by examination under a microscope.

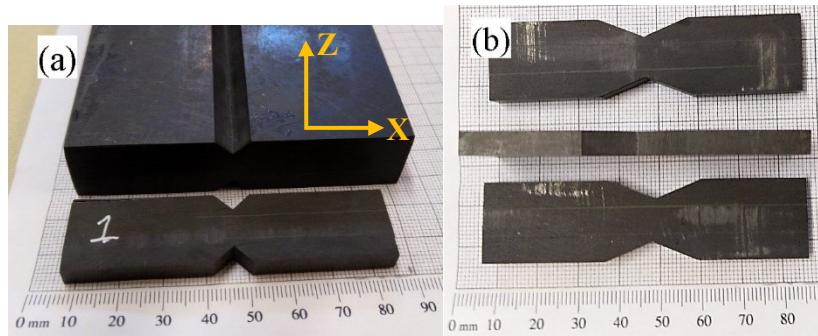


Figure 4.8: (a) Remanufactured XZ/YZ plane Iosipescu specimens with 90° V notch and (b) 135° V notch

The shear modulus of the material was determined with the use of dedicated Iosipescu strain gauges of specification A2P-08-C085C-500 connected to a data acquisition device, StudentDAQ MM01 in a half-bridge configuration. The Iosipescu strain gauge, bonded to the face of the specimen as shown in Figure 4.7 (a), had its resistors aligned in the +45° and – 45° directions and are overlapped in a polyamide film. Hence, when connected in a half-bridge network, shear strain is recorded and averaged over the entire length of the Iosipescu notch from Equation 4.3.

$$\gamma = \gamma_{+45} - \gamma_{-45} \quad (4.3)$$

4.4 Tension-Tension Fatigue

The fatigue behaviour of rCF composites was established in a tension-tension loading scheme, as represented in Figure 4.9, using the same dogbone Type-1 geometry as per ASTM D638, used for tensile tests. The fatigue behaviour was initially trialled with untabbed, rectangular shaped coupons as per ASTM D3039. The fatigue properties were obtained from a hydraulic, servo-actuated Mayes Fatigue Machine with mechanical wedge grips. Fatigue tests were load-controlled and run at a sinusoidal stress ratio of $R = 0.1$ at a frequency of 10 Hz. It was ensured that the specimens were cut from a single rCF panel to produce S-N curves, to reduce the variability in properties and analyse a particular rCF processing characteristic. All tests were performed at lab temperature and humidity conditions until fracture or until the set cycle limit at 10 million cycles. The fatigue stress intervals were gradually reduced from 90% of the material's ultimate tensile strength, usually in intervals of 10%, until the material endurance limit had been predicted to be achieved. A characteristic S-N curve was then established. The specimen was initially loaded until its maximum fatigue load, after which the cyclic loading began. The influence of the specimen geometry on the fatigue data was investigated first and foremost.

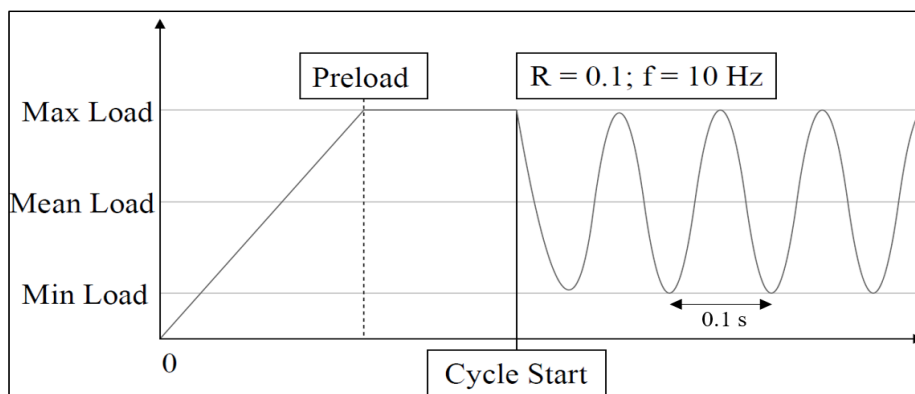


Figure 4.9: Fatigue loading experimental set-up

The fatigue data was studied using plots between fatigue stress and strain at a particular cycle in the fatigue test, i.e. hysteresis curves, at various load cases. The slope of the hysteresis curve, measured between the interval of fatigue strain at the minimum alternating load and at the maximum alternating load, was used to estimate the dynamic modulus of the material. The dynamic modulus provides a representation of the influence of fatigue on the material stiffness, possibly minimizing the errors of a quasi-static tensile test to monitor the elastic modulus mentioned in ASTM D3479 [180]. The results of these two methods were investigated in this study. Monitoring the dynamic modulus of the material over its fatigue life period was thus used as a measurement technique to monitor stiffness. A self-calibrated Epsilon extensometer model 3452-025M-010-LT, of gauge length 25 mm, with knife edges, was used to monitor specimen strain. The extensometer was connected to a Spider 8 data logger on which it was calibrated, via a signal conditioner, to amplify its 2 mV/V output signal to 10 V/V. The fatigue loads and machine strokes were transferred to a calibrated Rubicon digital control system, logged by a Spider 8 data logger and stored using Catman v4.5 software as shown schematically in Figure 4.10.

As part of the quasi-static tensile testing, the run-out specimens of an SMC IM56R cross-ply laminate, which remained unbroken after 10 million cycles, were subjected to tensile tests to estimate the residual strength properties of the material after fatigue. For further analysis, the cross-sections of the specimens that had failed due to cyclic loading were observed under an optical microscope to study the damage phenomena. The influence of various rCF processing parameters were also investigated.

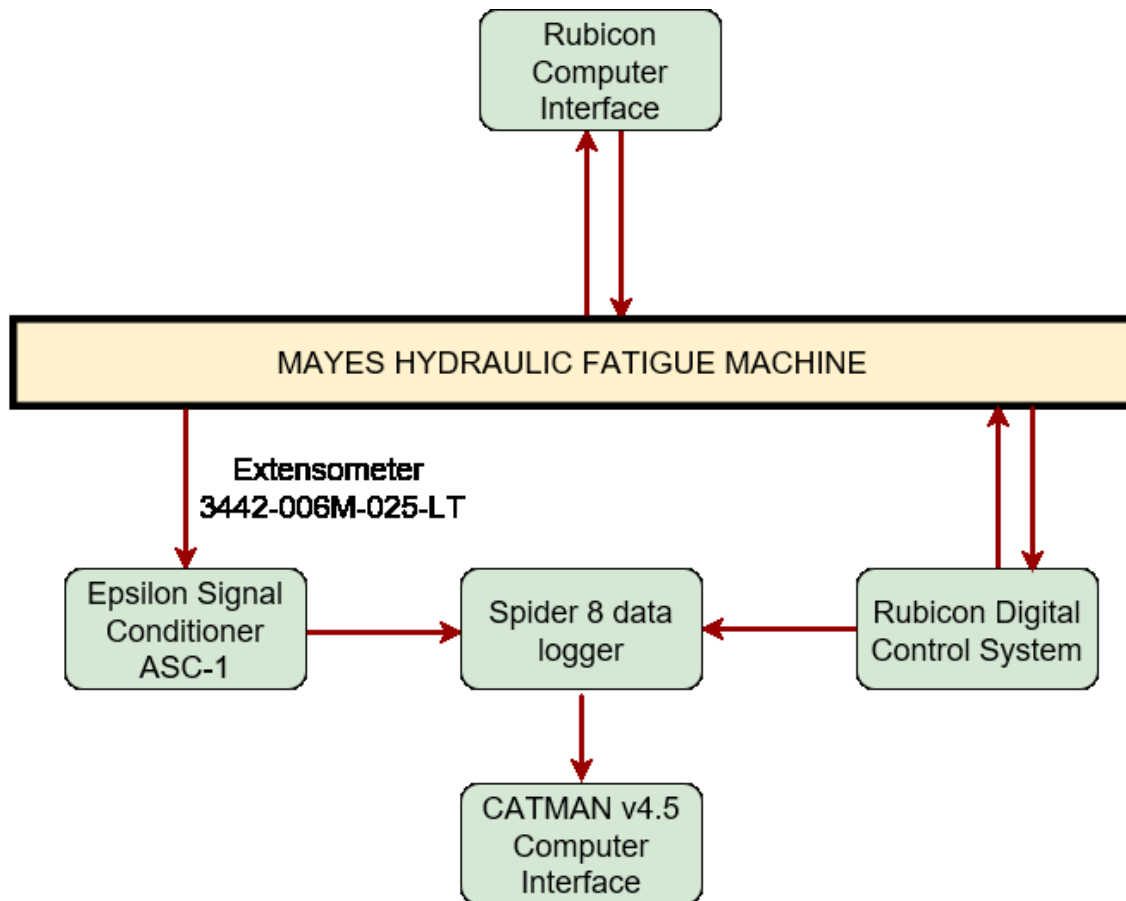


Figure 4.10: Experimental apparatus for tension-tension fatigue tests

4.5 Environmental Durability

4.5.1 Introduction

Moisture uptake and deterioration of mechanical performance of composites is critical in assessing the long term durability of composites, similar to the effect of rusting of metallic components during its operation life. The long term durability of rCF composite system was accomplished by its immersion in select liquid mediums that were expected to significantly weaken the performance of the material. The fluids taken into consideration were automotive diesel fuel in accordance to the EN590:1993 specification [181], deionised water from Brenntag [182] and Kilfrost TDIce Plus de-icing fluid [183] consisting of 60-100% of propylene glycol. The choice of the fluids was decided based on the potential application environments of rCF composites in the rail and automotive industries [184].

Compression cured, unreinforced epoxy plaques of Hexion™ EPIKOTE™ Resin TRAC 06605 + EPIKURE™ Curing Agent TRAC 06608 were also subjected to fluid immersion in deionised water at 23°C and 50°C, in addition to the rCF composite systems. 50°C was selected for all the durability tests so as to accelerate the ageing process at a temperature not too close to its T_g . The maximum moisture absorbed and glass transition temperatures were recorded before and after ageing.

4.5.2 Experimental procedure

The degradation of mechanical performance of rCF composites due to liquid absorption was estimated as per procedure B in ASTM D5229M – 12 [185]. Dogbone shaped tensile coupons were immersed in tightly enclosed fluid baths maintained at their respective temperatures in laboratory ovens. The samples were preconditioned for 24 hours at 23°C and 50% RH. The impact of environmental aging was assessed by a series of quasi-static tensile tests at periodic intervals until 1080 hours.

4.5.2.1 Stiffness

A set of rCF composite samples were kept aside to measure the stiffness changes to avoid inherent material variability interfere with the impact of immersion aging. Each sample set of 3 specimens was immersed in diesel and de-icing fluid at 23°C and deionised water at 23 and 50°C respectively in air tight sealed water baths. The tensile modulus was measured by a tensile test loaded until 0.3% of the material tensile strain. As the strain measured for the moduli are much lower than its ultimate tensile strains (~1.3%), the repeat loading was not expected to affect the material properties. The tensile modulus was monitored after 120, 240, 360, 720 and 1080 hours on the same set of specimens. The surface of the specimen was thoroughly wiped before the test and replaced into the specimen bag within 30 minutes.

4.5.2.2 Strength

The tensile strength of the material was monitored using different material sets. The material variability was kept to a minimum by extracting the samples from two panels of the same areal weight, thickness and ply number, and stacking sequence. The panel's tensile strength was initially measured before aging on a set of 5 specimens. The strength was monitored by tensile loading a set of 3 specimens until failure after immersion in each liquid medium after 120, 240, 360, 720 and 1080 hours.

In summary, the effect of immersion in fluid environments on the elastic modulus was monitored on the same set of 3 specimens tested at regular intervals and the impact on tensile strength was established using the test matrix as shown in Table 4.4:

Aging time	Number of specimens				
	Diesel 23°C	De-icing fluid 23°C	Deionised water		
			4°C	23°C	50°C
0 h	← 5 specimens →				
120 h	3	3	3	3	3
240 h	3	3	3	3	3
360 h	3	3	3	3	3
720 h	3	3	3	3	3
1080 h	3	3	3	3	3

Table 4.4: Test matrix used to evaluate the influence of fluid immersion on strength of rCF composites

All of the specimens were tested in the weft direction.

4.5.2.3 Gravimetric analysis

The gravimetric change in the moisture absorbed was monitored from the immersion of rCF composite in in deionised water at 23°C and 50°C, diesel and de-icing fluid at 23°C. Three square panels with unsealed edges, of dimensions 100 x 100 x 3 mm³ of LCM, SMC and autoclave cured composite systems were immersed in the fluid baths for thermo-gravimetric analysis. The moisture absorbed was measured by weighing the specimens periodically on a high precision balance with 0.1 mg resolution akin to the procedure A mentioned in ASTM

D5229 [185]. Care was taken during the weighing stage of the specimens by transferring the specimens into a sealed specimen bag from the conditioning chambers. The specimen surfaces were wiped thoroughly before weight measurements. The specimens immersed in de-icing fluid were rinsed in tap water and wiped before weighing. It was ensured that the specimens were not outside the conditioning chamber for more than 30 minutes. The moisture absorption rate was examined by plotting the change in mass of the specimen with square root of immersion time and the equilibrium moisture content is taken as the maximum absorbed moisture, M_m . The material was defined to be at its effective maximum moisture equilibrium when the material weight did not increase over 0.02% over two consecutive mass recording intervals. The moisture content at each interval, M_t , was determined from Equation 4.4:

$$M_t = \frac{W_t - W_o}{W_o} \quad (4.4)$$

where W_o and W_t are the initial dry weight of the specimen and wet weight at each interval at a given time t respectively. The moisture uptake readings were recorded either until mass saturation or until 65 days.

4.5.2.4 Glass Transition Temperature

The glass transition temperature (T_g) of rCF composites before and after fluid immersion was measured by Dynamic Mechanical and Thermal Analyser (DMTA) complying with ASTM D7028 [186]. A Triton Technology, Tritec 2300 DMA machine was used controlled by Universal Analysis 2000 software. The DMTA measures the stress due to a sinusoidal strain that is applied onto the test specimen. The stress and strain will be:

- a) Proportional and in phase for an ideal, elastic solid
- b) Proportional and out of phase by 90° for an ideal, Newtonian fluid

Since the matrices of composites are essentially viscoelastic polymers that exhibit characteristics of both solids and liquids, the phase angle (δ) will be in between 0 and 90

degrees. The tangent of this phase angle ($\tan \delta$) is measured by the DMTA as the ratio of the viscous energy dissipated (Loss Modulus, E'') to elastic energy stored (Storage Modulus, E'). The storage modulus drops substantially at T_g , the temperature at which the composite changes from its glassy state to viscous state, causing a spike in the $\tan \delta$ curve. The DMTA T_g is recorded as the temperature at which the peak of the $\tan \delta$ curve occurs.

Rectangular samples of $(35 \times 9 \times t)$ mm³ were subjected to sinusoidal oscillations of 1 Hz in a 3 point flexural dual cantilever loading mode. The rate of heating was set at 5°C/min. These experimental conditions were kept constant for both aged and unaged specimen to allow for comparison purposes. The aged laminates and epoxy plaques were dried at room temperature for 24 hours before being tested.

4.7 Data Analysis

Experimental test samples used are never identical in material characterisation. The data may appear to be scattered and rigorous data analysis is required to make meaningful judgements and interpretations. A population parameter assessed using a sample data set is never going to be free from errors and is expressed in terms of confidence intervals. Statistical analyses form a framework to describe potential sources of variability and incorporate them into decision making processes. It is important to verify that the sample data is significant enough to represent its population or if there may have been a sampling error [187].

A sample data set in material science is usually summarised with mean, standard deviation and coefficient of variation, which form the descriptive statistics of the data. In material characterisation, the sample statistics are expressed in terms of a sampling distribution, a bell curve which narrows around its mean. However, laboratory material characterisation is generally expensive and it becomes important to estimate from a smaller set of measurements with inferential statistics.

Rational decisions about the observed effects of the sample data for a population are conducted using hypothesis tests. A null hypothesis denotes no relationship between the population variables in the study. An alternative hypothesis is also established with which a decision is made with the aid of probability models that quantify the risk involved in the statistical inference. All statistical conclusions are made with reference to the null hypothesis. The null hypothesis, H_0 , is rejected or failed to reject based on a calculated probability p value, that is judged at an arbitrarily chosen significance level, α [187, 188]. If we reject the null hypothesis, we conclude that the data supports the alternative hypothesis, H_a . The error associated with this decision making rests with the significance level chosen and are classified as type I and type II errors. A Type I error refers to incorrectly rejecting the null hypothesis when it should not have been rejected. The probability of committing type I error is α . A Type II error relates to the failure to reject the null hypothesis when it should have been rejected and it varies with experimental factors.

Student's T-test and Analysis of Variance (ANOVA) are parametric tests that are commonly used to study two or more populations or subgroups of a population. It is assumed that the populations are normally distributed and that the variances of the samples and their respective population are equal. The student's T-test can be used to study the relationship between variables for two unrelated populations (Independent T-test) or two variables within the same population (Paired Samples T-test), as depicted in Figure 4.11. A T-test is limited to only two groups or populations whereas ANOVA can be used to make inferences by studying the means and variances of more than two populations without compounding the significance level by carrying out multiple t-tests. In this research, the descriptive and inferential statistical analysis were conducted using the software package IBM SPSS Statistics 25 [189].

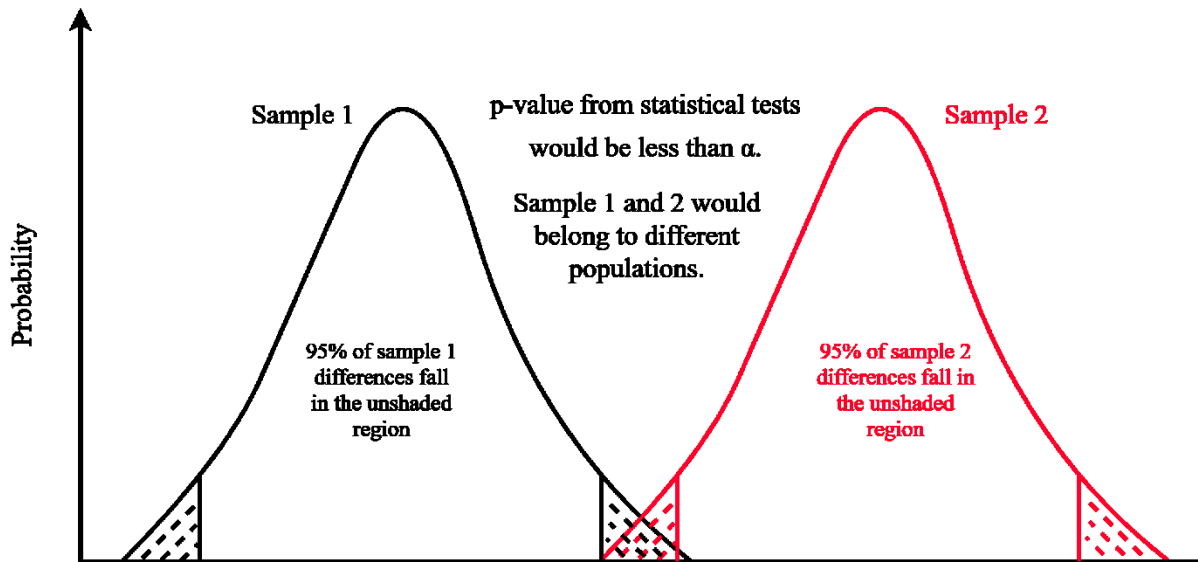
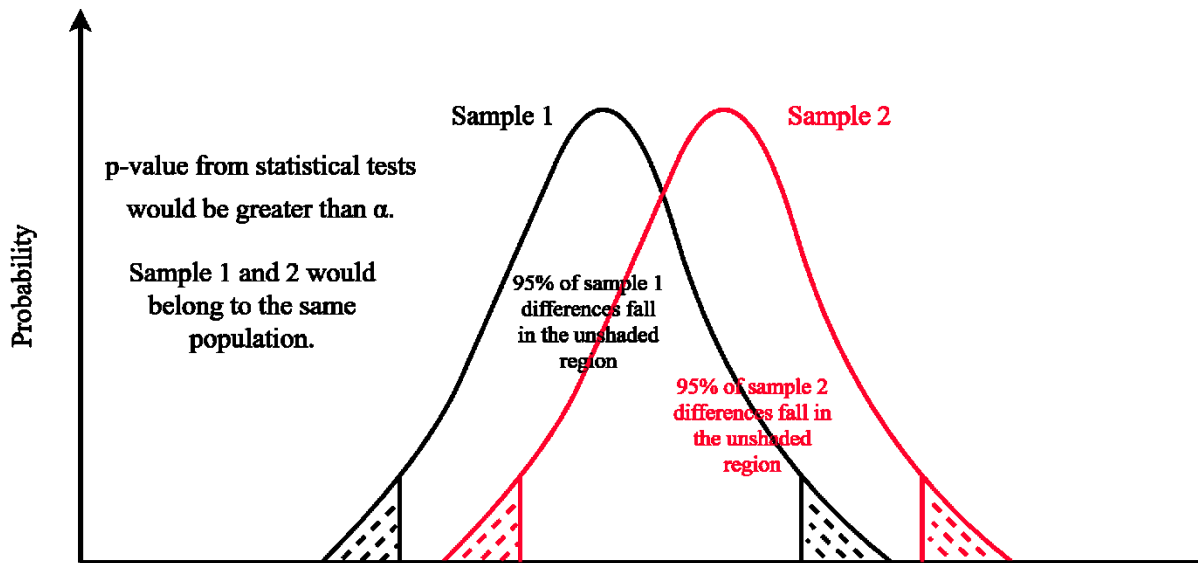


Figure 4.11: Statistical inference from two population groups from a t-test

Chapter 5: Static Tensile Behaviour

5.1 Development of tensile test practices for rCF composites

5.1.1 Introduction

Appropriate testing practices are required that reliably measure the tensile strength limits of rCF composites to assess the influence of rCF material processing variables. A suitable test methodology takes into account the selection of jaws clamping the coupon, specimen geometry and specimen preparation techniques to ensure uniform stress distribution to the gauge section, test speed and strain measurement techniques. International standards agree uniformly on most of these aspects, but they are ambiguous about the applicability of appropriate test method for rCF composites or composites of similar reinforcement architectures. As a result, as seen in Table 2.3, the selection of tensile specimen geometry and specimen preparation has so far not been consistent in literature. In this section, commonly tested specimen geometries are discussed, assessing their influence on the tensile results for rCF composites.

5.1.2 Test Coupon Geometry and Failure Characteristics

As described in Section 4.4.1, straight sided and dogbone shaped prismatic coupons were primarily evaluated. From a sample size of 145 specimens from LCM and SMC panels, 87.6% of the straight-sided rectangular coupons depicted a lateral mode of failure at or close to the grip section, irrespective of being untabbed or tabbed with aluminium, tapered GFRP end tabs and CFRP end tabs. The typical failure locations are shown in Figure 5.1. Debonding of the end tabs was not observed in any of the cases, indicating a good stress transfer from the tabs to the composite specimen. The use of end tabs is not a specific requirement in tensile test standards and their use depends traditionally on the test outcome. The lack of gauge section failure implied that coupon thickness increments at the grips does not result in good transfer of stress and strain into the specimen gauge length. The possible issue of excessive clamping force

(set at 100N) of the rectangular test specimen by the mechanical wedge grips was considered to be negligible. Additionally, having a 15° tapered end tab to reduce the abrupt change of thickness in rectangular prismatic specimens did not improve the load introduction into the specimen gauge length.

Preliminary trials with ASTM D638 Type 1 geometry dogbones specimens that were cut from the panels by waterjet cutting suggested a much improved stress distribution into the gauge length of the sample, with 8 of 10 specimens showing acceptable failure modes. Typical failure locations are shown in Figure 5.2. Although there was an indication of higher failure strength limits than that of rectangular geometries, further dedicated studies would be needed to validate this hypothesis given the variability posed by the fibre reinforcement architecture in rCF composites.

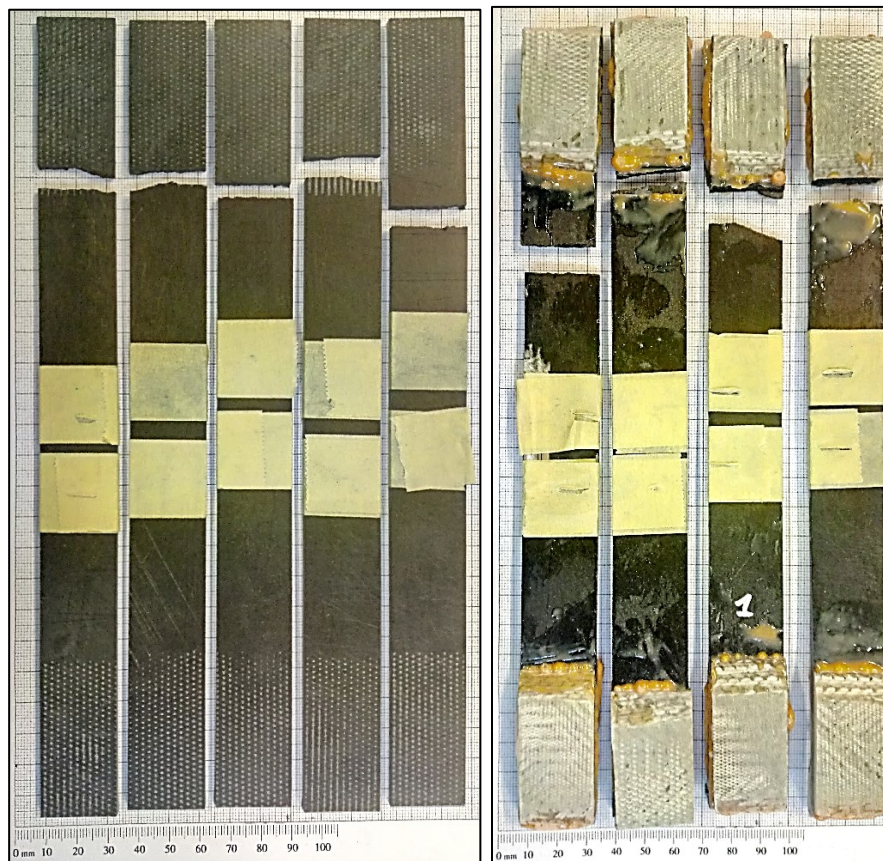


Figure 5.1: Failure modes in rectangular tensile specimens



Figure 5.2: Failure modes in dogbone specimens

The specimens henceforth were manufactured using an end mill bit tool in a composite milling machine, in conjunction with a bespoke steel mould and had shown similar repeatable results to coupons manufactured by waterjet cutting. The impact of the specimen geometry was assessed by cutting straight sided and dogbone geometry specimens from the same panel so as to reduce the variabilities that could arise from material processing. All of the specimens were oriented in the weft direction of an LCM processed panel of 3.5 mm thickness, reinforced with six 223 g/m² mats of IM56R fibres all laid in the same orientation. The impact of coupon geometry can be clearly seen with the tensile results plotted in Figure 5.3 and the difference in the data analysed is statistically significant (see Section 4.7).

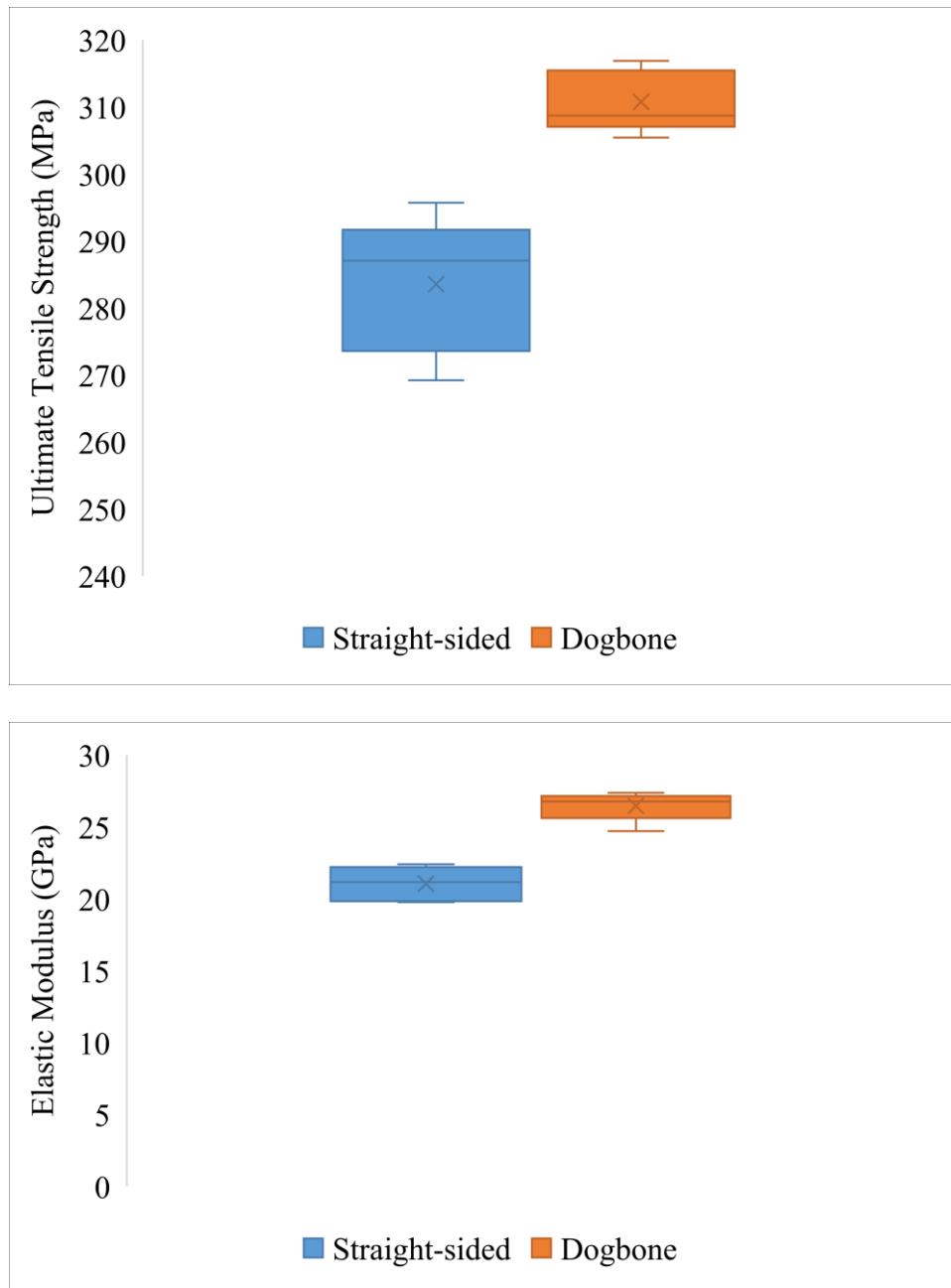


Figure 5.3: Tensile characteristics of rCF with straight-sided and dogbone specimens

The mean weft tensile strength of dogbone specimens (310.71 $\pm$ 4.62 MPa) was greater than the mean weft tensile strength for straight-sided untabbed specimens (283.5 $\pm$ 10.17 MPa). An independent samples T-test was significant below 0.05 level: $T(8) = -5.448$; $p=0.001$ two tailed. The 95% confidence interval for the difference was -38.73,-15.70 which does not contain the zero specified by the null hypothesis that the means are equal, and is thus rejected. The increase in the tensile properties with dogbone specimens and repeatable gauge length

failures, as observed in Figure 5.2, clearly suggests a better stress and strain introduction and distribution through the length of the specimen that can be attributed to a more suitable specimen design for rCF composites. End-tabbed specimens were not part of this study because only a limited number of straight-sided and dogbone specimens could be extracted from any one panel to limit manufacturing variability.

In any case, tabbed and untabbed samples tested from another panel indicated that the use of end-tabs did not guarantee any improvement in the properties, nor did they exhibit gauge length failures. All the specimens were taken in the warp direction from an LCM processed panel of 3.4 mm thickness, reinforced with 8 plies of 195 g/m² mats laid in the same orientation, reinforced with SM45D fibres. The results of untabbed and CFRP end-tabbed coupons are plotted in Figure 5.4.

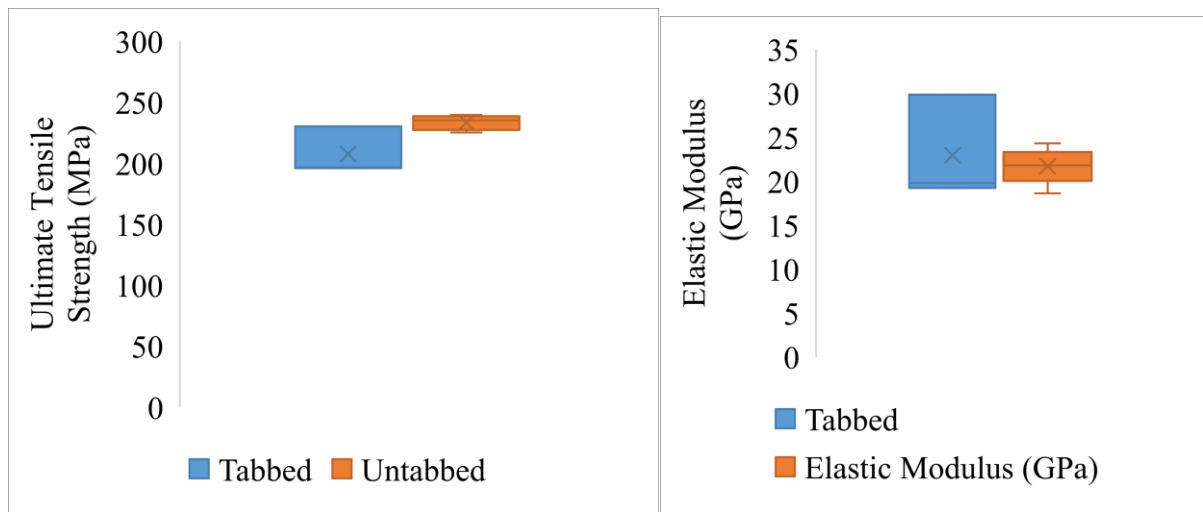


Figure 5.4: Tensile characteristics with CFRP end tabs

Similar results were obtained from aluminium end tabbed specimens. In this case, all the specimens were taken in the warp direction from an LCM processed panel of 2.3 mm thickness, reinforced with 5 plies of 176 g/m² mats laid in the same orientation, reinforced with IM56R fibres. The results are plotted in Figure 5.5. The use of rectangular prismatic coupons resulted in premature failures and an unreliable dataset.

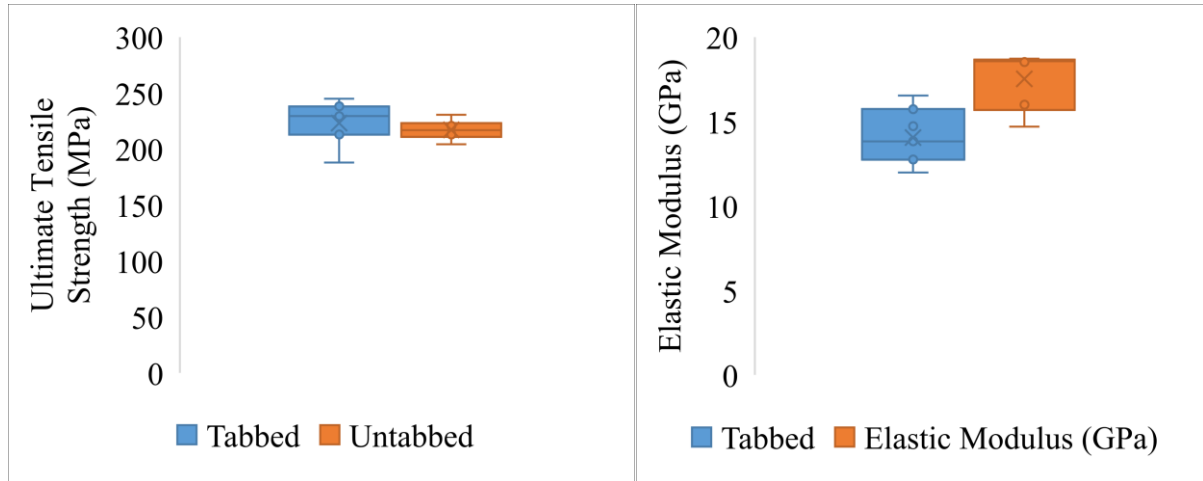


Figure 5.5: Tensile characteristics with Al end tabs

Another specimen geometry alternative is the ‘bowtie’ specimen that was introduced by Grumman [70] in support of the MIL-HDBK-17A [94] for composites reinforced with fibreglass mat. The dimensions of the test specimen are similar to the ASTM D638 geometry, but has a linear taper connecting the specimen grip to the gauge section instead of a radius of curvature. An 8 ply LCM laminate composed of 193.7 g/m^2 mats with SM45D fibres was used to assess the ‘bowtie’ geometry. However, only 45% of 20 ‘bowtie’ specimens resulted in acceptable failure modes. The majority of the specimens had a tendency to fail at this tapered region or at the end of the taper, rather than the gauge region as shown in Figure 5.6, and the ‘bowtie’ design was thus considered inappropriate for rCF composites.

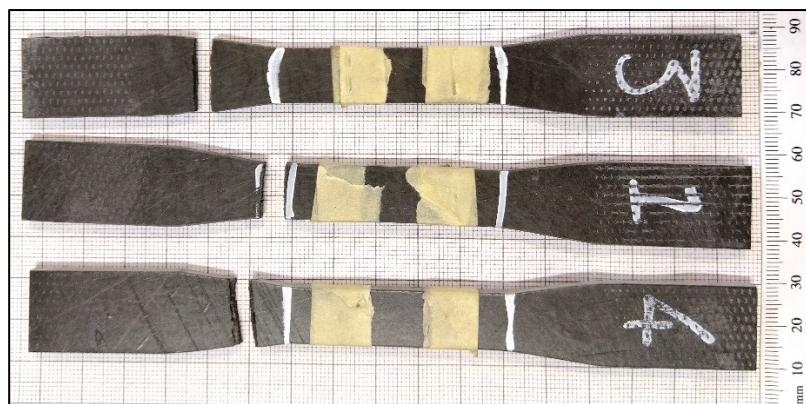


Figure 5.6: Tensile coupon failure in a bowtie specimen geometry

The effect of dogbone specimen machining was also assessed by comparing samples made from an end mill bit tool and from water jet cutting. A 3.3 mm thick, 6 cross-ply LCM laminate composite of 212 g/m² mats of IM56R fibres was used for this study. The specimens were taken from the same panel and were all cut along the same direction. The result, as plotted in Figure 5.7, suggests that the means of the tensile strength and modulus are not much different, confirming that the specimen manufacturing technique by end milling did not influence the results. The difference between the means was not statistically significant below the 0.05 level [i.e., $p > 0.05$] via the independent T test and the 95% confidence intervals for both the tensile strength and modulus contained their respective zeroes. This means that the null hypothesis statement considering the means were equal was failed to be rejected.

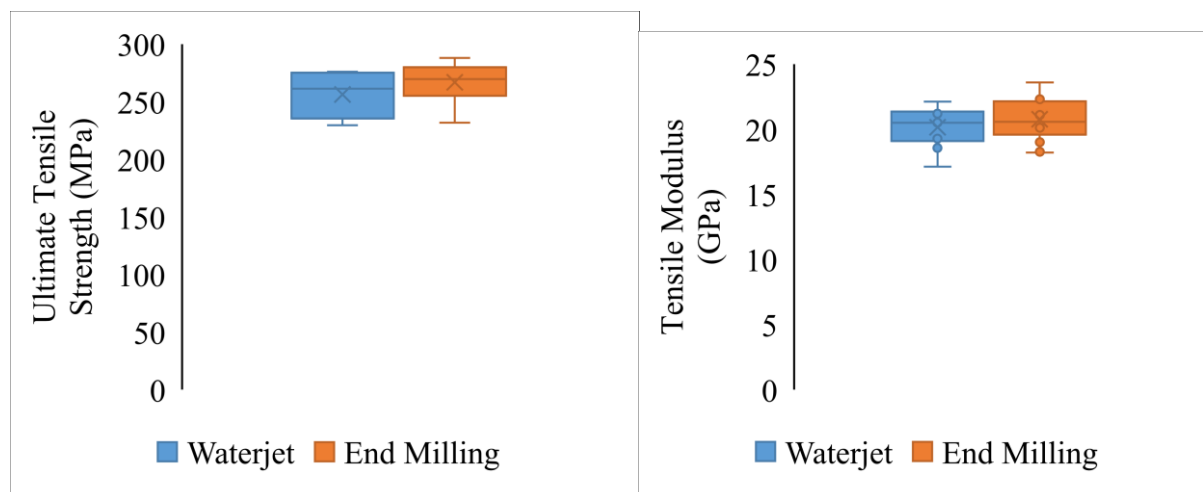


Figure 5.7: Impact of dogbone specimen manufacturing

For each of the independent test results stated above, at least 10 specimens were used for each sample set. A representative tensile stress-strain curve of an SMC IM56L laminate in the warp and weft directions are plotted in Figure A3.1. The curve is generally linear with a slight transition region initiating below 0.5% tensile strain.

5.2 Impact of rCF manufacturing processes

The impact of fibre V_f , composite remoulding techniques, fibre type and laminate lay-up on rCF composites were assessed using dogbone geometry coupons. Figure 5.8 depicts the 95% confidence interval of the UTS of rCF composites based on the testing orientation in the primary x-axis (as warp and weft for laminates with unidirectionally laid plies and cross-ply) and moulding process conditions in the secondary x-axis. At least 6 specimens were used for each data point. The results are segregated in the secondary y-axis based on the V_f range between (a) 0.18 – 0.22, (b) 0.23 – 0.29 and (c) 0.30 – 0.34. The V_f was calculated from Equation 5.1.

$$V_f = \frac{nA_w}{\rho t} \quad (5.1)$$

where n is the number of plies in the laminate, A_w is the fabric areal weight, t is the thickness of the cured laminate and ρ is the density of carbon fibre.

The fibre type is indicated in respective panels of Figure 5.8. However, the influence of the fibre type is difficult to assess due to the large number of parameters, but could be understood better from Figure 5.9 which depicts a plot for 95% of CI of UTS (see Fig. 4.11) of rCF composites in the weft direction for all V_f ranges. The results from Figures 5.8 and 5.9 are discussed in the subsequent sections.

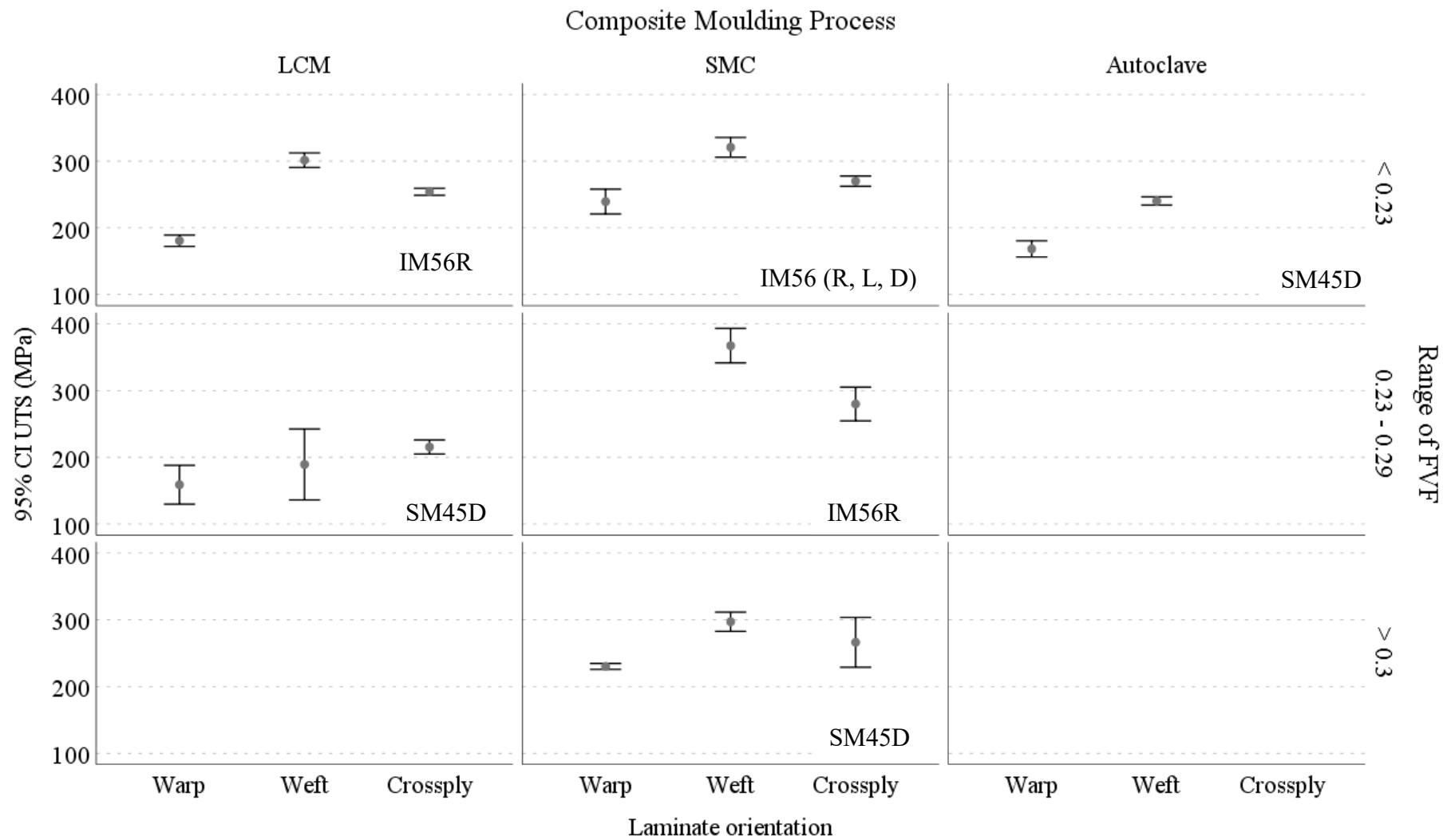


Figure 5.8: Influence of rCF processing parameters on tensile strength

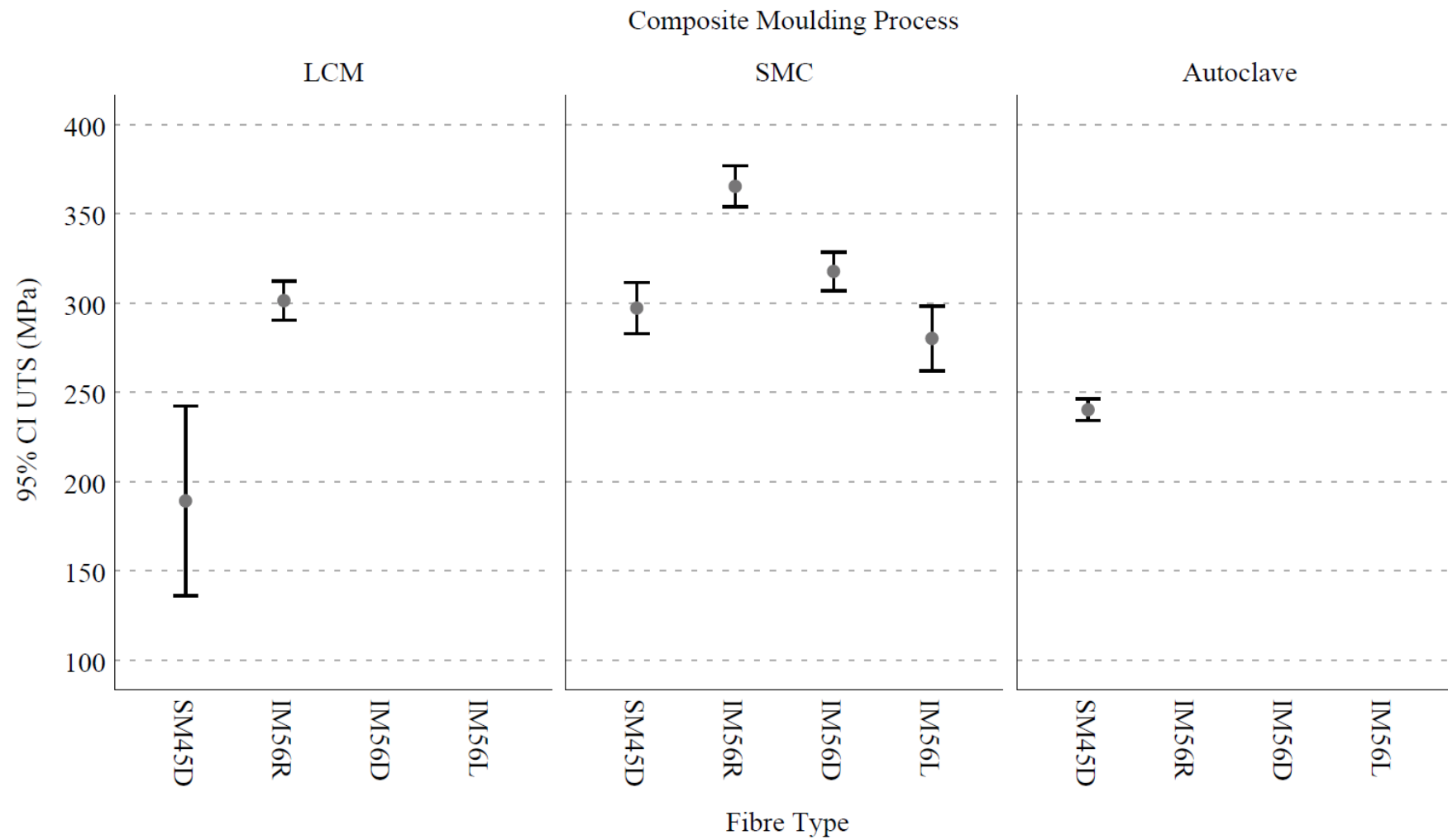


Figure 5.9: Impact of fibre type on rCF tensile strength along the weft direction

5.3 Discussion

5.3.1 Selection of Coupon Geometry

Preliminary experimental studies on rCF composites in this research began with tensile tests with straight-sided coupon geometry as per the ASTM D3039 and ISO 527-5 standards. However, the commonly used rectangular shaped test coupons for evaluating composites resulted in premature grip failures to the extent that certain specimens would not sustain loads over 50 MPa. This led to high variability in test results whose causes could not be pinned down to material manufacturing defects, testing practice or measurement errors. End-tabbing of straight-sided coupons did not improve the failure characteristics of rCF composites either. The use of end tabs themselves could impart additional stress concentrations and stress peaks leading to other undesirable failure modes. The reinforcement architecture of rCF composites, especially with the introduction of fibres along the z-plane due to the needle punching process during the carding stage, results in a less anisotropic material than unidirectionally reinforced composites. Hence straight-sided coupons could not accurately reflect the true strength of rCF composites as the random, discontinuous, needle-punched, non-woven fabric reinforcement prevent the efficient load introduction into the specimen gauge length. An improved coupon design to assess tensile properties of rCF composites was necessary.

Waterjet cut dogbone specimens dramatically improved the failure characteristics of rCF composites. Premature failures were avoided and no end-tabbing was necessary. The consistent gauge length failures enabled the reliable analysis of material manufacturing processes like fibre type, composite moulding methods, fibre packing efficiency, etc. The influence of specimen geometry on rCF composite response can be specifically understood from the differing results and failure modes of rectangular and dogbone test coupons cut from the same

panel. The out-of-gauge length failures due to the poorer stress transfer from the grip into the gauge length thus lead to premature grip failures of the rectangular coupons.

The lack of specific guidance for testing rCF composites or discontinuous, non-woven composites leads to errors in material evaluation in the literature and, eventually, design data specifications for engineering applications. The ASTM D3039 standard recommends the use of rectangular coupons for discontinuous composites reinforced with high-modulus fibres. ISO 527-4 recommends dogbone coupons only for injection moulded composites and vaguely suggests the use of any adequate specimen geometries that garners acceptable failures for thermoplastic and thermoset based composites. This resulted in incoherent tensile test practices for similarly reinforced composites in the literature, as tabulated in Table 2.3. For non-woven rCF composites however, Section 5.1 clearly shows the influence of an inappropriate coupon geometry.

Rectangular tensile test coupons are easy to prepare and may be suitable for an approximate and preliminary evaluation of rCF composites provided the occurrence of gauge failures. However to study the effect of various processing parameters and record design based values, it is highly recommended that variability in results is controlled through adequate test practices by adoption of dogbone coupons. The manufacture of such dogbone coupons could either be from waterjet cutting or from end milling as they did not show any significant differences to tensile loads as depicted in Figure 5.7.

5.3.2 rCF Process Parameters

This section discusses the impact of rCF process parameters such as V_f , fabric directionality, composite moulding process, fibre type and pyrolysis from Figures 5.8 and 5.9.

5.3.2.1 Directionality of non-woven rCF mat

The higher strength in the weft direction over the warp direction in laminates with unidirectionally laid non-woven mats across all paradigms in Figure 5.8 is a result of the preferential orientation of the fibres along the carding machine transverse direction that is unique to the fabric processing machine as explained in Section 1.3. The difference in the tensile strengths between the warp and weft is not as high as that seen in longitudinal and transverse directions of continuous, unidirectional laminates and thus non-woven rCF composites are less anisotropic in nature.

The cross-ply laminates show intermediate properties but lean towards the respective weft strengths. It is however ideal to have higher disparity in material characteristics between the warp and weft directions, i.e., more alignment of fibres along the weft direction, so as to achieve even higher strength limits in rCF composites, closer to that of continuous UD composite systems. Thereby, having a cross-ply laid rCF laminate does not serve any significant purpose, unless an equal mechanical property distribution along warp and weft is desired – in which case the lay-up configuration would need to be even to avoid the influence of any additional residual strain.

5.3.2.2 Composite Moulding Process

It is evident from both Figures 5.8 and 5.9 that across similar fibre reinforced composites, SMC laminates have higher strengths than LCM and Autoclave laminates.

Amongst compression cured laminates, the improved performance of SMC laminates over LCM could be linked to their improved processing technique and higher curing pressures. In

SMC laminates, epoxy resin is applied on the surfaces of the non-woven fabrics before lay-up but in LCM laminates, a less viscous epoxy resin system is applied onto the top-most ply of the non-woven fabric lay-up and pressed. It may be possible that the latter processing methodology leads to poor resin distribution through the thickness of the laminate, although this was not observed in cross-sectional optical micrographs for LCM laminates. The characteristics of the EPIKOTE™ TRAC 06170 resin system and its compatibility with carbon fibres themselves may be another factor. The higher standard deviation in the LCM SM45D laminates between 0.23 - 0.29 V_f range could be attributed to the lower affinity of the CF size with the resin system, explained further in Section 5.3.2.4. SMC pressed laminates may have a higher degree of in-plane anisotropy due to the realignment of fibres along the resin flow direction during the manufacture of non-woven, pre-impregnated sheets. The LCM pressed laminates may have a higher variability due to the multi-directional resin flow during compression moulding.

Despite the presence of inter-ply voids in autoclave laminates, there was no evidence to suggest it had an impact on their tensile properties. It could be argued that for SM45D reinforced composites, autoclave laminates outperform LCM laminates as seen in Figure 5.9.

5.3.2.3 Fibre Volume Fraction

Similar to conventional composites, an increase in V_f improves the tensile properties of rCF composites as seen from IM56 reinforced SMC laminates in the < 0.23 and $0.23 - 0.29 V_f$ ranges in Figure 5.8. However, due to the needle-punching stage during the carding textile process, the fabrics are quite porous in nature which limits the maximum performance of the V_f to around 0.3. Furthermore, laminates pressed at even higher volume fractions may experience fibre breakages at high compression pressures due to the mechanical entanglement of the fibres within the rCF fabrics, leading to higher variability of the laminate.

5.3.2.4 Fibre Type

The performance of rCF composites depends on the reinforcement fibre type, particularly the strength of the fibre. rCF laminates reinforced with IM56- fibres outperform laminates with SM45- fibres, despite their random fibre distribution. From Figure 5.9 for LCM and SMC laminates, it can be seen that IM56 reinforced laminates, that also happen to have lower V_f , have higher UTS than SM45D reinforced laminates. The plot shows that IM56R and IM56D fibres generally have higher strengths over SM45D. For SMC cured laminates, it is seen that there is little difference amongst SM45D and IM56L. It is encouraging that rCF composites reinforced with pyrolysed fibres are not inferior to those reinforced with repurposed fibres.

The needle-punching process may be detrimental to the strength of IM56R/IM56L fibres as they are devoid of any sizing that protect the fibres as opposed to IM56D/SM45D. Figure 5.10 highlights the impact of IM56- fibres on the rCF composite strength in the weft direction of SMC laminates of $< 0.23 V_f$. It can be seen that IM56R SMC laminates have been found to outperform IM56D SMC laminates. This seems to imply that pyrolysis of CF did not have an impact on the static strengths of non-woven rCF composite. Recovering fibres from shredded, cured laminate waste may have caused further fibre damage than recovering from other waste types and thus resulted in a reduced laminate strength and higher standard deviation.

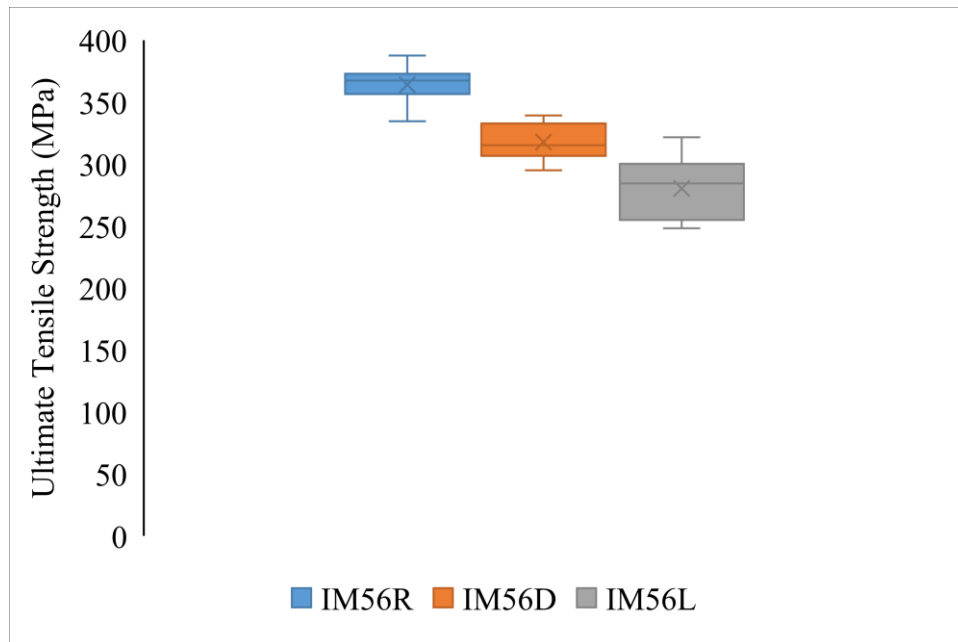


Figure 5.10: Influence of fibre type on the weft tensile strength of SMC laminates below $0.23 V_f$

The presence of sizing on carbon fibres did not ensure the higher strength as thus evidenced in IM56D and IM56R fibres. The superior performance of IM56R reinforced SMC may be due to the better fibre-matrix adhesion by improved micro-mechanical inter-locking with epoxy chains as a result of rough surface features after pyrolysis of fibres as discussed in Section 2.1. Pyrolysed CF was reported to be rich in oxygen containing functional groups that facilitates better bonding with epoxy resin. Sizing and surface treatments on CF are not universal to all fibre/matrix systems. Sizing is generally applied as a protective coating to the CF surface during the processing stages of vCF. They thus act as merely handling agents that help in improving vCF production rates and may not aid in adhesion to epoxy resin. The surface treatment procedures (such as electrolytic treatment) involve adding functional groups like carboxyl, hydroxyl and carbonyl, on the sized CF, optimal for a particular resin system. For example, the presence of more carbonyl groups on the CF surface impact the adhesion with epoxies negatively but may be preferred for other resin systems [190]. The information on the type of sizing layer on the IM56D fibres was not given out or lost due to the industrial confidentiality of the CF waste suppliers. Thus IM56D (and SM56D) fibres may or may not

offer superior interfacial strength with epoxy resin systems. Another disadvantage with sizing on rCF composites is that it may cause agglomerations of the shorter, discontinuous fibres that lead to fibre-rich locations in the composite. Therefore, although this study proves that IM56R SMC laminates perform better than IM56D SMC, had the surface treatment on IM56D been optimised for the respective epoxy resin system, the results may have been different.

5.3.2.5 Variability

The uncharacteristically high variability of the warp and weft strengths of SM45D LCM laminates in Figures 5.8 and 5.9 could be the result of a poorly manufactured batch or a result of the variability of the LCM moulding process. It may also be argued from the discussions from 5.3.2.4 that the sizing present on the SM45D fibres here was incompatible. The sizing may also cause clusters of fibres to stick to one another that lead to fibre-rich and resin rich zones in the cured laminate. The availability and selection of recycled fibres nevertheless depends on the type of feedstock waste available.

Variability may exist amongst panels manufactured with the same processing variables. The differences can be attributed to the manufacturing variability, fibre history and quality at the fabric and cured laminate levels. At the fabric stage, variability could arise due to the damage to the fibre through various processing and carding steps and differences in areal weight at different sections of the fabric. At the cured laminate stage, variability is due to the presence of fibre rich and matrix rich areas in the panel, alignment errors during hand lay-up and the random fibre distribution of the laminate in three directions itself. The classification of laminates based on fibre types, moulding methods, needle punching density, areal weight and fibre volume fraction are valuable parameters to define rCF composites.

5.4 Summary

The results from this chapter recognise a marked difference in the material properties of rCF composites on the use of an inappropriate coupon geometry for tensile tests. The use of dogbone geometry coupons led to a larger percentage of acceptable, gauge length failures. The straight sided coupons and their variations are easy to prepare and most commonly used for tensile tests but, due to the reinforcement architecture of rCF composites, the stress distribution into the gauge length of such coupons is unsatisfactory leading to premature failures.

This chapter also reviewed the effect of rCF manufacturing processes on the material properties. The porous nature of needle-punched, non-woven rCF fabrics restricts the best performance of their cured laminates below 0.3 fibre V_f . The SMC moulding process outperforms LCM and Autoclave processes due to the better laminate consolidation achieved. The influence of recycled fibre type was also studied and it was found that laminates reinforced with IM56R exhibit the best performance.

Chapter 6: Static Shear Behaviour

This chapter discusses the static shear response of rCF composites. Greater emphasis was placed on the development of a reliable interlaminar shear testing practice over analysing shear properties of rCF composites quantitatively.

6.1 Development of shear test methods

6.1.1 Interlaminar shear

The objective was to identify and develop a test method to realise ‘true’ interlaminar shear failure for recycled, discontinuous, non-woven composites validated by the failure modes of the test specimens.

6.1.1.1 Short Beam Shear (SBS)

The SBS test method by three point bending, as described by ASTM D2344 [97] and ISO 14130 [98], was used to determine the interlaminar shear strength (ILSS) in the XZ (or YZ) plane of the composite laminate by the use of a short beam specimen with the span to thickness ratio described in Table 4.3. LCM, SMC and Autoclave moulded laminates were used.

The typical failure mode of rCF composites when subjected to SBS test in a three point bending set up with both ASTM and ISO standard specifications, irrespective of the laminate thickness and number of plies, is a tension failure at its bottom plane which is deemed as an unacceptable failure mode as shown in Figure 6.1. Adaptations to the SBS geometry on compression cured laminates, as suggested by literature, including the I-beam specimen, use of a sandwich beam specimen and remanufacture of a thick short beam specimen, did not induce shear failure in the laminate. A tension dominant failure was observed across all the above mentioned SBS adaptations.

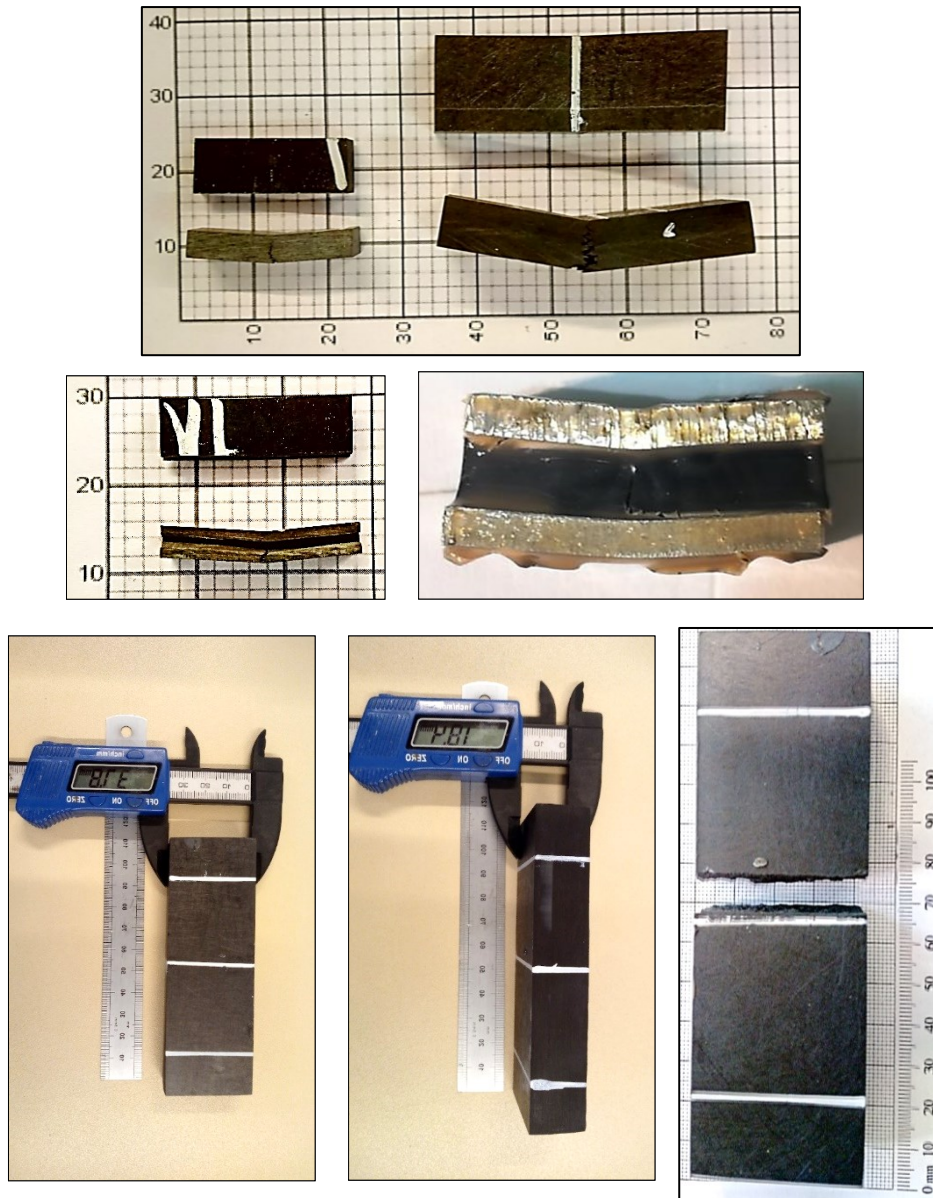


Figure 6.1: SBS failed specimen as per standards and modifications to specimen geometry

6.1.1.2 Double Notch Shear (DNS)

The DNS test uses an axial compressive load to generate a shearing action between the plies in a stagger-notched rCF composite specimen. A shear failure as per the DNS test is characterised by a crack along the shearing plane between the staggered notches of the specimen. An autoclave cured laminate was used in this test. The compressive load applied to the ZX plane resulted in an instantaneous failure with the specimen being crushed at one of the notches, instead of an expected delamination crack between the notches, as seen in Figure 6.2. The

apparent shear strength in Table 6.1 was calculated as the ratio of the failure load to the notch area because of the absence of a shear crack plane in autoclaved specimens. This mode of failure was expected for LCM and SMC cured laminates too.

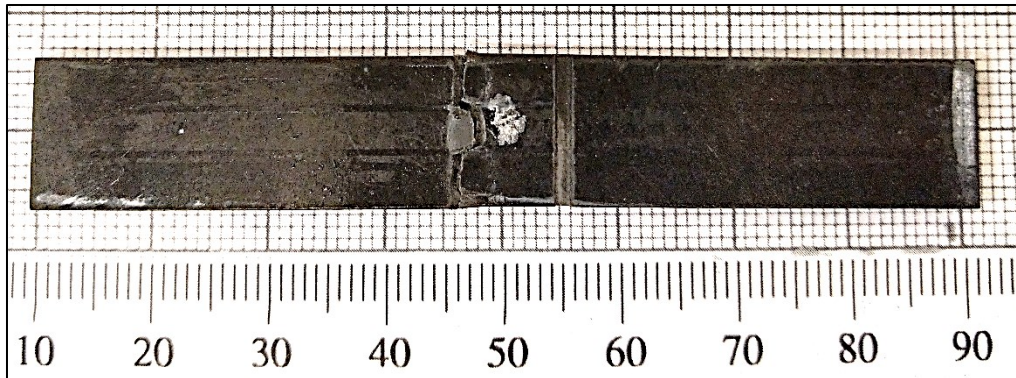


Figure 6.2: Failure mode of a DNS specimen

6.1.1.3 Double Beam Shear (DBS)

The objective of the DBS test is to induce interlaminar shear failure in the mid-plane of the specimen by means of a delamination between plies or an interlaminar crack in the XZ plane of the composite material. A five point bending load is applied on a short beam specimen in the DBS test method that subjects the laminate to a complex state of stress. LCM, SMC and autoclave laminates were used for this test.

None of the LCM or SMC laminates showed any indication of an interlaminar shear failure, as they failed with a double tensile failure at the bottom plane of the samples as shown in Figure 6.4.

Two out of the seven autoclave specimens tested failed with interlaminar cracks in the specimen as shown in Figure 6.3 whereas the remaining specimens failed by two tensile cracks at the bottom plane in between the support rollers. Although these two specimens also had cracks at the bottom plane, the interlaminar cracks were independent from them.

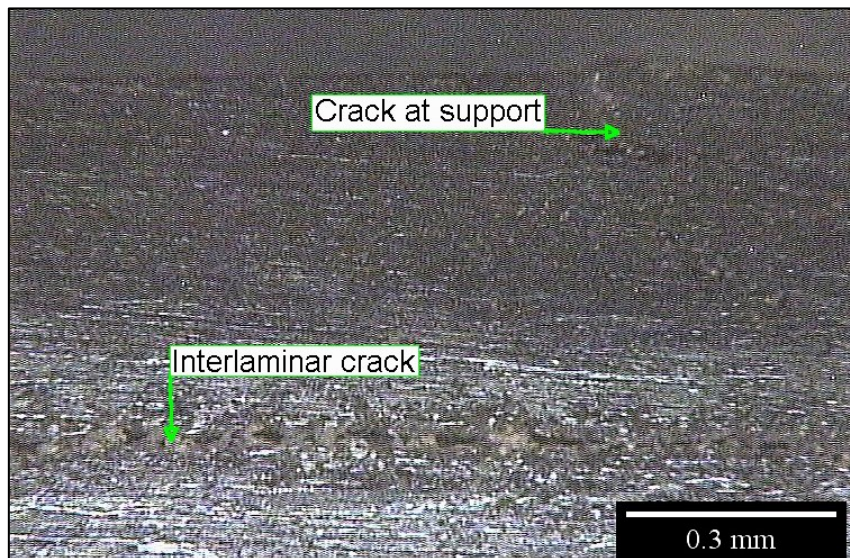
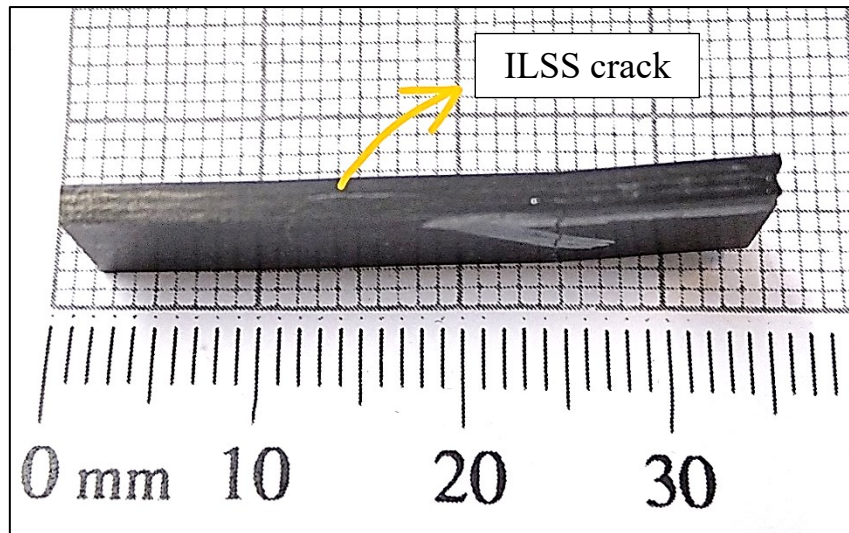


Figure 6.3: Interlaminar crack observed with autoclave cured laminates

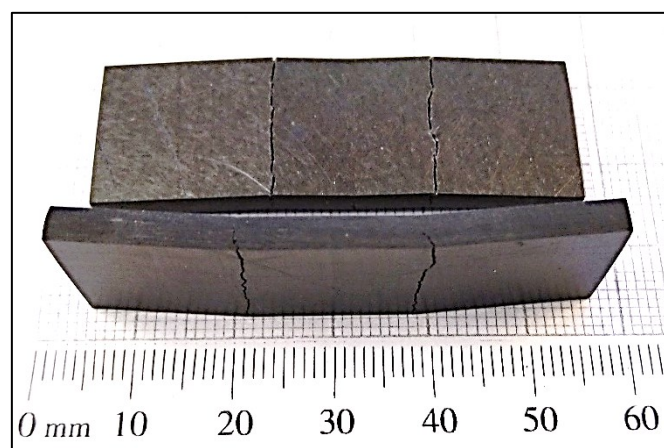


Figure 6.4: Failure mode of LCM and SMC specimens subjected to DBS tests

6.1.1.4. Iosipescu for interlaminar shear

The Iosipescu shear test was conducted on specimens in the XY, XZ and ZX planes of the rCF composite laminate. The XZ and ZX planes correspond to the measurement of interlaminar shear and the specimens have to be modified to introduce shear loads in these planes. A 20 ply, 200 gsm, SM45D reinforced SMC laminate was specifically used for Iosipescu Interlaminar Shear tests. The remanufactured specimens tested in the ZY/ZX planes of the composite laminate exhibited pure shear failure characterised by a notch to notch shear crack as shown in Figure 6.5 (a). The shear failure occurred within the laminate in the ZX plane and not at the bond-lines between the cured laminates, which demonstrates a delamination failure in the rCF composite. The interlaminar shear strength was calculated at its failure load in these two planes. The shear modulus was estimated with the use of dedicated shear strain gauges bonded between the notches of the specimens that recorded the out of plane shear strain of the material.

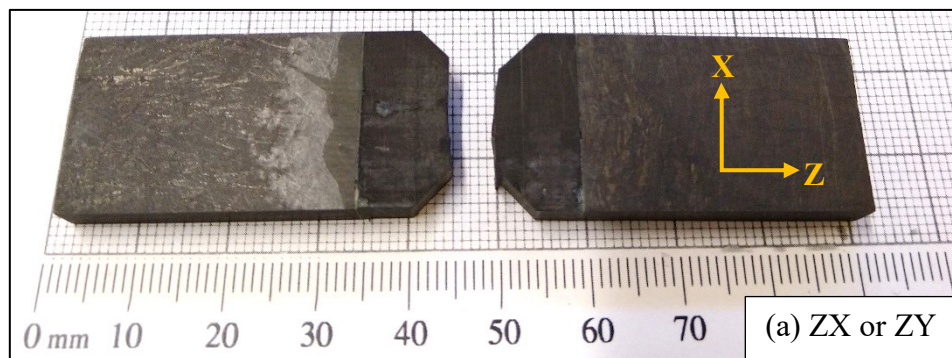


Figure 6.5: (a) Typical out-of-plane notch to notch shear failure in ZX/ZY plane and (b) delamination by splitting at the notch in the XZ/YZ plane with 90° V notch

The specimens tested in the XZ/YZ plane with a 90° V notch angle failed with delaminations by splitting near the notch as shows in Figure 6.5 (b). These cracks change the shear stress distribution in its deformed specimen that prevents failure between the notches in the gauge section. The delaminations are depicted as a drop in load in the load-displacement curve shown in Figure 6.7. The cracks followed to propagate through the width of the specimen away from the gauge section. The splitting delaminations are also seen with the 135° V notch angle specimens as shown in Figure 6.6. It was observed that the failure strength taken from the first occurrences of laminate splitting of the 135° V notch specimens were higher than the 90° V notch specimens.

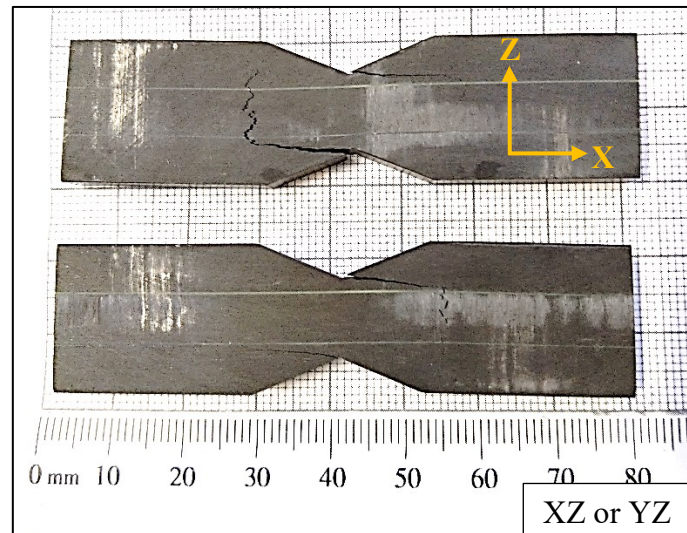


Figure 6.6: Laminate splitting in XZ/YZ plane on 135° V notch Iosipescu geometry

The shear strengths estimated by the four test methods are summarised in Table 6.1. The load-crosshead displacement plot is plotted in Figure 6.7 for typical SBS, DBS, DNS and 90° V-notch Iosipescu specimens in the ZX and XZ planes.

S.No.	Test Method	Testing plane	Specimen Geometry	Sample Size	Failure Strength or Shear Strength (MPa)	Failure Mode
1.	Short Beam Shear (SBS)	XZ/YZ	ASTM D2344*	8	34.72 +/- 0.64	Tensile
			ASTM D2344 + Longitudinal notch of 1 mm depth*	6	37.64 +/- 1.58	
			ASTM D2344 + Aluminium plates of 2 mm thickness*	6	78.24 +/- 9.86	
			ASTM D2344 by co-bonding three 20 ply laminates**	1	33.12	
2.	Double Beam Shear (DBS)*	XZ/YZ	ISO 19927	10	60.61 +/- 2.87	Tensile
3.	Double Notch Shear (DNS)***	ZX/ZY	ASTM D3846	10	30.59 +/- 3.10	Crushing at notch
4.	Iosipescu In-plane Shear*	XY/YX	ASTM D5379 (90° notch angle)	5	148.31 +/- 5.52	Tensile
			ASTM D5379 (90° notch angle) + CFRP and GFRP end-tabbed	3	128.58 +/- 12.97	
			ASTM D5379 with 60° notch angle	3	127.35 +/- 21.69	
			ASTM D5379 with 120° notch angle	3	133.01 +/- 8.23	
			ASTM D5379 with 8 mm notch to notch distance	3	147.52 +/- 3.49	
5.	Iosipescu Out-of-plane Shear**	XZ/YZ	Remanufactured ASTM D5379 geometry (90° notch angle)	6	46.90 +/- 4.96	Delamination/splitting
			Remanufactured ASTM D5379 geometry (135° notch angle)	6	60.81 +/- 4.22	
6.	Iosipescu Out-of-plane shear**	ZX/ZY	Remanufactured ASTM D5379 geometry	6	47.1 +/- 4.02	Shear

Table 6.1: Failure strengths of rCF composites to different shear test methods

Data tabulated for

* LCM laminate

** SMC laminate and

*** Autoclave laminate

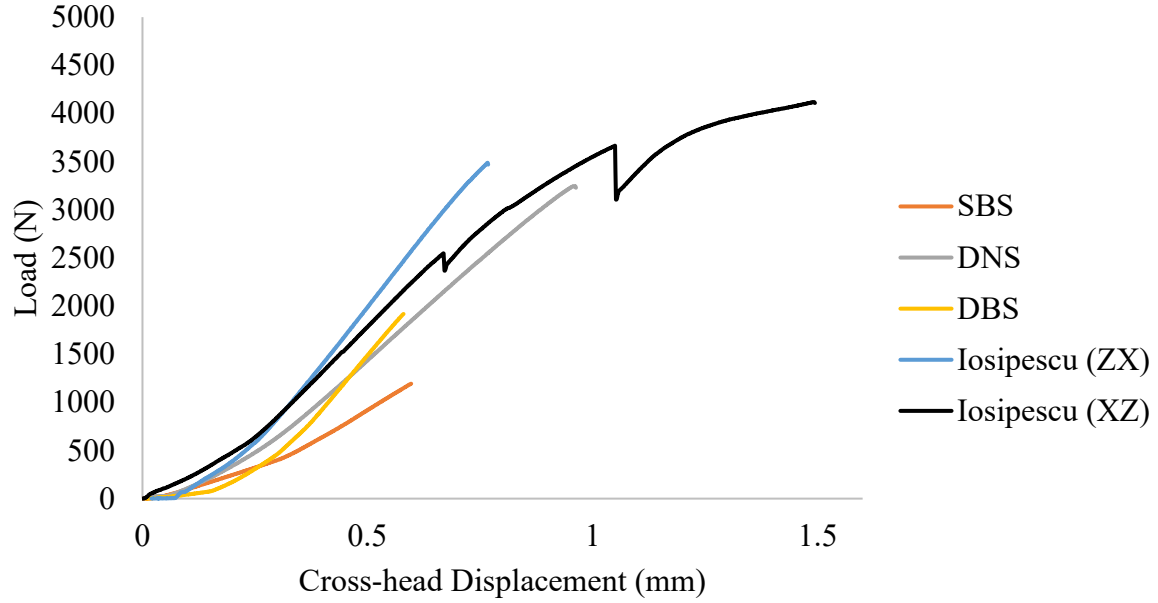


Figure 6.7: Load-Crosshead displacement curves for the out-of-plane shear tests

The average shear modulus from the Iosipescu shear test was derived in the ZX plane from its stress-strain plot in Figure 6.8. The shear modulus, termed as shear chord modulus of elasticity (G^{chord}) in ASTM D5379, was calculated in the shear strain range between 1500 $\mu\epsilon$ to 5500 $\mu\epsilon$ from Equation 6.1.

$$G^{chord} = \Delta\tau/\Delta\gamma \quad (6.1)$$

where $\Delta\tau$ is the difference in shear stress and $\Delta\gamma$ is the difference in shear strain between the two strain points. The shear chord modulus of elasticity of six specimens averaged to 2.81 +/- 0.52 GPa. The strain gauges de-bonded from the specimen before reaching the failure stress of the composite.

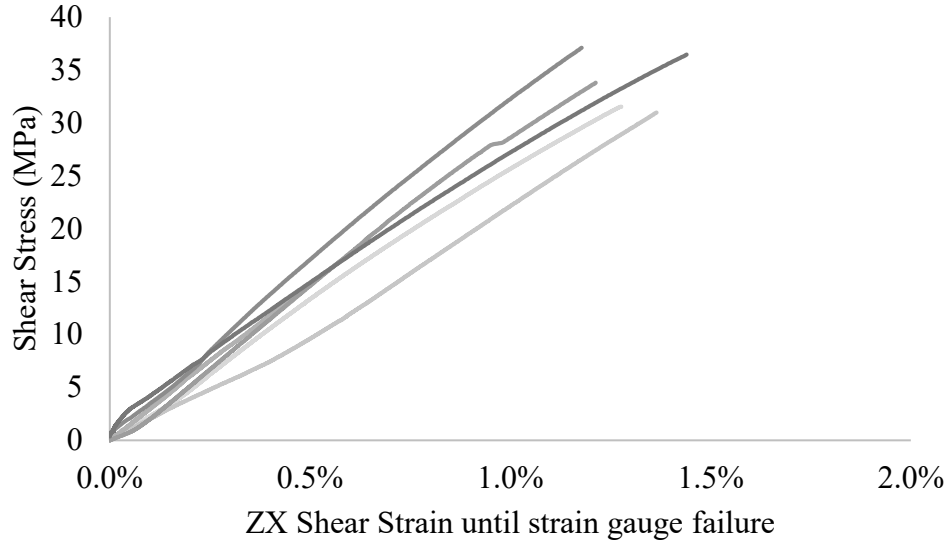


Figure 6.8: Shear Stress-Strain curves of 5 remanufactured specimens subjected to Iosipescu shear test in the ZX plane

6.1.2 Iosipescu for In-plane shear

4 mm thick, 20 plies of 83 g/m² LCM laminates were used for in-plane Iosipescu shear tests. The Iosipescu specimens in the XY plane of rCF laminates failed with 45° tensile cracks between the notches. End-tabbing the specimens with GFRP or rCF themselves, also resulted in a tensile failure mode. The modifications to the Iosipescu geometry by altering V-notch angles to 60° and 120°, 105° V notch angle calculated from Equation 2.2, and by reducing the notch to notch distance of the 90° V notch, all failed by a tensile crack as shown in Figure 6.9. A sample size of three specimens were selected for these modifications as the failure modes were expected to be consistent. The typical stress-strain curve for a standard 90° V notch angle, LCM cured specimen is shown in Figure 6.10 and the average failure strength listed in Table 6.1. The failures and results were also identical for a 3.7 mm thick, 12 plies of 200 g/m², SMC cured laminate in the standard 90° V notch geometry.

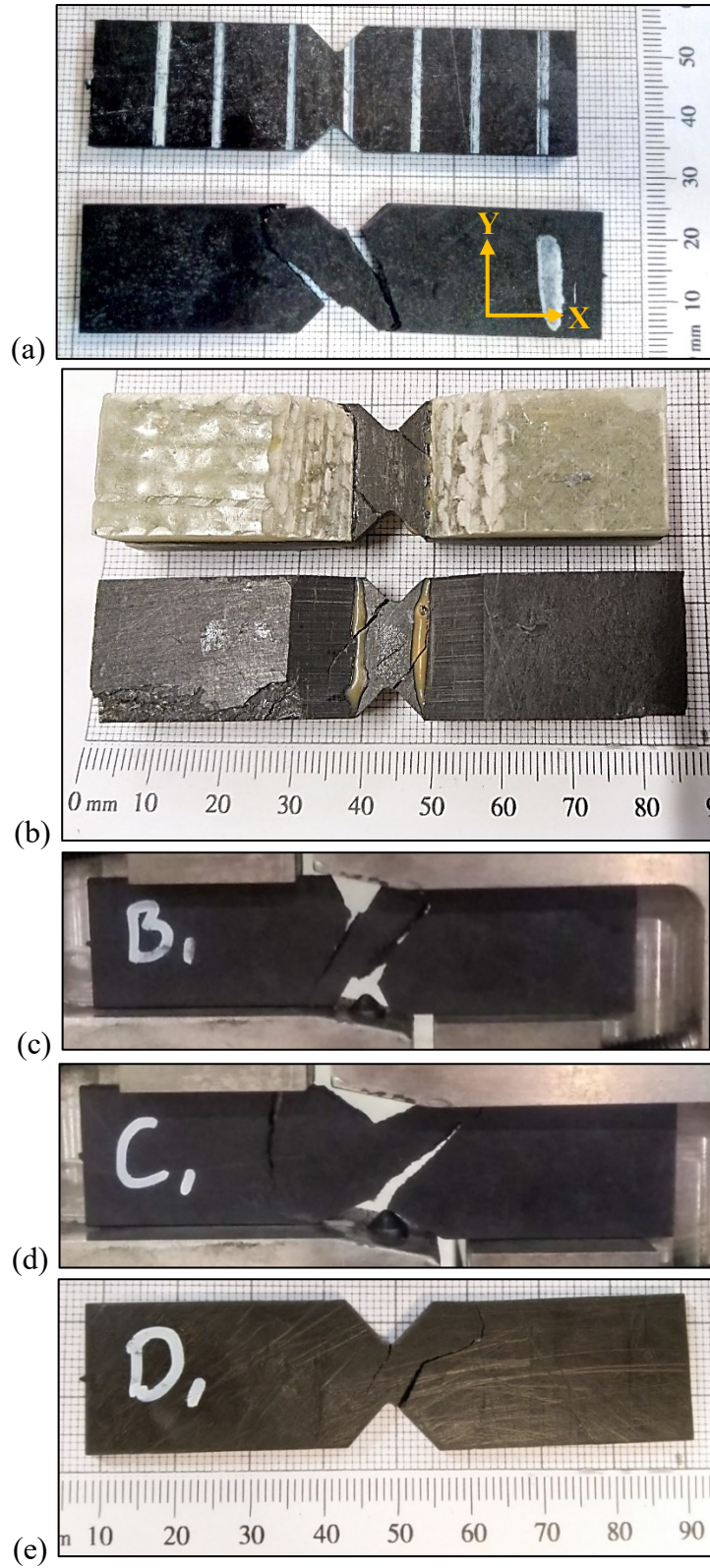


Figure 6.9: Typical in-plane (XY) shear failure by Iosipescu shear test for (a) standard ASTM D5379 geometry and modified geometries (b) End-tabbed, (c) 60° V notch, (d) 120° V notch and (e) shorter notch distance

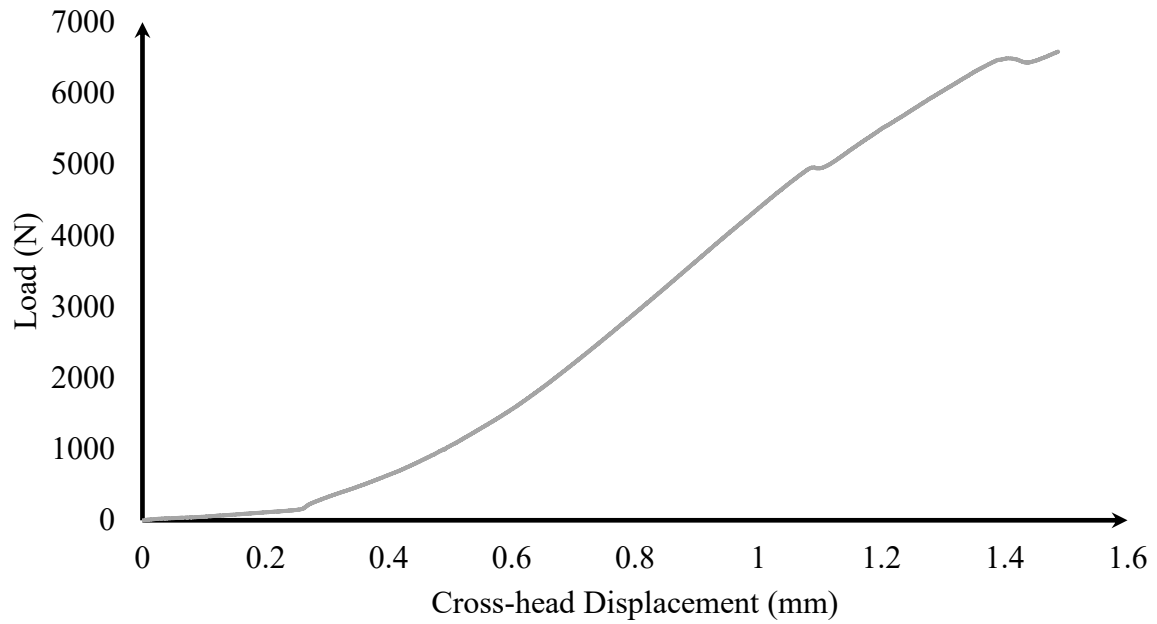


Figure 6.10: Typical load-Crosshead displacement of the standard 90° V notch Iosipescu in-plane shear test (XY plane)

6.2 Discussion

Analysis of the failure modes in rCF composites indicates the relevance of the above mentioned test methods for this class of composites.

6.2.1 Short Beam Test methods

The load-displacement curves (Figure 6.7) shows that the short beam specimens under SBS and DBS have distinct regions where the slope increases after a certain load, whereas the Iosipescu and DNS curves are relatively linear in nature. This could possibly be the result of the complex stress states that the SBS and DBS specimens are subjected to during the test. Both of the short beam test methods are unable to subject a pure shear load to the test specimen.

The SBS test is generally used for shear characterisation in the XZ or YZ plane. Its adaptations, as recommended in the literature (i.e., laminate with over 60 plies, introduction of notches and the sandwich beam specimen), all resulted in a tensile failure at its bottom plane. This failure mode with SBS is not limited to discontinuous laminates as this has been the commonly

reported failure mode with numerous other composite reinforcements too. The advantage of this method has always been the simplicity of the test, ease in the manufacture of the specimens and the fixture, and has been adopted as a rapid quality check for composites by determining their ‘apparent’ interlaminar shear strength.

While DBS may have had better success in continuous fibre composite systems as reported in the inter-laboratory study in Annex 2 - ISO 19927 [164], the test did not induce shear failures in non-woven, compression cured, rCF composites used in this study. The DBS method was slightly more successful than the SBS method in obtaining an interlaminar shear failure in the XZ/YZ planes for autoclave cured laminates, but this could be driven by the presence of severe inter-ply voids. Nevertheless, the repeatability of observing shear failure was low, even in autoclave cured laminates.

6.2.2 Double Notch Shear

The DNS test was conducted only on autoclave laminates, on expectation that their poor inter-ply consolidation would facilitate a shear failure in the laminate, however the method did not result in a shear failure. The crushing failure at the specimens’ notches could be because of the non-uniformity of the stress field in the gauge section of the specimen between the notches and the existence of highly concentrated stresses at the manufactured notches. The inability of the DNS test to generate a uniform shear fracture plane could possibly be because of the nature of the porous non-woven reinforcement composite that results in a moderately transversely isotropic material in the XY plane [118]. In addition to this, it has been reported in the literature that the distance between the notches and depth of the notches can result in variable results and the DNS has very little scope as a shear test alternative at least for the reinforcement structure used in this study.

6.2.3 Iosipescu Tests

6.2.3.1 In-plane shear (XY plane)

The use of the Iosipescu shear test in the determination of the in-plane shear component along the XY or YX plane of the material did not generate a shear failure that is characterised as a notch to notch crack. Changes to the V-notch geometry of the Iosipescu specimen set at 120°, 60° and a reduced notch distance did not change the failure pattern of the 45° tensile crack observed. This can be explained by the distribution of the fibres in the XY plane of the laminate that offers resistance in the warp and weft directions, which prevents the matrix dominant shear failure in this plane. The influence of the lay-up and fibre distribution is also explained in a continuous fibre reinforced cross-ply [0/90] GFRP/epoxy laminate where different failure modes were observed when tested at different off-axis angles in the Iosipescu test [109, 179]. Increasing the cross-sectional area of the test specimen in the XY plane, akin to Arcan test methods [108], was not found to be successful in a random fibre reinforced GF/epoxy composite and thus not studied with rCF composites.

6.2.3.2 Interlaminar shear (ZX plane)

The remanufacture of the laminate to characterise the composite in the ZX or ZY plane resulted in a pure shear failure between the V notches characterised as an instantaneous and straight crack between the notches. This fracture is synonymous to that of a delamination failure between the plies of the cured laminate and is consistent across all of the specimens tested. The shear strength calculated here should comply with the interlaminar shear strength of rCF composites because the gauge region of the Iosipescu specimen is subjected to a state of pure shear. The limited amount of fibres dispersed in these planes relative to that in the XY plane facilitated a matrix dominated crack. The influence of the epoxy bond between the cured

laminates can be neglected because the cracks observed occurred within the central laminate and not at the bond-line.

The disadvantage is that careful specimen remanufacture can be cumbersome and requires the use of thick cured laminates, of at least 6 mm in thickness, to minimise the influence of external epoxy bond-lines. ASTM D5379 requires that the laminate must either be at least 76 mm thick or be co-bonded to 76 mm thickness [177]. The manufacture of a 76 mm thick laminate is challenging for compression moulding techniques, especially on a fabric such as rCF non-woven mats that are by nature, lofty due to the mechanical bonding enabled by the needle punched fibres in the Z direction. The hypothetical case of manufacturing a 76 mm thick laminate would suggest the presence of flaws, defects, voids and a poorly cured material through the thickness of the laminate that would result in poor experimental values. The maximum thickness of the laminate in this study was thus restricted to 6 mm. This ensured a suitably cured laminate through the thickness of the material with minimum manufacturing defects. The alternative option of co-bonding up to 76 mm thickness was also considered, but this may likely introduce several undesirable variables during the test. Firstly, the bond-lines between the cured laminates have to be minimal to reduce the influence of adhesive in the test. Secondly, successful co-bonding over 13 cured 6 mm thick laminates in an experimental laboratory setting without imperfections or misalignments was deemed unlikely. Thirdly, in the case of such a manufactured material, the length of the V notch specimen may well undergo some amount of damage that could influence the test. Hence, only the critical section of the V notch geometry was manufactured and bonded to laminates in the XY plane, which tend to exhibit higher load resistance than those loaded in the ZX/ZY plane, as the results of this study would suggest. The fulfilment of interlaminar shear in the refabricated V notch specimen was realised with cracks that occurred within the central laminate between the V notches with the exclusion of any cracks originating from the bond-lines between the cured laminates, as seen

in Figure 6.5. Although the specimen remanufacturing may be cumbersome, it remains a valid method for the determination of the critical shear strength in the ZX/ZY plane of rCF composites.

The shear modulus was estimated with the use of dedicated shear gauges bonded onto one face of the Iosipescu specimen. The influence of any twisting in the specimen was checked by measuring the shear strains by bonding strain gauges on both the sides of one Iosipescu specimen and these are plotted in Figure 6.11. A difference of 0.31 GPa in the shear modulus was calculated but this error could be averaged out by the use of a larger sample size. The variance could arise due to errors in bonding alignment of the central gauge section to the remaining sections of the Iosipescu geometry, possible twisting of the specimen by the jig, differences in thickness across the specimen, the relatively small strain considered (up to 13 MPa load), variability in the distribution of the fibres in the gauge section or the material, and errors from the strain gauge itself. However this inconsistency in shear strains from the two faces of the same specimen falls within the standard deviation of the sample considered here.

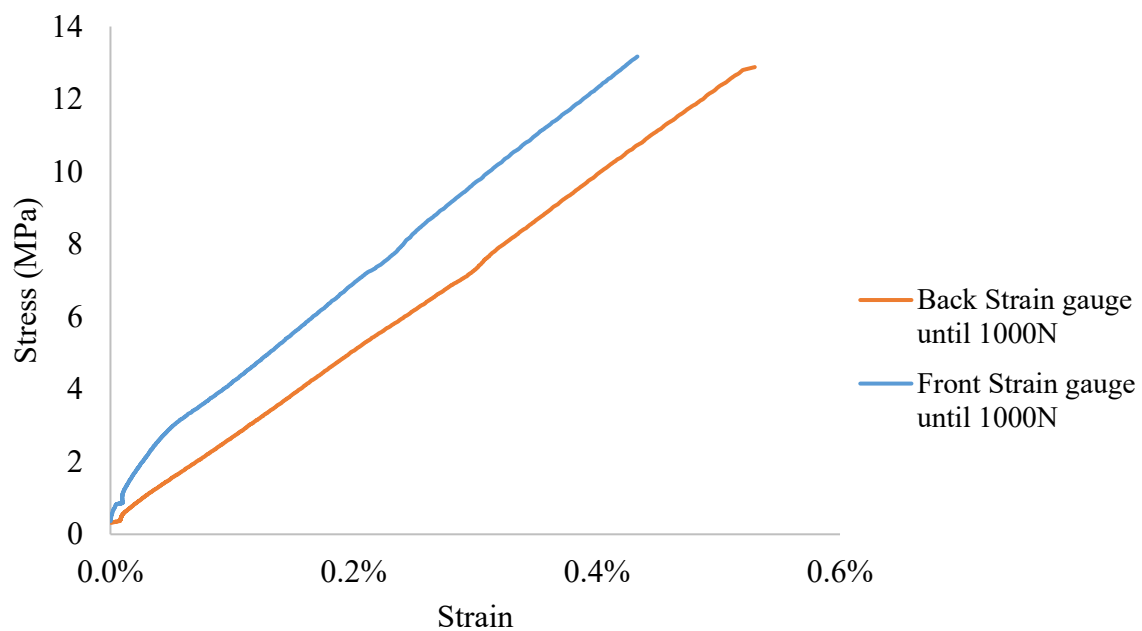


Figure 6.11: Shear Modulus calculated from both faces of the ZX/ZY Iosipescu specimen

6.2.3.3 Interlaminar shear (XZ plane)

The delamination failure observed in the 90° V notch Iosipescu specimen in the XZ/YZ plane is similar to the failure modes reported in continuous fibre reinforced UD composite specimens tested along the 90° direction [100, 106, 107]. The specimen failed by splitting near the notches before shear failure was observed in the gauge section. The splitting of the top and the bottom laminates, represented by drops in load in Figure 6.7, may have been followed by a non-uniform stress distribution in the remaining specimen geometry that prevents further delaminations between the 90° V notches. Wider notch angles such as the 135° specimen used did not result in the occurrence of a shear failure but, rather, the failure strength of the modified specimen appeared to depend on the angle of the V notch. The dependence of the failure strength on the angle of the V notch calls for the continued use of the 90° V notch as recommended by the international standards. The failure strength was taken as the first occurrence of a delamination crack in the test material, but whether this can be considered as an interlaminar failure is debatable, just as in the case with unidirectional continuous fibre composites discussed in literature [100, 106, 107].

The occurrence and determination of out-of-plane shear failure in a multidimensional reinforced composite such as the needle-punched, non-woven rCF composite discussed here involves the identification of the shear plane in which pure shear failure is most likely to occur. Interlaminar failure is likely to occur in the weakest shear plane of the laminate wherein the reinforcement fibres along that particular plane are minimal. The Iosipescu shear test for the determination of interlaminar shear requires a specific fixture, re-fabrication of planar laminates for manufacturing specimens, bonding of strain gauges for the determination of shear moduli and, overall, it becomes a relatively expensive test procedure. Despite this, this method remains the only viable method that can repeatedly and precisely determine the interlaminar shear strength and modulus for the rCF composites used here. This re-fabricated V notch

geometry and test method may also be applicable to textile composites with similar reinforcement architectures.

6.3 Summary

The nature of the internal fibre architecture in rCF composites means that pure shear failures are difficult to realise from conventional testing methods. The difficulty in obtaining a shear failure was evident with three point bending set-up by SBS test (including modified geometries), five point bending set-up by DBS test and staggered notch specimen in the DNS test. The DBS test could induce interlaminar shear in a limited amount of autoclaved specimens, but this was driven by the presence of inter-ply voids.

The reinforcement architecture restricted pure in-plane shear failure for the V-notch Iosipescu shear test. The Iosipescu test seemed to be the most successful for interlaminar shear but the specimen geometry needed to be remanufactured and redesigned with thick laminates (at least 6 mm thick) so as to observe pure shear failure in the material, introducing load into the weakest planes of the material. Identification of the shear plane in which interlaminar failure is likely to occur was key in the determination of the critical limit of shear strength in rCF composites. Based on the results of this study, the Iosipescu Shear test is advised as the recommended shear test practice for discontinuous, needle-punched carbon fibre composites.

Delamination along the ZX/ZY plane was the cause of interlaminar shear failure. The interlaminar shear strength of SMC rCF composites was measured to be 47.1 +/- 4.02 MPa. Shear modulus of the rCF composite was determined with the aid of dedicated strain gauges, which were also used to check for any evidence of specimen twisting during the Iosipescu test. The interlaminar shear modulus of SMC rCF composites was measured to be 2.81 +/- 0.52 GPa.

Chapter 7: Influence of Cyclic Loading

This chapter discusses the tension-tension fatigue behaviour of different non-woven rCF composite systems, the stiffness evolution in the laminate with cyclic loading and damage mechanisms.

7.1 Specimen geometry

The selection of specimen geometry imparted a significant influence onto the stress transfer mechanisms within the coupon, similar to that observed in static tensile tests. Both straight sided, untabbed rectangular coupons and dogbone geometry coupons were cut from the same panel in a preliminary study. The coupons were subjected to sinusoidal, load controlled fatigue at a stress ratio of 0.1 and frequency of 10 Hz. As seen from Figure 7.1, the number of cycles to failure with rectangular coupons at a maximum alternating stress of 197.57 MPa (corresponding to a tensile strain of 0.9%¹), as recommended and commonly used for fatigue based tests, could range anywhere between 758 cycles to over 3 million cycles. In addition, the number of specimens failing within the gauge length was minimal, indicating a poor stress and strain transfer from the grip into the material. The higher variability observed in rectangular coupons would have resulted in a poor understanding of the fatigue response due to various rCF material processing techniques. By contrast the use of a dogbone specimen geometry at two different stress levels of 223 MPa (1% strain) and 195 MPa (0.9% strain), resulted in a distinct clustering of fatigue performance with a majority of the samples failing in the gauge length. Furthermore, the improved stress/strain transfer was verified with the temperature distribution measured via an infrared thermometer along the length of the specimen. It was found that the central gauge section showed a temperature rise of 2°C from ambient lab temperature and gradually reduces towards the grip section.

¹ Material used in this case - SMC IM56R, with maximum tensile strain of 1.24%

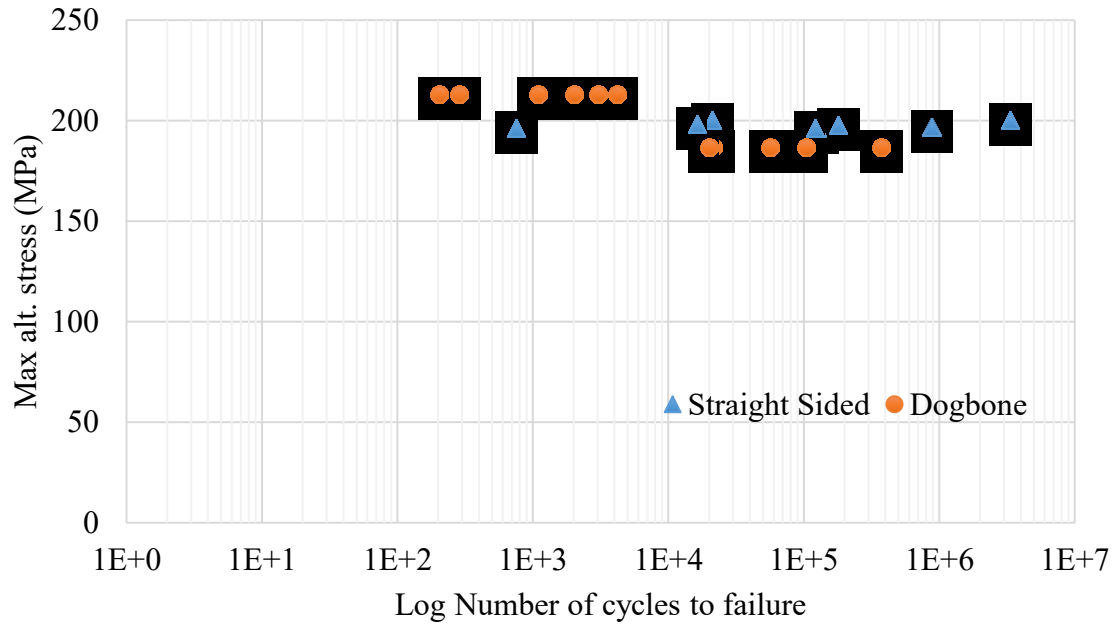


Figure 7.1: Variability in cycles to failure with specimen geometry

7.2 Fatigue life envelope of rCF Composites

The fatigue sensitivity of rCF composites was found to be typically low. Figure 7.2 compares the SN curve of SMC IM56R rCF cross-plyed laminate (from the current study) with reported values of select engineering materials from the literature namely, aluminium 6061 alloy, Woven CFRP/epoxy of $[(+/-45), (0/90)]_{3s}$ layup, chopped strand GF mat/polyester and plain weave E-glass fibre composite [191-194]. Although their static strengths are at different levels, it can be seen that the general fatigue resistance of rCF composites, represented by the slope of the SN curves, was found to be better than certain traditional materials. It should be noted that composites made with straight, aligned and continuous fibres, UD CFRP composite or non-crimp CF composites, tend to have much higher fatigue resistances. However, rCF composites have improved fatigue resistances over materials of comparable static strengths and reinforcement architectures, such as chopped strand mat GF composites. The fatigue curve of a GF mat reinforced SMC laminate, using the epoxy matrix system of Hexion™ 06605 is shown in Figure 7.3.

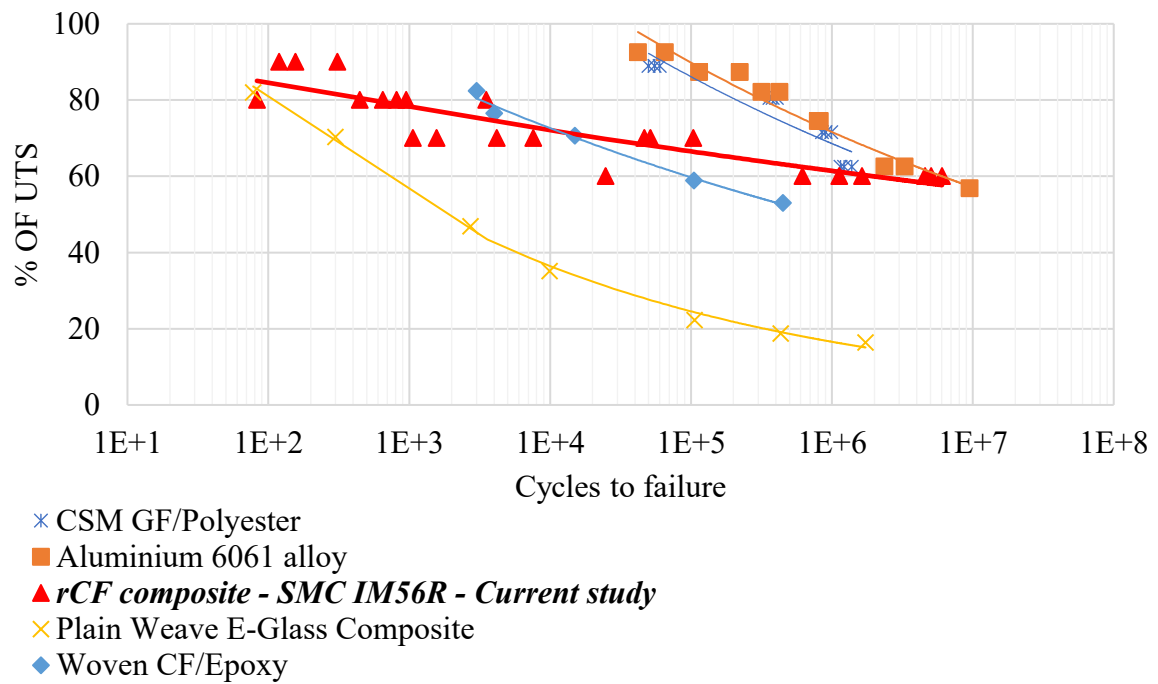


Figure 7.2: Fatigue resistance of SMC IM56R with respect to traditional materials [191-194]

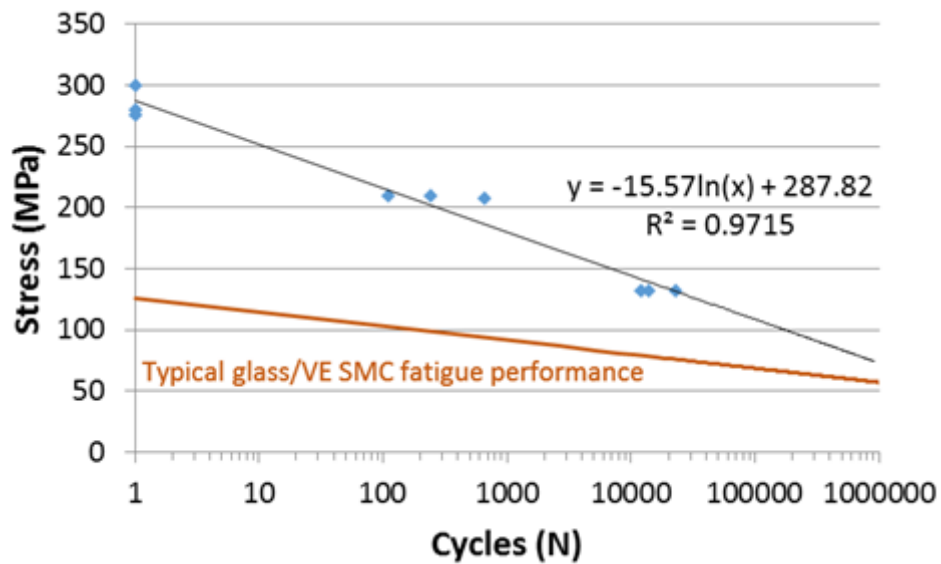


Figure 7.3: Fatigue curve of GF reinforced SMC laminate of Hexion™ 06605 resin system; Test Standard: ASTM D3479, Test Frequency: 7Hz; Stress Ratio (R): 0.1 [172]

Figure 7.4 depicts the average number of cycles to failure at each stress level for eight different rCF composite systems (see Table 7.1), irrespective of fibre volume fraction, composite moulding process, fibre type, lay-up and laminate loading direction. The S-N curves of each individual laminate are collected in Figures A4.1 to A4.8. The endurance limit of rCF composites, set at 10 million fatigue cycles, was realised at loads lower than 50% of the material ultimate strength that corresponds to a maximum alternating stress level of at least 100 MPa. As the readings at 100% stress level were static ultimate tensile strengths, run at different strain rates to the fatigue failure points, the SN curve could be classified into two distinct regions, i.e., at high stress levels above 60% and low stress levels below 60% of material UTS.

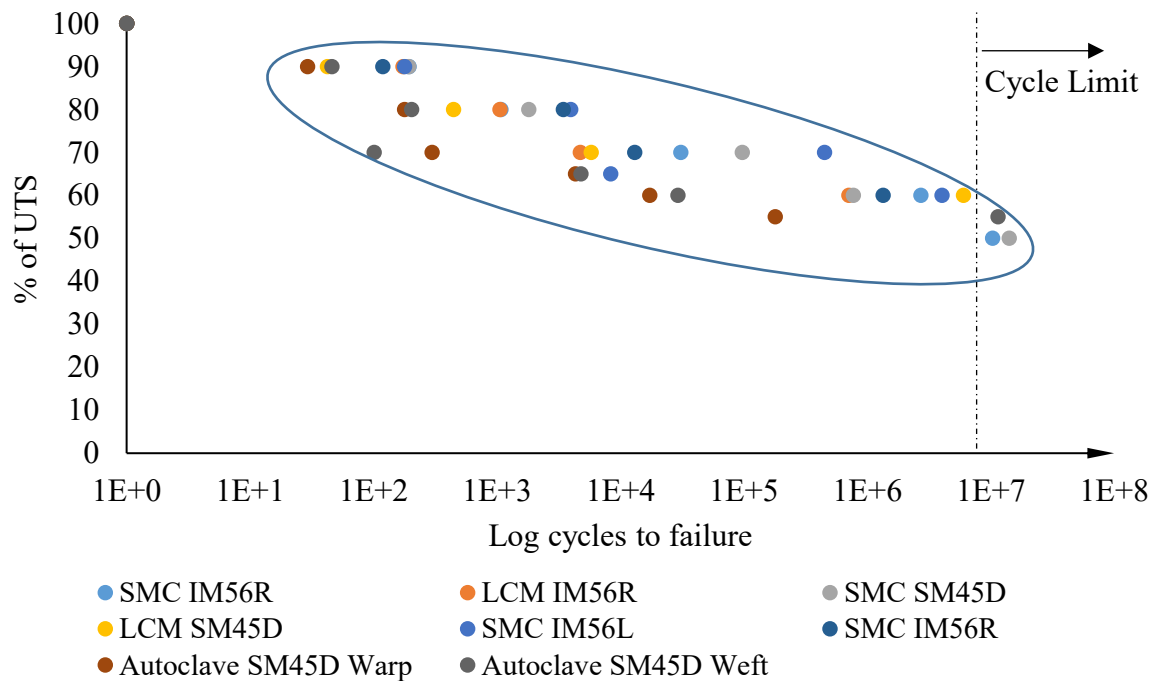


Figure 7.4: Average fatigue life diagram across different rCF composite systems

Non-woven rCF/epoxy composites typically have an average ultimate tensile strain of 1.11% +/- 0.24%, the variation arising due to the fibre type, remoulding process and laminate directionality. The data points plotted in Figure 7.4 estimates the number of cycles to failure for strain limits that are typically much higher than that used in engineering applications. As

the endurance limit is realised at 50% of the material UTS, it is safe to assume that rCF composites are predictable materials with good fatigue resistance.

7.3 Influence of material processing parameters

The following section discusses the fatigue response in non-woven rCF composites by assessing the recycling and remanufacturing process parameters.

7.3.1 Laminate directionality

The effect of fatigue load based on the laminate directions was analysed using Autoclave 0.22 V_f moulded laminates, where four 200 g/m² non-woven mats of SM45D fibres were laid in the same orientation. Samples were taken in the warp and weft directions for fatigue testing. Their static strengths were measured as 203 +/- 7.64 MPa in the warp and 297 +/- 16.2 MPa in the weft directions and their fatigue resistances are shown in Figure 7.5.

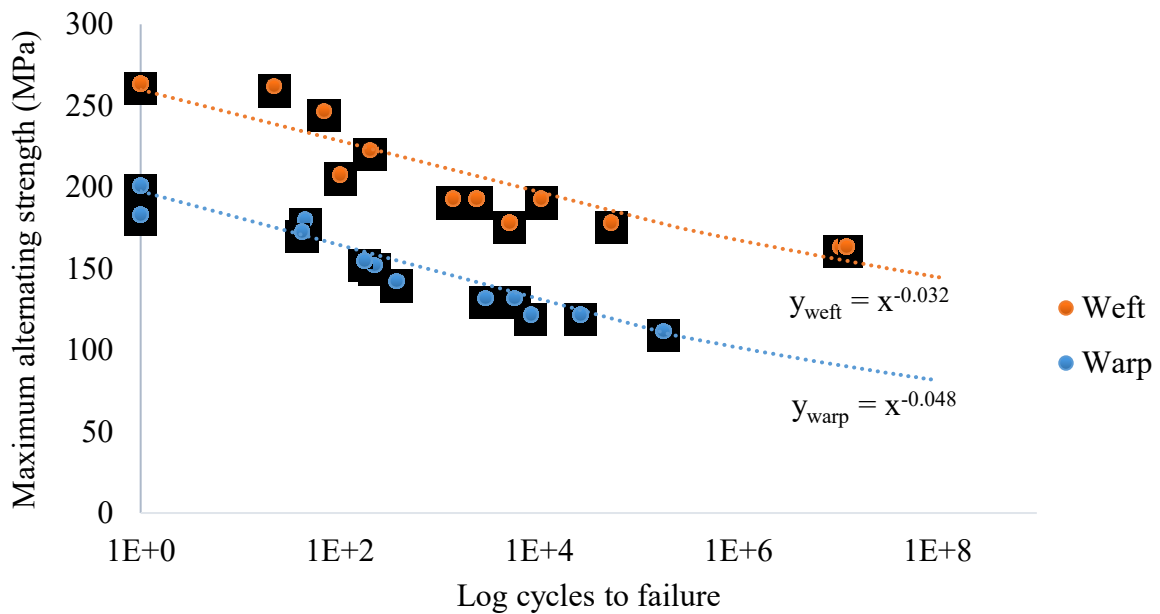


Figure 7.5: SN curves of Autoclave SM45D laminate in warp and weft directions

A clear distinction between the static strengths in two directions can be observed from Figure 7.5. The fatigue resistance, taken as a measure of the slope of the SN curve, is indicated by the

exponent of the power law equation in this figure. The power law equation was used because its curve better represents the two linear phases at higher and lower stress levels than a logarithmic chart, as explained in Section 7.2. A steeper slope has a higher negative exponent that corresponds to a more fatigue sensitive material. As indicated by their respective coefficients in Figure 7.5, the fatigue resistance in the weft was seen to be higher than that in the warp. Similar to its static properties, this could be a result of the preferential fibre placement in the weft direction of the non-woven mat during the carding process.

7.3.2 Influence of fibre content

Table 7.1 shows the fatigue endurance limit, calculated from their respective curve fitting equations at 10 million fatigue cycles, was generally at 50% of the respective material UTS, across different rCF composite systems, based on the processing, fibre type, fibre content and laminate direction.

Irrespective of the process technique, the fatigue endurance limit is seen to be proportional to the material UTS. The common trend amongst the cross plied laminates and the SMC based warp laminates is that the endurance limit increases with the fibre volume fraction in the material. The lower endurance limit of the LCM SM45D warp and Autoclave SM45D warp laminates result from inferior processing in comparison to SMC laminates. Despite this, Autoclave SM45D weft has a higher endurance limit which suggests that the fatigue resistance corresponds with the fibre content in the direction of fatigue loading.

S.No.	rCF composite system	Fibre V_f	UTS (MPa)	Tensile Modulus (GPa)	Fatigue Endurance limit (MPa)
1	LCM IM56R cross	0.21	254.91 +/- 9.83	25.25 +/- 1.11	129.05
2	SMC IM56R cross	0.25	279.72 +/- 24.05	21.39 +/- 1.9	157.68
3	SMC SM45D cross	0.33	266.39 +/- 35.65	25.13 +/- 0.11	156.40
4	SMC IM56R warp	0.17	197.46 +/- 28.66	15.79 +/- 1.05	107.49
5	SMC IM56L warp	0.19	197.23 +/- 22.32	24 +/- 2.46	114.67
6	LCM SM45D warp	0.27	194.06 +/- 18.91	19.07 +/- 1.93	109.49
7	Autoclave SM45D warp	0.22	203 +/- 7.64	17.54 +/- 1.31	91.12
8	Autoclave SM45D weft	0.22	297 +/- 16.2	26.75 +/- 1.35	155.12

Table 7.1: Fatigue endurance limit across different rCF composite systems

7.3.3 Influence of pyrolytic processes

Figure 7.6 represents the SN curves from a 0.19 V_f SMC, IM56L laminate of UTS 197.23 +/- 22.32 MPa, a 0.17 V_f SMC, IM56R laminate of UTS 197.46 +/- 28.66 MPa and a 0.22 V_f , autoclaved, SM45D laminate of UTS 203 +/- 7.64 MPa, all tested in the warp direction. It was found that the fatigue resistances of both the IM56L and IM56R laminates, moulded in the same epoxy resin, were quite comparable. Comparison between autoclave SM45D and SMC IM56L/IM56R laminates highlighted the poorer fatigue performance of the autoclaved laminates, but this could be attributed to the poor consolidation due to the additive used in the epoxy system that renders it to be more viscous over the SMC epoxy system. The standard modulus fibres may have also contributed to the poorer fatigue resistance.

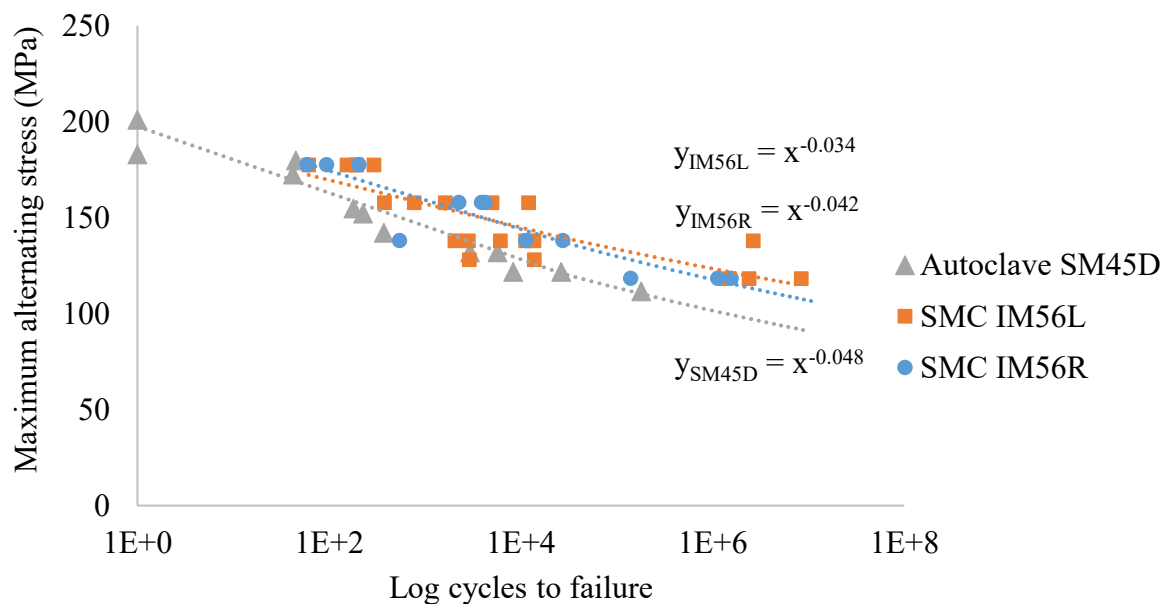


Figure 7.6: Influence of pyrolysis on fatigue resistance

7.3.4 Influence of fibre grades

The influence of fibre type was studied using cross-ply SMC processed laminates of different fibre modulus grades, namely, standard modulus fibres and intermediate modulus fibres. A 0.25 V_f IM56R reinforced laminate of UTS 279.72 $\pm$ 24.05 MPa was compared with a 0.33 V_f SM45D reinforced laminate of UTS 266.39 $\pm$ 35.65. Their fatigue resistances are plotted in Figure 7.7. No distinct difference in the fatigue resistances between the two laminates was found. The exponent is merely an indication for the fatigue resistance, and the common observation that the endurance limit was reached at the same stress levels holds true in this case. Although it could be argued that an enhanced performance of the SM45D laminate is because of its higher V_f than the IM56R laminate, their static strengths were similar. This could be the case where a higher V_f compensated for the static and fatigue strengths of the SM45D reinforced laminate. Hence there is no conclusive evidence to justify the influence of fibre type. A much improved static and fatigue strength could be expected from the IM56R laminate too, had the V_f been higher than 0.25. In this context, it is postulated that IM56R reinforced laminates had a better fatigue resistance than SM45D reinforced rCF composites.

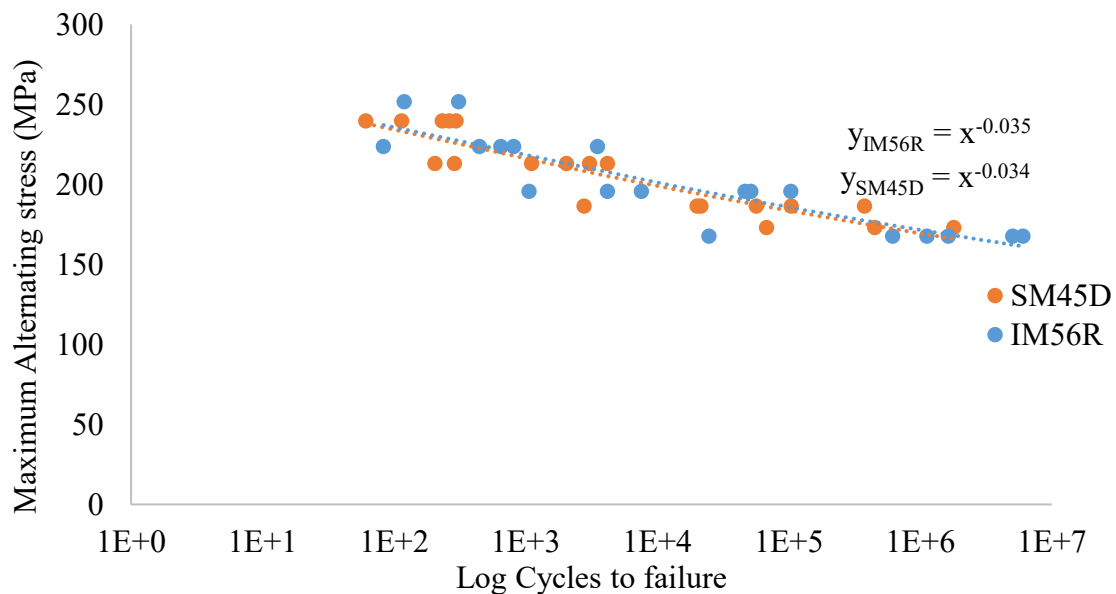


Figure 7.7: Fatigue sensitivities of SMC laminates of different fibre grades

7.3.5 Influence of laminate moulding processes

The impact of the laminate remoulding process was studied using cross-ply IM56R reinforced laminates. A 0.25 V_f SMC laminate of UTS 279.72 +/- 24.05 MPa was compared with a 0.21 V_f LCM processed laminate of UTS 254.91 +/- 9.83 MPa. Their fatigue resistances are plotted in Figure 7.8 and it can be seen that the SMC laminates have a better fatigue resistance than the LCM laminate. The improved fatigue performance of SMC laminates could be attributed to their superior consolidation over LCM processed laminates.

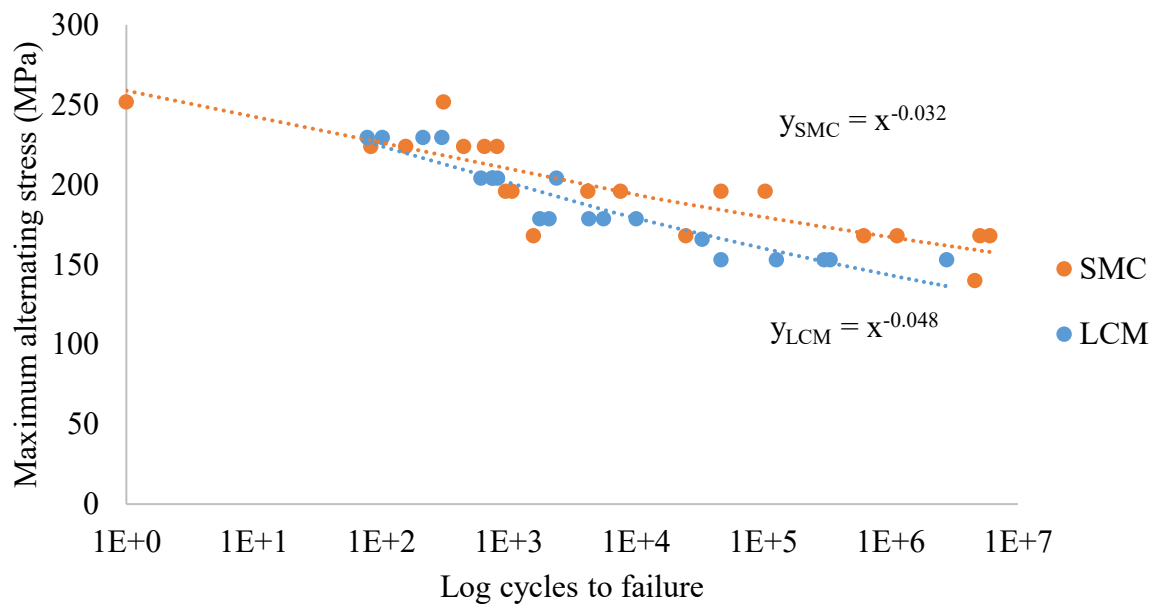


Figure 7.8: Fatigue resistance based on laminate remoulding process

7.4 Fatigue Damage

7.4.1 Modulus as a damage metric

Composite materials undergo a loss of stiffness with fatigue as explained in Section 2.4. For random fibre reinforced SMC composites, a damage parameter D is expressed in terms of modulus reduction from Equation 7.1 [195]:

$$D = \frac{E_0 - E}{E_0} \quad (7.1)$$

where E_0 is the initial stiffness and E is the stiffness after N fatigue cycles. The following section discusses the results of stiffness evolution in rCF composite systems, established using a destructive methodology in quasi-static tensile tests evaluating strength and stiffness, and also using a 25 mm gauge length dynamic extensometer.

7.4.1.1 Quasi-static Tensile tests

A 0.25 V_f , cross-plyed, IM56R fibre, SMC laminate was used to assess a suitable methodology to monitor stiffness. A method to quantify the loss in stiffness due to fatigue, as per ASTM D3479 [180], is to evaluate the tensile properties upon discontinuation of the cyclic loading at selected intervals, referred to as quasi-static tensile tests. A pilot test evaluating the residual properties of three specimens fatigued to 7 million cycles at 10% UTS and three specimens at 50% UTS for 12 million cycles was carried out and the results are plotted in Figure 7.9. The residual properties were compared with the static tensile properties of a sample from the same panel.

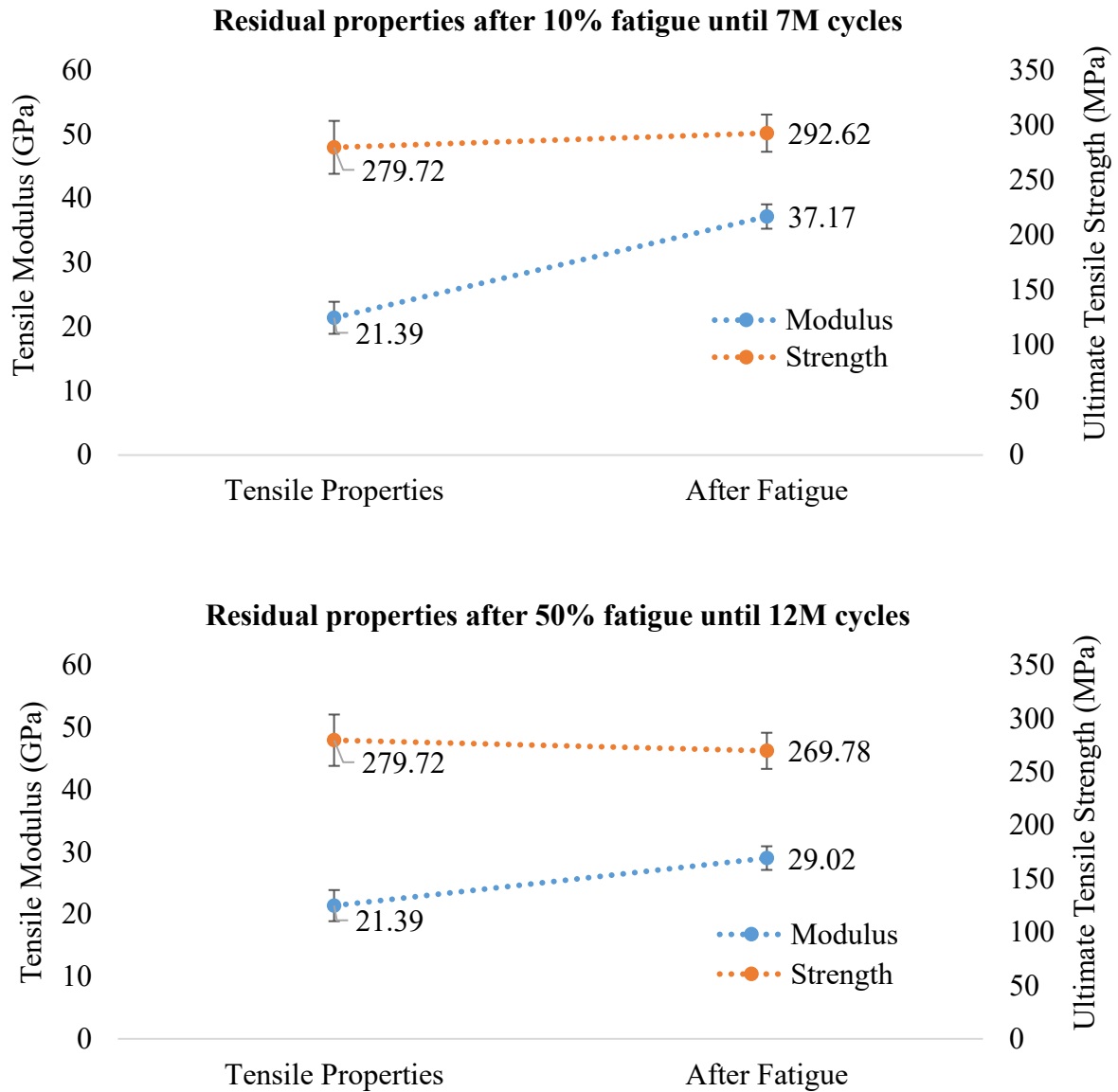


Figure 7.9: Residual characteristics of SMC IM56R laminate after fatigue cycling - a preliminary assessment

From Figure 7.9, it can be seen that the average residual tensile strength of the samples was within the material standard deviation before fatigue, but the tensile modulus increased after fatigue cycling. This unexpected increase at both the fatigue stress levels may be attributed to smaller sample size and the natural material variability too. Furthermore, it was observed that the sample average tensile strain to failure dropped from 1.34% to 0.98% in the fatigued samples. Nevertheless, the above quasi-static tensile test results were part of a *preliminary investigation* of the residual properties post-fatigue testing on rCF composites and a more

rigorous approach to monitor the material properties was needed. The samples considered before and after fatigue were different and further studies using a dynamic extensometer to measure the loss in stiffness is recommended.

Henceforth, the material stiffness due to fatigue cycling was monitored using its dynamic moduli, calculated from the slope of the hysteresis loops as explained in Figure 7.10.

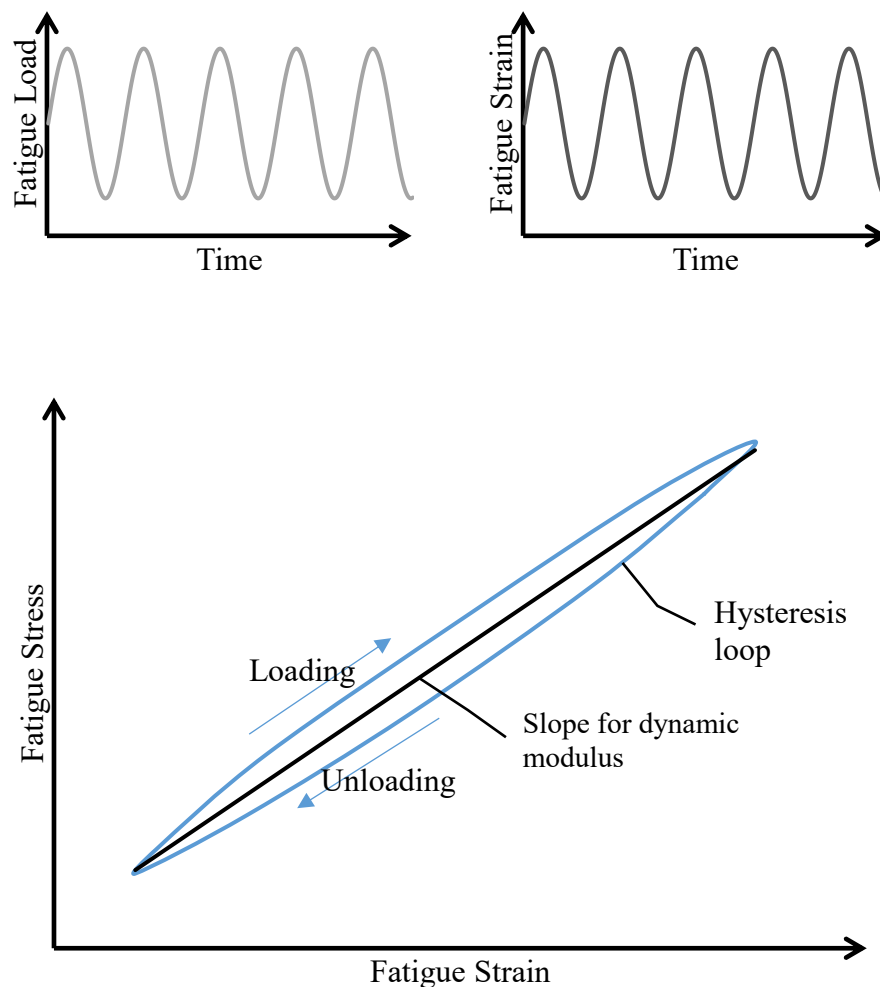


Figure 7.10: Fatigue data recorded transformed into a hysteresis loop for dynamic modulus calculation

The stiffness change was thus assessed by calculating the dynamic moduli with the aid of a dynamic extensometer attached to the samples during fatigue cycling. As a pilot test, two new sets of three specimens taken from the same laminate panel as used above, were subjected to 3 million fatigue cycles at stress levels of 50% and 10% UTS and plotted in Figure 7.11. No

significant change in the resultant dynamic stiffness before and after fatigue was observed. It must be noted that the dynamic modulus does not equate to tensile modulus, but this methodology provides a more reliable indication of stiffness evolution in the laminate due to fatigue. Thus material variability, that may have been an influence as seen in Figure 7.9, was avoided.

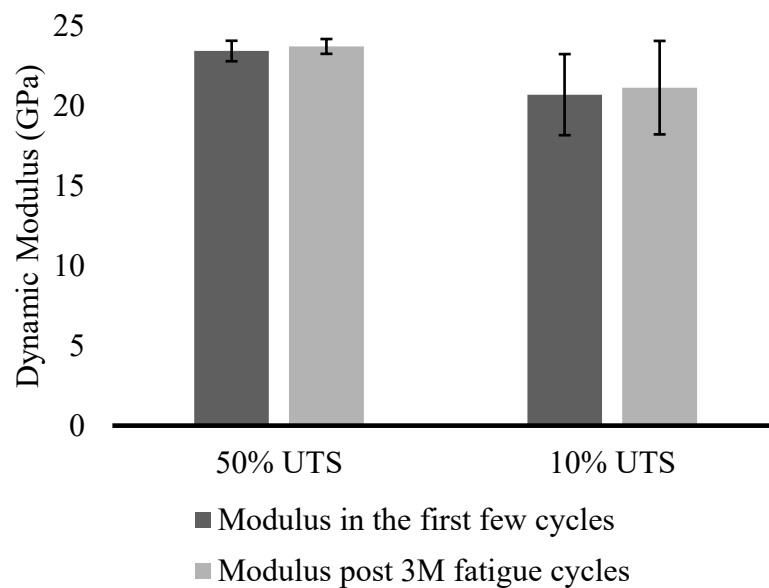


Figure 7.11: Dynamic modulus change due to fatigue loading in SMC IM56R laminate

Furthermore, the residual tensile strength of the laminate after fatigue cycling at 50% and 10% stress levels was estimated by a quasi-static tensile test and plotted in Figure 7.12. The residual strength of all samples fell within the standard deviation of the panel's ultimate tensile strength, indicating no significant loss after fatigue cycling.

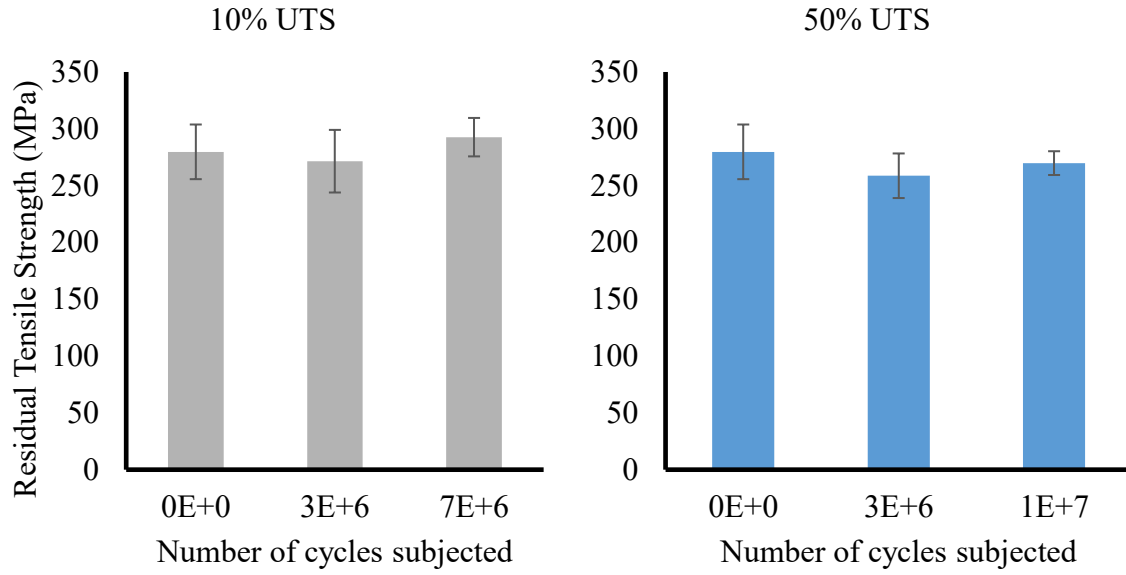


Figure 7.12: Residual Tensile Strength of IM56R SMC laminate after fatigue loading

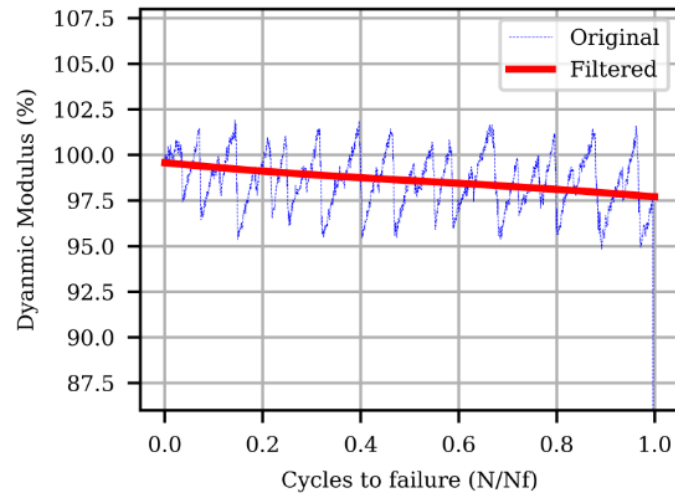
7.4.1.2 Dynamic Moduli

The methodology, established in Section 7.4.1.1, was used to further study the stiffness evolution at high stress levels for the rCF composites systems listed in Table 7.1.

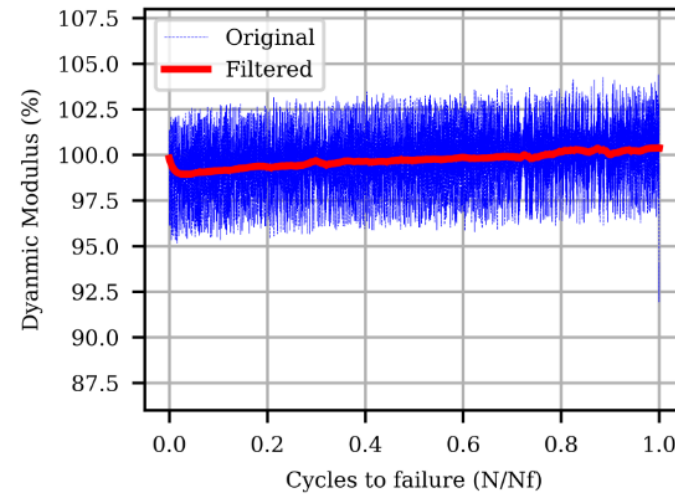
The dynamic moduli was similarly recorded at every fatigue cycle for the composite systems used in this research, plotted as a percent change in dynamic stiffness over time until sample failure in Figure 7.13. The large amount of raw data was handled on IDLE Python 3.6.

The raw signals recorded from the data logger were noisy, possibly due to electrical signal errors. Hence, the dynamic moduli signals were filtered/smoothened to isolate the true underlying signal by a first-order Butterworth low-pass filter at a cut-off frequency of 0.001 via a python code and plotted in the figure. It should be noted that the filtered data curve only shows the trend of the fatigue stiffness until failure.

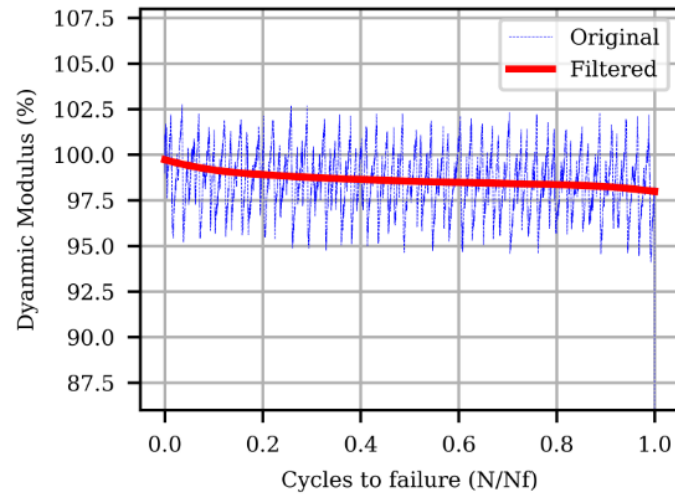
Stiffness change in Autoclave SM45D weft at 80% UTS



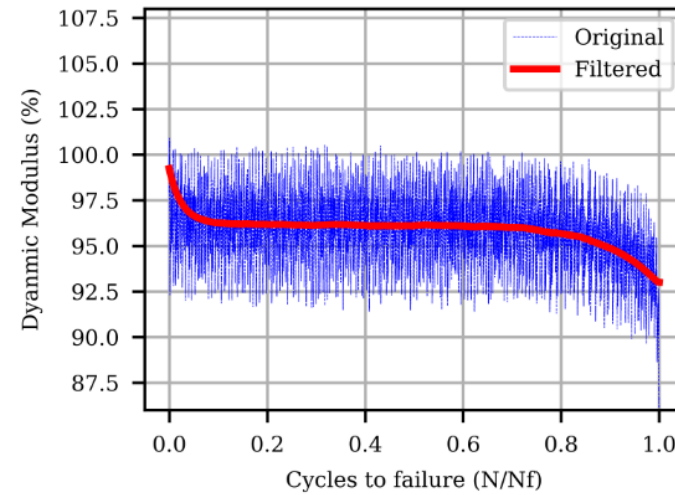
Stiffness change in LCM IM56R crossply at 65% UTS



Stiffness change in LCM SM45D warp at 70% UTS



Stiffness change in SMC IM56L warp at 70% UTS



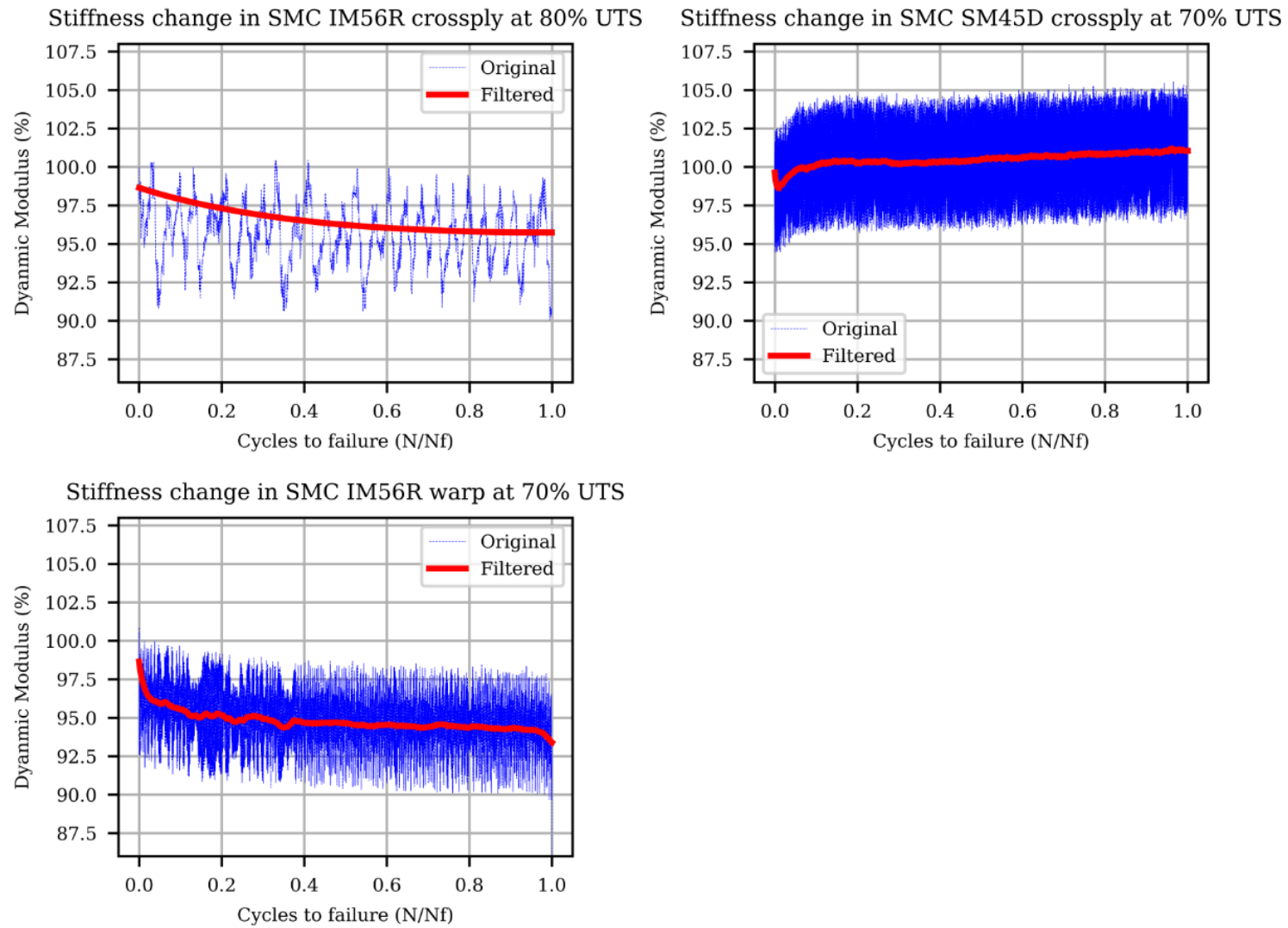


Figure 7.13: Normalised dynamic moduli evolution in different composite systems

The drop in dynamic modulus from the first cycle to the last cycle is shown in Table 7.2. The change in stiffness was calculated using Equation 7.1.

S.No.	rCF composite system	Stress Level (%)	Stiffness Change (GPa)	Stiffness Change (%)
1	LCM IM56R cross	65	+ 0.480	+ 2.40
2	SMC IM56R cross	80	- 0.561	- 3.12
3	SMC SM45D cross	70	+ 0.429	+ 1.71
4	SMC IM56R warp	70	- 0.653	- 4.03
5	SMC IM56L warp	70	- 1.841	- 8.76
6	LCM SM45D warp	70	- 0.42	- 2.47
7	Autoclave SM45D weft	80	- 0.151	- 0.76

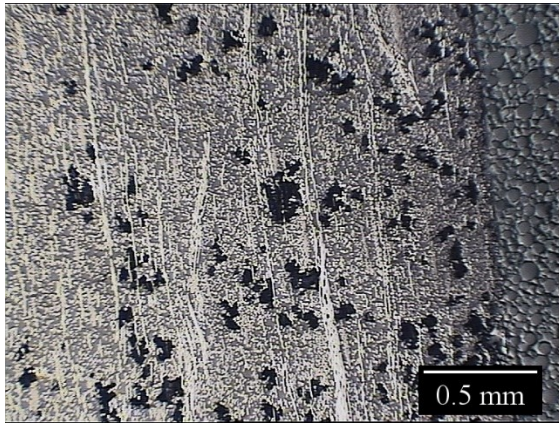
Table 7.2: Change in dynamic stiffness from the first cycle to the last cycle across rCF composite systems

It is evident that from Figure 7.13 and Table 7.2 that the stiffness changes have been within the material standard deviation for all rCF composite systems with the exception of SMC IM56L tested in the warp direction, whose stiffness degraded gradually towards the last 20% of its fatigue life period.

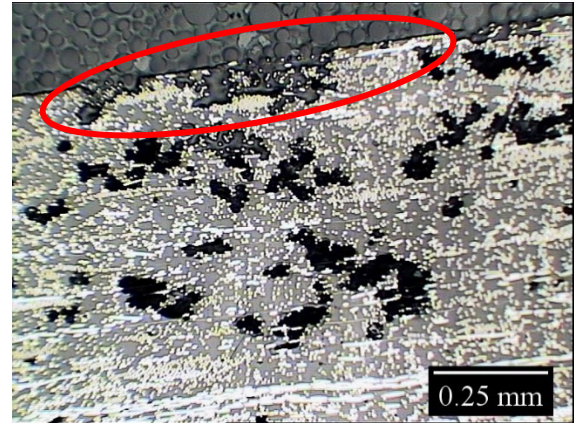
7.4.2 Micrographic analysis

The damage mechanisms can be classified at low stress and high stress levels, based on the difference in patterns observed. In autoclave laminates, brittle, lateral failure of specimens was common at high stress levels. At low stress levels, delamination between plies was more common. In LCM and SMC laminates, the mode of failure was the same as the tensile failures at all fatigue stress levels – a brittle, matrix dominated lateral fracture of the specimen in the gauge section. At high stress levels, typically as observed in Figure 7.14, there were increased signs of matrix damage in the fatigued samples. This occurred through the thickness of the material and might possibly originate from pre-existing manufacturing defects such as voids that exaggerate and develop over cyclic loading. This may lead to surface roughness and deformities through the thickness, all of which act as stress concentration regions after their formation. Additionally, the samples showed development of cracks on the surface of the specimens, transverse to the direction of the fatigue loading, which were visible to the naked eye at high stress levels as shown in Figure 7.15. It is hypothesised that at high stress levels, matrix damage accumulates, cracks develop through the voids across the specimen thickness and eventually cause specimen rupture.

Instances of fibre meta-delaminations were also spotted (Figure 7.14 (c)) in these locations where a bulk of fibre and matrix separates out. However, there were no conclusive signs of fibre breakage.



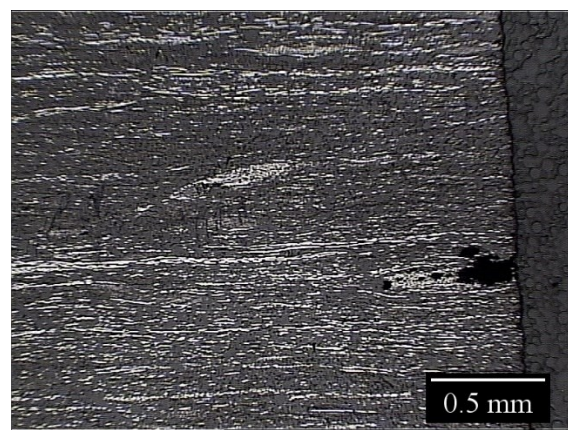
(a)



(b)



(c)



(d)

Figure 7.14: Cross-sections of fatigued LCM and SMC samples at high stress levels

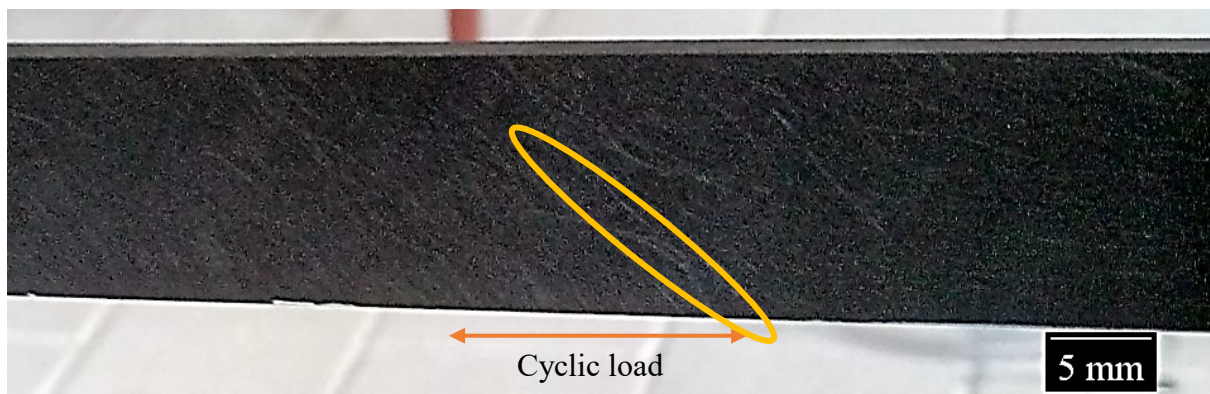


Figure 7.15: Transverse cracks on the specimen surface visible as faint lines across the specimen thickness

Yet another phenomenon that could propagate matrix damage within the laminate is spots of fibre rich and matrix rich regions that are inherent to the material structure in rCF composites. The presence of fibre rich locations, as seen in SMC SM45D in Figure 7.16, leads to debonding between the fibre and matrix, specifically at these locations. Debonding between the fibre and the matrix is uncommon at locations where there is a relatively even spread of fibres within the matrix. Fibre rich locations occur when tows of pyrolysed or repurposed carbon fibres do not separate at the beginning of the carding process. This could occur more frequently with repurposed fibres due to the presence of a sizing layer on the fibre surface. The consequence of debonding within fibre rich locations is that these become regions of poor stress transfer and promote matrix damage around them. Similar to fibre rich regions, instances of matrix rich locations promote fatigue matrix damage due to their inferior load carrying capability.

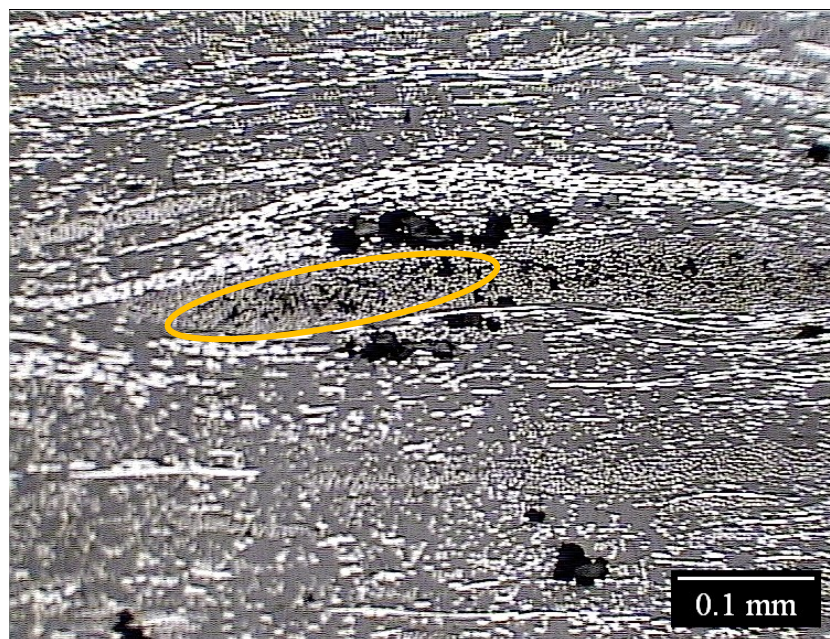


Figure 7.16: Debonding at fibre rich locations at high stress levels

The optical micrographs give indications of fatigue damage mechanisms where the cross-sections of the laminate are examined a few millimetres from the specimen rupture location. Given that fatigue damage phenomena have been observed at such locations for samples

subjected to high stress levels, it is safe to assume that the damage spreads throughout the length of the sample. However, at lower stress levels, matrix damage were scarcely observed. Typical micrographs from a sample subjected to low stress fatigue can be seen in Figure 7.17. The damage mechanisms could possibly be localised at the point of fracture and could have originated from the presence of a manufacturing defect.

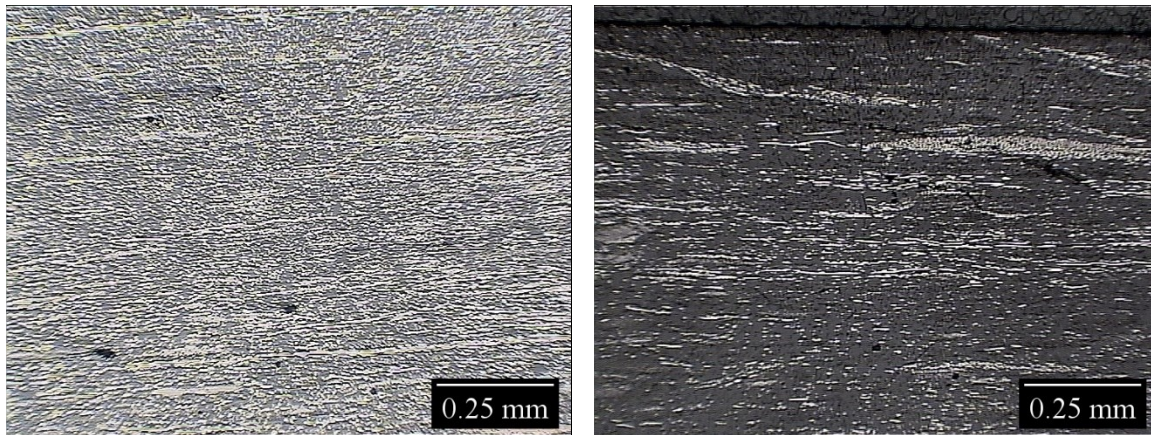


Figure 7.17: Typical cross-section of laminate subjected to high cycle fatigue

7.5 Discussion

The residual tensile properties after fatigue loading for 7 million cycles at 10% UTS, and for 10 million cycles at 50% UTS for SMC IM56R, showed unexpected increments in the tensile moduli and no significant loss in tensile strength from a quasi-static tensile test. Furthermore, the tensile strain to failure dropped by $\sim 0.3\%$ after the respective fatigue cycling at both stress levels. To further study this irregularity, a dynamic extensometer was selected to monitor the rate of damage via stiffness measurements.

Thermoset composites generally do not exhibit significant creep characteristics, especially in the given time frame of the fatigue tests at room temperatures. The tensile stress-strain curves for rCF composites exhibit an evident knee as seen in Figure A3.1. The stress-strain response during the first loading cycle of fatigue would be similar to this, but may not follow the same path during the unloading cycle, causing a hysteresis loop. Therefore, a residual strain may have been permanently inflicted onto the specimen after the first unloading cycle during fatigue as explained in literature [196]. It should be noted from the fatigue cycling pattern used in this study (see Figure 4.9), that the first fatigue cycle starts from the maximum fatigue load. That is, the specimen was already stretched to the maximum alternating load before the fatigue cycling started.

From the residual tensile results (Figure 7.9), it may be reasoned that a permanent increment in the specimen length was imparted due to fatigue loading. The first few fatigue cycles may have caused the non-woven reinforcement to break away from the matrix at certain sections of the laminate. This explains the higher intensity of matrix damages at high fatigue stress levels, as seen in Figure 7.14, compared to low fatigue stress levels as seen in Figure 7.17.

The stiffness measurements at high stress levels with the dynamic extensometer did not show significant degradation in the dynamic modulus of the samples as shown in Figure 7.13 and

Table 7.2, with the exception of SMC IM56L. The fluctuating nature of the dynamic stiffness readings, plotted in Figure 7.13, could be attributed to a high amplification gain of the signal from the extensometer by the Epsilon Signal Conditioner ASC-1 as shown in Figure 4.10. The filtered data curve thus gives an indication of the trend to the dynamic stiffness. In all of the laminates, the stiffness decreases initially until it stabilises at a particular value. This could be an indication of modulus decrease at the initial stages of fatigue loading due to development of damage in the laminate. However, from the filtered data curves in the initial fatigue life period in Figure A4.9, it seems that the initial apparent decrease in stiffness may be influenced by the electronic noise generated from the high degree of signal amplification. The pattern after the settlement of the filtered data curve is more relevant to the discussions related to the material. The changes in the stiffness, both increase and decrease, for rCF composite systems in Table 7.2 could be attributed to variance due to electronic errors and other possible errors such as extensometer slip. From Figure 7.13, the recorded stiffness change in Table 7.2 and the quasi-static tensile test results in Figures 7.9 to 7.11, it is hypothesised that the dynamic modulus of rCF composites under tension-tension fatigue would remain constant until failure. This pattern was observed until failure in Figure 7.13 in all of the rCF composite systems except for SMC IM56L (warp) (8.6% drop) and SMC IM56R (warp) (4.03% drop), where both the original and filtered data curves drop off towards failure. This drop in stiffness could be attributed to:

- (a) Directionality of the laminate tested – The laminate along the warp has a lower aligned fibre content, and thus poorer resistance to fatigue. This is also supported by no drop in stiffness observed for the Autoclave SM45D laminate, tested in the weft direction, that has significant inter-ply voids.
- (b) Lower fibre V_f – Both these laminates have over 80% matrix volume fraction (see Table 7.1) that limits the influence of the reinforcement on cycling loading.

The matrix damages observed depended on the respective fatigue stress levels it was subjected to. It could be argued that the damage may have had an effect on the rCF composite stiffness, as it would in the case of continuous UD composites. However, we have also seen the case of autoclave-cured laminates where the presence of severe inter-ply voids did not result in low tensile strength values. In fact, from Figure 5.8, it can be seen that their tensile strength values are on par with LCM laminates and slightly lower than SMC laminates.

Other possible explanations, albeit *less likely*, for the absence of stiffness degradation in rCF composites could be:

- (a) the forced alignment of the fibres in the direction of the fatigue load with increasing fatigue cycling, balancing any drop in stiffness that would be expected with matrix damage. It can be postulated that the rate of composite damage and fibre straightening reach a state of dynamic equilibrium, and the cumulative effect of composite damage eventually results in composite failure.
- (b) realignment of epoxy polymer chains and local carbon fibre stiffening due to a change in crystalline orientation [200] could also contribute to composite stiffening due to fatigue.
- (c) some further curing of the epoxy resin in the laminate may have taken place during the cyclic loading period.

Propagation of matrix damage could be the predominant type of fatigue damage mechanism in rCF composites. It could begin with the development of cracks on the specimen surface transverse to the direction of the load, at higher fatigue stress levels similar to the phenomenon for quasi-static tension in textile composites [197]. As seen from the micrographs at high stress levels, specimen fracture occurs due to the accumulation of internal matrix cracks with increasing number of cycles. At lower fatigue loads, matrix damage is limited and failure is

highly localised at the point of failure where there could exist a possible manufacturing defect. Other fatigue damage mechanisms such as fibre meta-delaminations, interface damage and debonding were observed in optical micrographs.

The effect of fatigue loading on the mechanical properties of the rCF laminate was evaluated and quantified with a real time system of dynamic modulus measurement. This proved to be more reliable than quasi-static tests because of the incorporation of errors that can arise due to variation in the sample set, and human errors such as misalignment of the extensometer that can result in unreliable readings. Another problem is the natural variability that rCF discontinuous composites possess, which is separate from the influence that fatigue loading has on the material. The dynamic stiffness measurements however could be improved if the amplification of the output signals were controlled.

One of the major damage metrics due to cyclic loading at the specimen level in the literature is stiffness degradation, but its applicability is doubtful for rCF composites given their fatigue behaviour. The limited occurrence of stiffness degradation in some rCF composite systems may only apply to tension based fatigue tests for stress ratios between 0 – 1. It is quite possible that degradation in stiffness would be observed at stress ratios below 0, i.e., in tension-compression fatigue or compression-compression based fatigue.

7.6 Summary

The tension-tension fatigue load behaviour of rCF composites is very different to that of vCF composites. The nature of the reinforcement in non-woven rCF composites was seen to have a significant impact on the fatigue resistance and the cyclic load response. Discontinuous SMC based composites generally exhibited a low fatigue resistance, but the presence of needle punched z fibres in rCF composites seems to improve the cyclic load resistance. Stiffness as a damage metric is inappropriate for assessing the performance of rCF composites with fatigue loading, at least in tension-dominant load cycling. rCF composites have a relatively long life at low stress levels and structural designs for suitable applications can take advantage of this stable stiffness over its fatigue life.

Chapter 8: Influence of Environmental Conditioning

This chapter discusses the physical and mechanical strength degradation of rCF composites upon immersion to particular environmental fluids. The fluid absorption rates and their implication on tensile properties of rCF composite systems are discussed, with the aim to predict their long-term degradation using Arrhenius equation. The changes to the glass transition temperatures due to fluid immersion are also recorded.

8.1 Exposure to environmental fluids

Epoxy based composites are sometimes prone to degradation in their physical and mechanical properties due to the hydrophilic nature of the matrix. The diffusion of liquids into composites softens the matrix by plasticisation, causing changes (although reversible) to its physical characteristics and possible damage inflicted onto the fibre-matrix interface. The environmental durability of the following laminates, whose non-woven plies were unidirectionally laid, was assessed by hygrothermal ageing studies by immersion in deionised water, de-icing fluid and diesel. It must be noted that the autoclave processed laminates resin system is different.

1. IM56R reinforced LCM laminate of 0.21 V_f , 3.4 mm average thickness
2. IM56R reinforced SMC laminate of 0.28 V_f , 2.1 mm average thickness and
3. SM45D reinforced Autoclave cured laminate of 0.21 V_f , 2.1 mm average thickness.

8.1.1 Gravimetric Analysis

To determine the fluid uptake in rCF composites, the percentage change in the mass of a 100 mm² square plate with unsealed edges was recorded until either 65 days or mass saturation, whichever was reached first. The edge area was not considered to be significant in comparison to the surface area and the differences in the laminate thickness was ignored. The fluid absorption of rCF composites is shown as a function of square root of time in days over

laminate thickness in Figure 8.1. Both the LCM and SMC laminates were able to reach their saturation limit in all the environmental conditions tested. The autoclave laminates were stopped after the established time frame of 65 days had been reached.

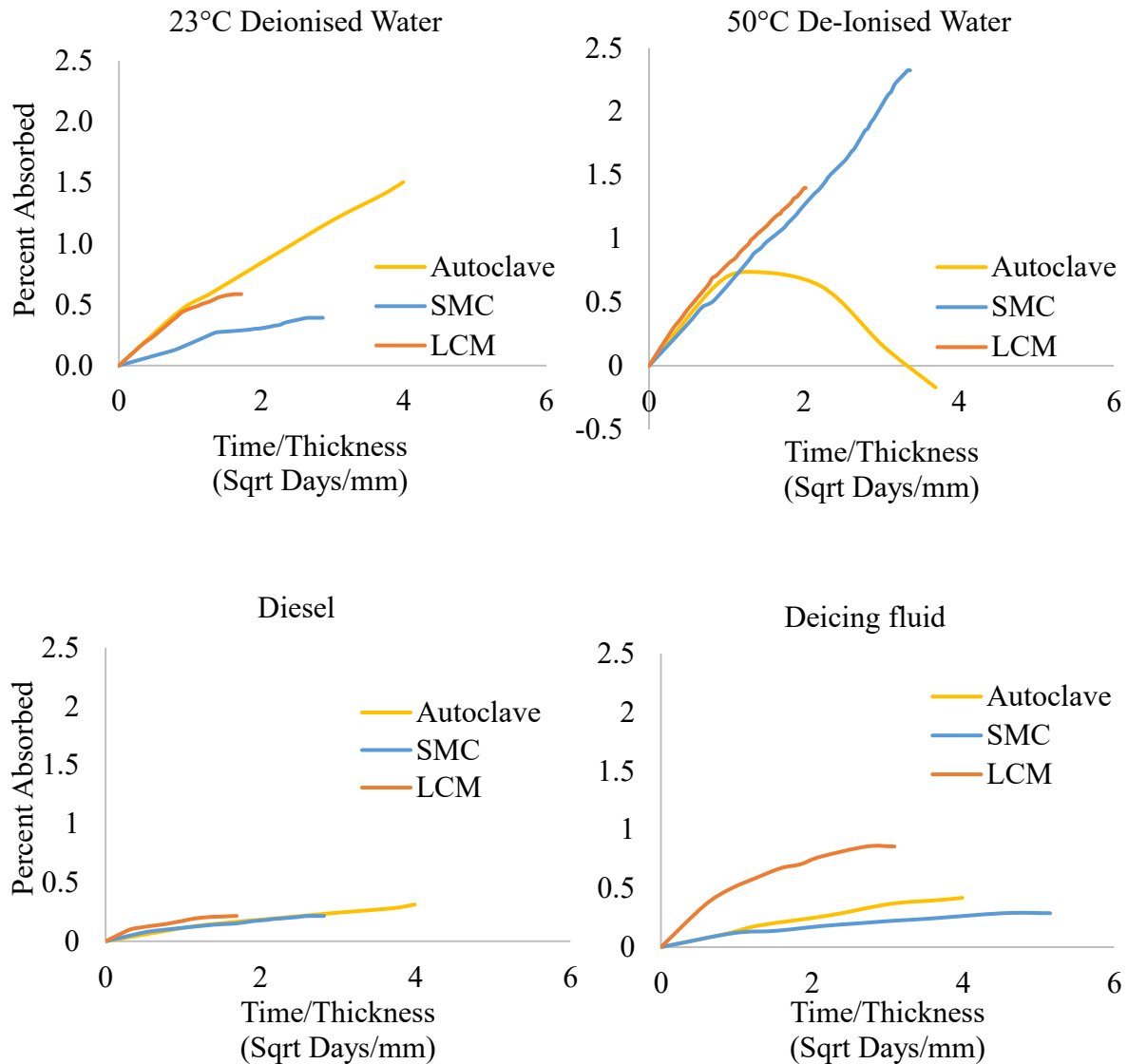


Figure 8.1: Fluid absorption of rCF composites

The water absorption rate was relatively high in the first 10 days and thereafter, the uptake rate slowed down until they stabilised at the saturation limit at their respective time frames. The maximum absorbed by LCM laminates was 0.59% at 23°C and 1.40% at 50°C. The maximum amount absorbed by SMC laminates was 0.39% at 23°C and 2.32% at 50°C. The role of temperature in the Fickian absorption of deionised water is exemplified by these results. The

greater absorption by the SMC laminates over LCM at 50°C indicates that SMC are more prone to fluid uptake at higher temperatures. These results are consistent with experimental results on aerospace quality epoxy resin, achieving 4% water uptake with a composite lay-up consisting of 0.62 V_f UD CFRP, whereby a saturation limit of just over 1.3% after 3 years of immersion at 60°C [198]. Both the SMC and LCM laminates attained saturation at 0.22% when immersed in diesel at 23°C. In de-icing fluid, the SMC laminate absorbed 0.29% while the LCM laminate absorbed a maximum of 0.86% at 23°C. A high water saturation point was observed at 23°C for autoclave laminates. Erratic readings in water uptake were recorded at 50°C and it is postulated that these results could be linked to the presence of inter-ply voids in autoclave laminates (as shown in Figure 4.1 (c)). The average void fraction of the autoclaved laminates is 13.75% as opposed to the SMC and LCM laminates with 0.54% and 1.18% respectively from Archimedes tests (see Table A7.1).

The deionised water absorption behaviour at 23°C and 50°C in a bulk of Hexion™ Epikote 06605 + Epikure 06608 cured epoxy plaque is plotted in Figure 8.2. The maximum absorption at 50°C and 23°C in the cured epoxy plaque is 3.69% and 2.19% respectively. The pattern is similar to SMC laminates, wherein the absorption is higher at 50°C than at 23°C.

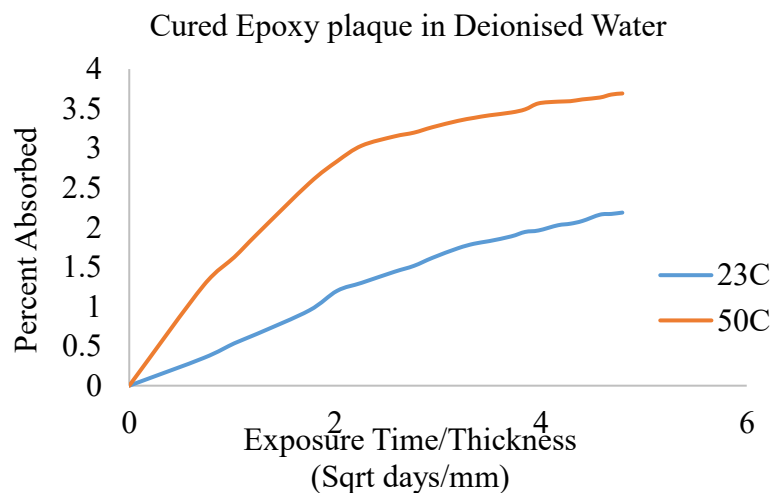
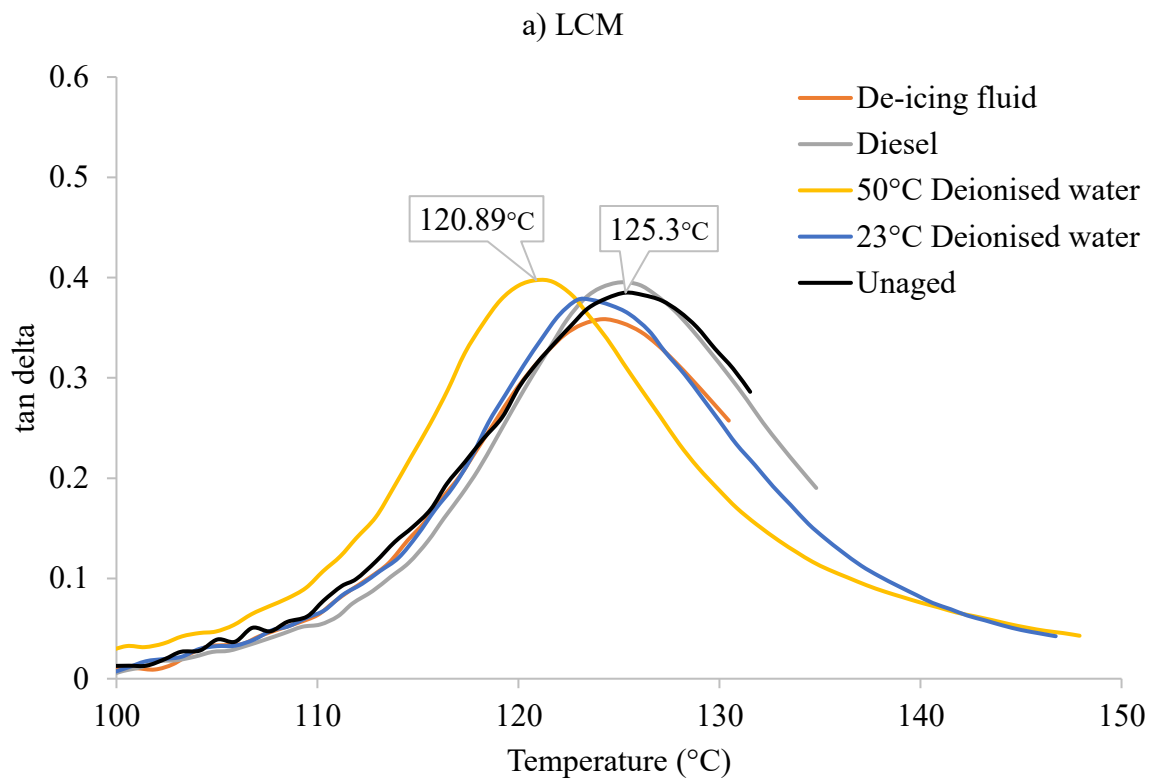


Figure 8.2: Percent water uptake of Epikote 06605 + Epikure 06608 epoxy to deionised water immersion

8.1.2 Glass Transition Temperature

The glass transition temperature (T_g) was taken as the peak temperature of the tan delta curve, as seen in Figure 8.3, beyond which the polymer chains lose rigidity and begin to soften. The T_g was measured for unaged samples and for aged samples prepared from the 100 mm² panels subjected to various fluid immersions. The aged samples were then dried at room temperature for at least 24 hours before testing.



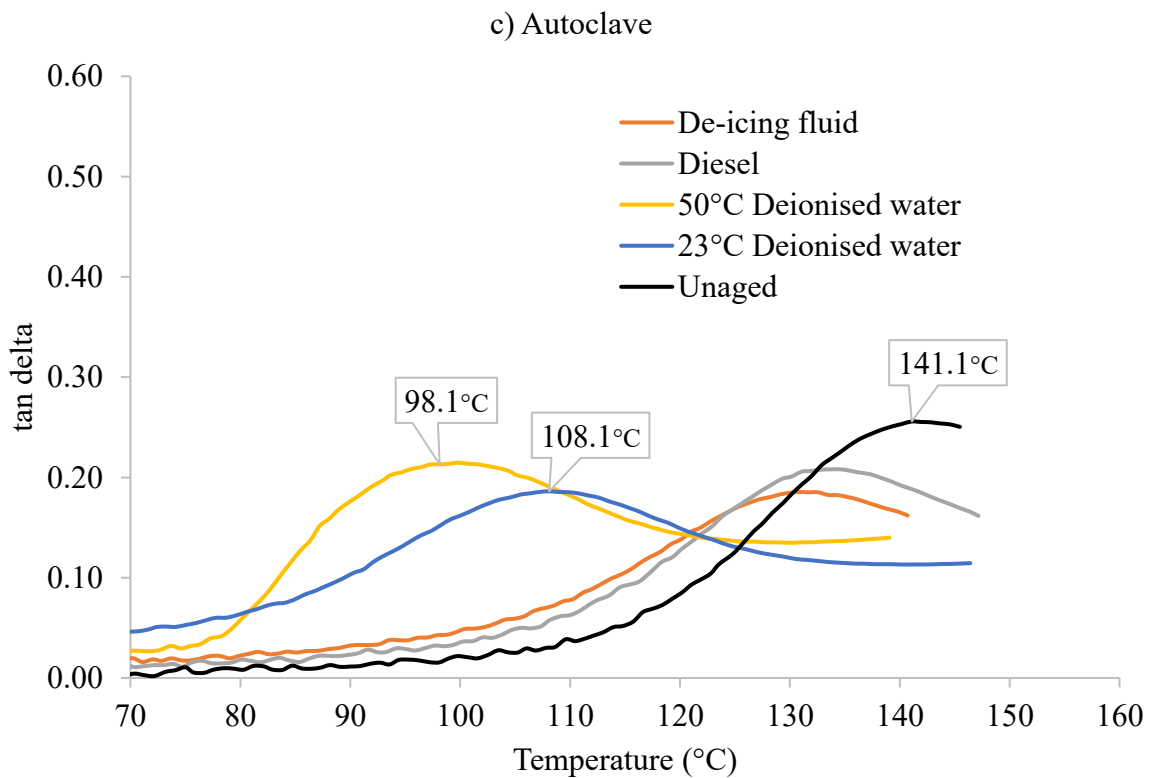
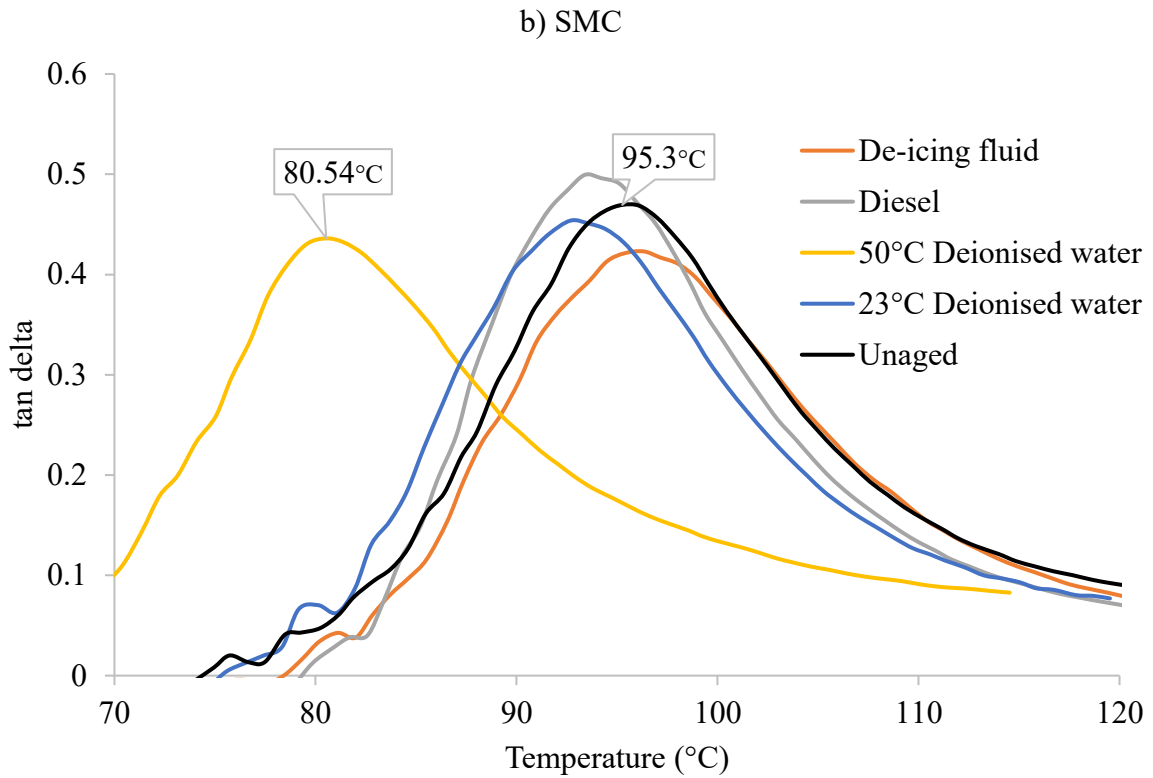


Figure 8.3: Shift in glass transition temperatures due to fluid immersion in a) LCM b) SMC and c) Autoclave

The T_g of unaged LCM laminate was recorded to be 125.3°C with no significant shift ($\pm 2^\circ\text{C}$) observed after immersion in diesel, de-icing fluid or deionised water at 23°C. The T_g shifted by 4.4°C after immersion in deionised water at 50°C.

The T_g of an unaged SMC laminate was 95.3°C and again no significant shift ($\pm 2^\circ\text{C}$) was recorded after immersion in de-icing fluid and diesel. A drop in T_g of 2.6°C and 14.7°C was recorded after immersion in deionised water at 23°C and 50°C respectively.

The T_g of autoclaved samples was recorded to be 141.1°C. On immersion in diesel and de-icing fluid at room temperature, the T_g dropped by 6.7°C and 10.4°C respectively. Ageing in deionised water drastically reduced its T_g by 33.1°C and 42.2°C upon immersion at 23°C and 50°C respectively.

The shift in glass transition temperature due to immersion of Hexion TM Epikote 06605 + Epikure 06608 cured epoxy plaque in deionised water at 23°C and 50°C is shown in Figure 8.4. The aged epoxy plaques reveal a double peak in their $\tan \delta$ curves (solid line curves) that were not observed for the aged SMC laminates. The loss modulus curves (dotted line curves), also shown in Figure 8.4, have only a single peak. This may possibly indicate the presence of two separate phases in the resin system used in SMC composites and is discussed in Section 8.2.

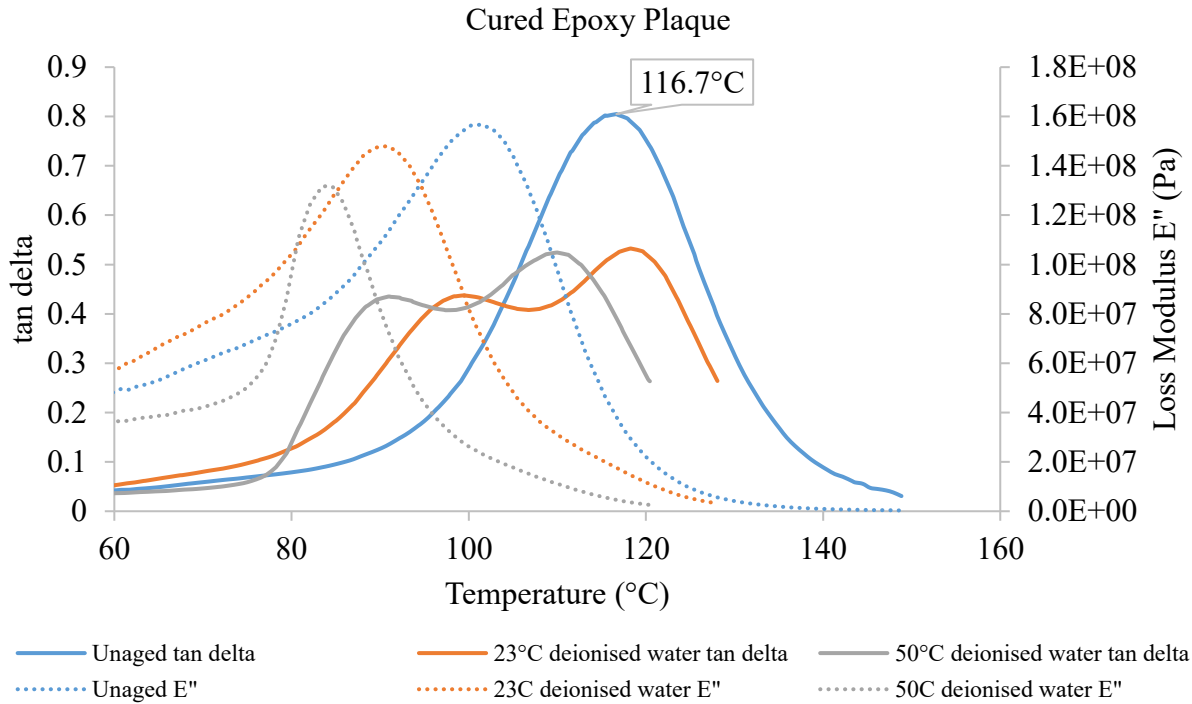


Figure 8.4: Shift in glass transition temperature of cured Hexion™ Epikote 06605 epoxy plaque due to immersion in deionised water

8.1.3 Influence of hygrothermal ageing on mechanical properties

Figure 8.5 depicts the tensile characteristics of LCM laminates after 45 days of immersion. The samples used for the measurement of tensile moduli were identical and there was no evidence of significant degradation in any of the environments. As the samples used for the measurement of tensile strength could not be identical, the dataset was analysed statistically as shown in Table 8.1, the terminology of which was explained in Section 4.7. The independent samples T test was not significant below the 0.05 level and the 95% confidence intervals do not contain the zero specified by the null hypothesis in all cases. The null hypothesis, that the mean values of tensile strength are equal, has therefore failed to be rejected indicating there was no significant strength degradation was observed in LCM laminates. This pattern is similar across intervals of 11, 21 and 32 days also, as shown in the Figure A5.1.

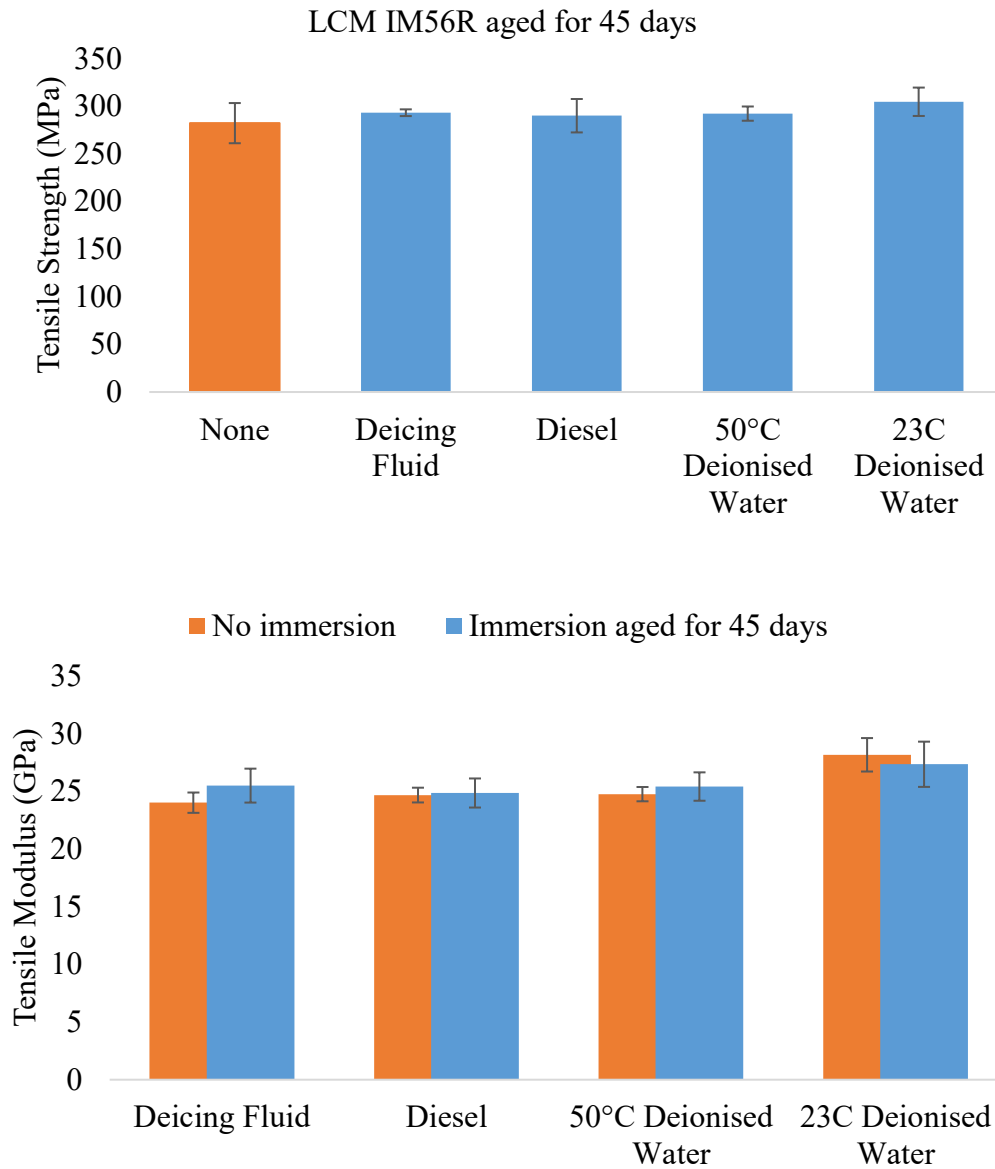


Figure 8.5: Mechanical characteristics due to hygrothermal ageing of LCM laminates²

² The samples used in each fluid medium to monitor the change in tensile moduli were the same before and after immersion. Refer Section 4.5.2.1.

Independent Samples Test											
		Levene's Test for Equality of Variances			t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
										Lower	Upper
Tensile Strength in deionised water at 23C	Equal variances assumed	0.66	0.43	-1.69	11.00	0.12	-22.43	13.24	-51.57	6.70	
	Equal variances not assumed			-2.06	4.75	0.10	-22.43	10.89	-50.88	6.01	
Tensile Strength in diesel	Equal variances assumed	0.37	0.55	-0.58	11.00	0.58	-7.79	13.49	-37.48	21.91	
	Equal variances not assumed			-0.64	3.95	0.56	-7.79	12.13	-41.63	26.06	
Tensile Strength in deicing fluid	Equal variances assumed	4.24	0.06	-0.87	11.00	0.40	-10.94	12.60	-38.67	16.79	
	Equal variances not assumed			-1.57	10.35	0.15	-10.94	6.97	-26.40	4.53	
Tensile strength in deionised water at 50C	Equal variances assumed	2.59	0.14	-0.79	11.00	0.45	-10.00	12.73	-38.03	18.02	
	Equal variances not assumed			-1.26	10.13	0.24	-10.00	7.94	-27.68	7.67	

Table 8.1: Independent Samples T-test for Strength of LCM laminates

Figure 8.6 depicts the tensile characteristics of SMC laminates after 45 days of immersion. No evidence of degradation in tensile stiffness was recorded in any test case. The tensile strengths of SMC laminates on immersion in deionised water and diesel shows degradation but after 45 days of immersion, only the loss in strength in diesel was statistically significant below 0.05 level as shown in Table 8.2. This would mean that the null hypothesis that the strengths are equal before and after ageing is rejected for diesel but is failed to be rejected in other environmental media. It must be noted that the p-value for immersion in deionised water at 50°C is 0.09 and it is quite possible that there may be further strength degradation beyond 45 days. This is supported by the gradual reduction in the tensile strengths at intervals of 5, 11, 18, 30 and eventually 45 days in this medium as shown in the Figure A5.2.

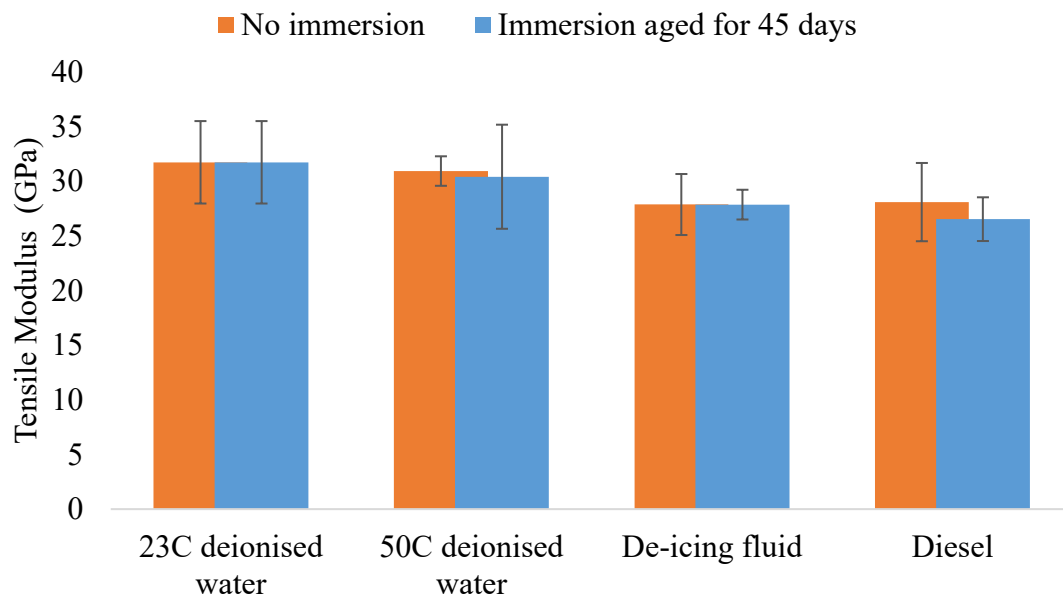
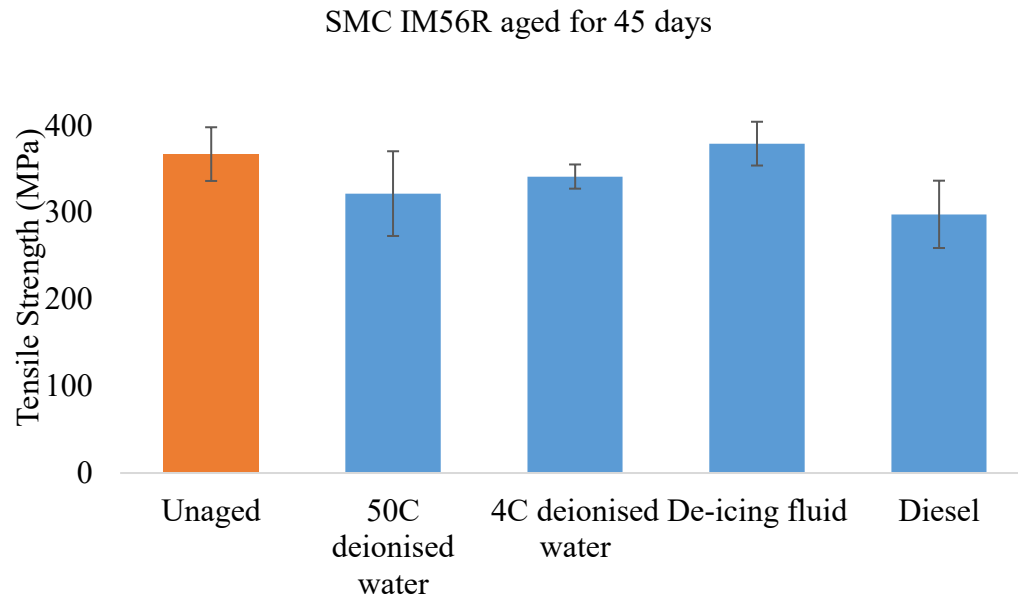


Figure 8.6: Mechanical characteristics due to hygrothermal ageing of SMC laminates³

³ The samples used in each fluid medium to monitor the change in tensile moduli were the same before and after immersion. Refer Section 4.5.2.1.

Independent Samples Test										
		Levene's Test for Equality of Variances			t-test for Equality of Means					
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Tensile Strength in deionised water at 23C	Equal variances assumed	0.50	0.50	1.23	9.00	0.25	29.07	23.57	-24.26	82.40
	Equal variances not assumed			1.01	2.72	0.39	29.07	28.69	-67.89	126.03
Tensile Strength in diesel	Equal variances assumed	0.15	0.70	3.12	9.00	0.01	69.35	22.23	19.08	119.63
	Equal variances not assumed			2.78	3.02	0.07	69.35	24.91	-9.64	148.35
Tensile Strength in deicing fluid	Equal variances assumed	0.06	0.81	-0.73	11.00	0.48	-12.05	16.52	-48.41	24.30
	Equal variances not assumed			-0.77	10.01	0.46	-12.05	15.70	-47.04	22.93
Tensile strength in deionised water at 50C	Equal variances assumed	1.25	0.29	1.88	9.00	0.09	45.51	24.15	-9.12	100.13
	Equal variances not assumed			1.51	2.63	0.24	45.51	30.21	-58.71	149.72

Table 8.2: Independent Samples T-test for Strength of SMC laminates

Figure 8.7 depicts the tensile characteristics of Autoclave cured laminates after 45 days of immersion. Any degradation in strength or stiffness was not statistically significant at any period of ageing recorded at 5, 11, 20, 30 and 45 days, as depicted in the Figure A5.3.

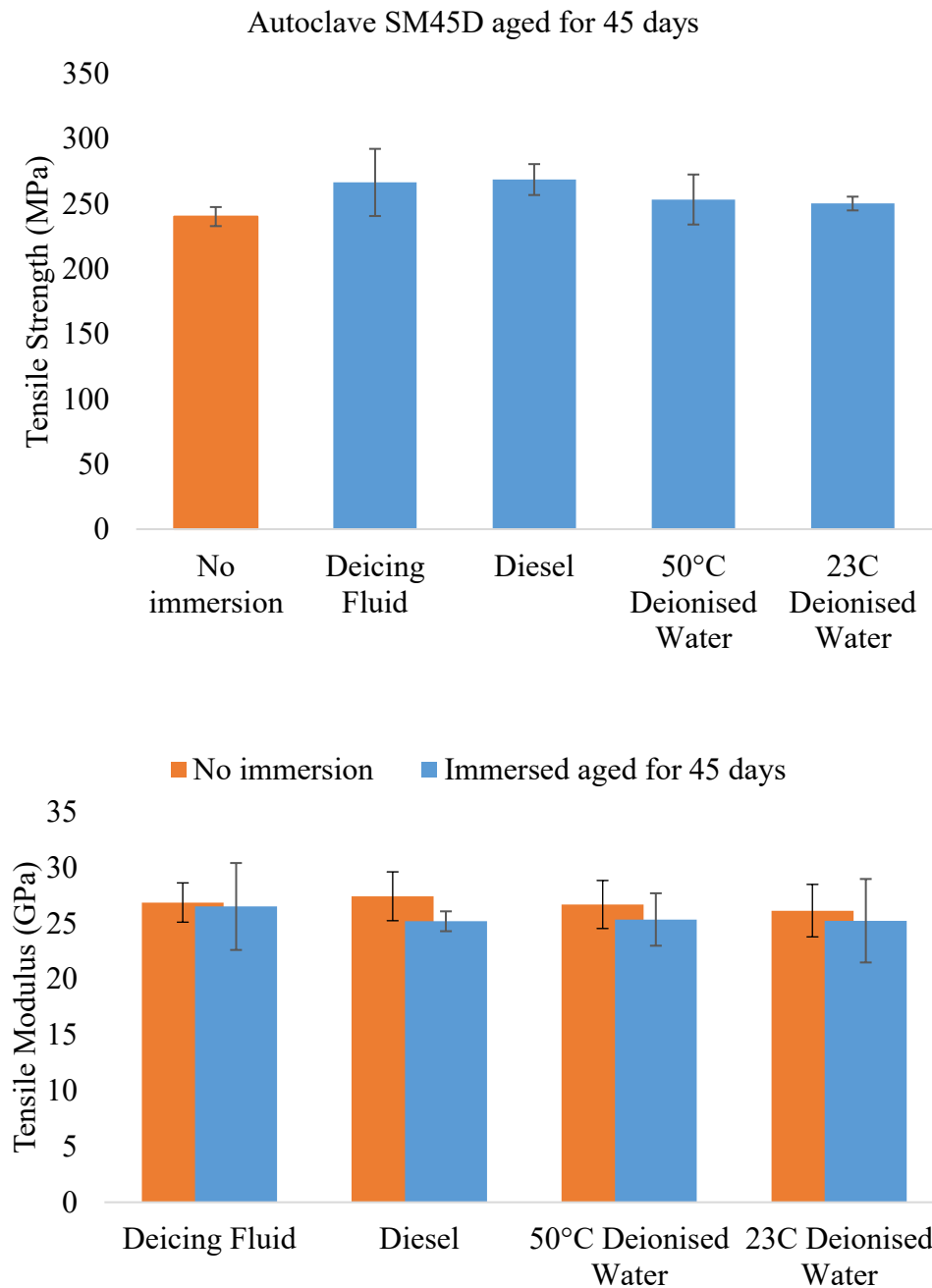


Figure 8.7: Mechanical characteristics due to hygrothermal ageing of Autoclave laminates⁴

⁴ The samples used in each fluid medium to monitor the change in tensile moduli were the same before and after immersion. Refer Section 4.5.2.1.

8.2 Discussion

As discussed in Section 2.5, the general effect of fluid immersion of a polar polymer is to introduce a degree of plasticisation, which increases with temperature due to increased diffusion. For an unreinforced material, a deterioration in mechanical characteristics would be expected. The changes in the physical attributes of the epoxy resin used in SMC laminates was also assessed in this study. Figure 8.4 shows that there are two peaks with the aged epoxy samples and a single peak with unaged epoxy sample from their respective tan delta curves. The loss modulus (E'') curve however depicts only a single peak for both aged and unaged epoxy samples. The single peak could be attributed to the fact that the loss modulus curve depicts the initiation of the softening of the epoxy matrix rather than the stage where complete softening occurs throughout the polymer matrix chains [199]. The dual glass transition temperature peak in the tan delta curves for aged epoxy resin is significant in terms of the water plasticisation phases of the resin. The polymer chains of the epoxy matrix may not be necessarily cross-linked homogeneously in the cured resin structure, especially considering the snap-cured epoxy resin used here. The lesser cross-linked sections with shorter molecular chain lengths are more likely to be plasticised with water and vice-versa. Hence the lesser cross-linked sections would have a highly plasticised region that corresponds to the lower glass transition temperature peak and the higher cross-linked sections have a lower plasticised region that corresponds to the higher glass transition peak in the tan delta curves [200, 201].

This plasticisation behaviour and dual transition peaks for cured epoxy resins is however reversible as had been shown in the literature where the lower transition disappears on drying [200, 202]. Figure 8.4 corresponds to cured epoxy resins subjected to a temperature sweep in a DMTA after 48 hours of drying, whereas Figure 8.8 shows the temperature sweep of the same cured epoxy resin immediately after water immersion period. It can be seen that the first transition peak begins to rescind gradually on drying. It is postulated that the peak may coalesce

to a single transition peak on further drying, but across a wider temperature range, in comparison to that of an unaged sample. The glass transition temperature at this peak is also expected to be lower than the transition peak of an unaged material. In any case, only a single glass transition temperature peak was observed in unaged and aged SMC laminates as seen in Figure 8.3 (b).

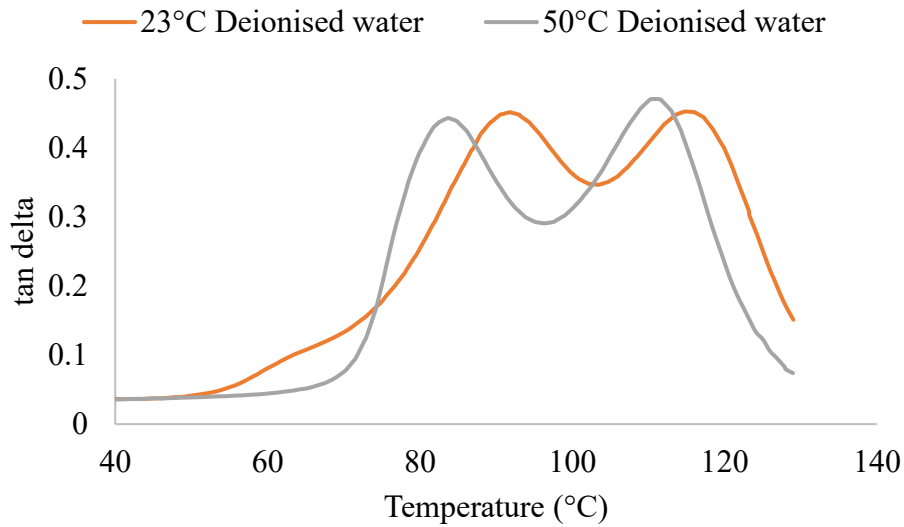


Figure 8.8: Dual tan delta glass transition temperature peak of cured Hexion™ Epikote 06605 epoxy plaque due to immersion in deionised water, without drying the samples

The T_g of the unaged cured SMC laminate was lower by 21.4°C than the unaged cured epoxy resin. The T_g of cured unaged LCM laminate was 15°C lower than the T_g mentioned in the TDS datasheet for the unreinforced epoxy resin system [171]. The reduction in T_g could be due to the influence of the reinforcement and the curing process. The effect of durability on a fibre-reinforced polymer depends on the resin, the fibre architecture, the quality of adhesion between the matrix and the fibre, and the consolidation of the laminate [145]. Immersion ageing did not significantly degrade the mechanical strength characteristics of LCM IM56R and Autoclave SM45D laminates in comparison to SMC IM56R laminates exposed to the same environmental conditions. It can be seen that the amount of water absorbed by the laminate in Figure 8.1 is proportional to the drop in glass transition temperatures across all laminates. The ageing

temperature played a crucial role in the shift of the T_g and the amount of water absorbed, the effects of both reflected in their resulting ultimate tensile strengths. It is possible that the immersion period was not long enough to observe any mechanical degradation in rCF composites, especially LCM IM56R and autoclaved SM45D.

Mechanical defects and voids are major contributors to moisture ingress as evident from the water ingress pattern and corresponding glass temperature drop in autoclaved SM45D shown in Figures 8.1 and 8.3. Both LCM and SMC laminates attained their saturation limits in various fluid environments, but the presence of voids between the plies in Autoclave cured laminates may have contributed to the increased water absorption and absence of any saturation limit within 45 days. It must be noted that the saturation period was limited to 45 days in this study, but it may take over 2 years to achieve complete saturation of moisture absorption [198]. The immersion in liquid media is a more complex and accelerated ageing process than subjecting composites to an environmental conditioning chamber. This was evidenced from a preliminary study of this research work. A pilot study in this research subjected three LCM IM56R plates to an environmental chamber maintained at 75°C and 95% relative humidity and the results of moisture absorbed are plotted in Figure 8.9. The statistical variability that arises with fluid immersion is much larger than humidity testing and presents irregularities that renders it difficult to evaluate the effects of particular variables due to hygrothermal ageing [145].

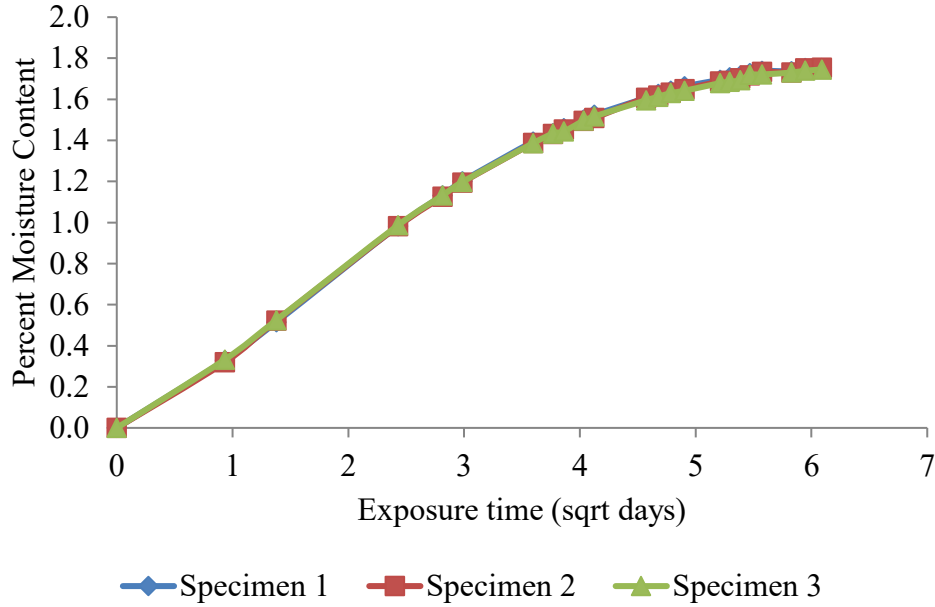


Figure 8.9: Preliminary gravimetric study on LCM IM56R plates

CF itself is generally insensitive to moisture uptake but the primary interest here was to quantify the impact of moisture on the fibre-matrix interface. The surface treatment of carbon fibres have been reported to improve the environmental performance of UD vCF composites [151, 153, 203-205]. It has also been reported that the presence of a size compatible with the matrix, or application of a coupling agent, resists fibre-matrix debonding and results in less absorbed moisture for unidirectional CF composites [151, 203, 206]. For example, a silane surface treatment forms hydroxyl chemical bonds with the sizing layer on the carbon fibre on one side, and cross-links with the epoxy matrix through epoxide functional groups on the other, improving the fibre-matrix adhesion in vCF composites [204]. The affinity of pyrolysed CFs and their impact on the UTS has been recorded in Chapter 5. As mentioned in Chapter 2, there are expected to be strong covalent bonds between the functional groups of the oxidised CFs and the epoxy resin. From Figures 8.5 and 8.6, the plasticisation of epoxy may have happened at temperatures closer to the matrix glass transition temperature and their effects were evident on the residual strengths. The degradation of the fibre-matrix bondlines by the possible occurrence of capillary action discussed in Section 2.5, may not have had a significant effect

due to the discontinuous, random reinforcement nature in the laminate. It could be concluded that the type of fibre in rCF composites does not seem to affect its environmental durability, but could rather be pinned down primarily to the resin system used. Alternatively, there was no sufficient evidence to prove that the presence or absence of sizing, or the use of pyrolysed fibres, dictated the fibre-matrix adhesion degradation to fluid.

A popular theory in the literature is that the difference in thermal expansion coefficients between the fibre and the matrix affects their adhesion. Fluid induced swelling facilitates the development of micro-cracks along the bondlines [151, 153]. However, such thermal expansions are in the range of microstrains, which the two constituent elements may withstand without causing sufficient damage to the fibre-matrix interface, and it is more likely that the softening of the resin system at temperatures closer to its T_g will play a more important role. This was exemplified by the reduction in the mechanical strength of SMC IM56R laminates ($T_g = 95.3^\circ\text{C}$) on exposure to deionised water at 50°C over LCM IM56R laminates ($T_g = 125.3^\circ\text{C}$).

The absorption of water tends to swell the laminates through their thickness, effectively increasing the thickness of the laminate, albeit non-uniformly. Furthermore, in the case of SMC and Autoclave cured laminates, discolouration was observed as shown in Figures 8.10 & 8.11. The rust coloured discolouration in SMC laminates was seen only on the surface of the laminate, similar to earlier observations that also found no evidence of chemical changes through the material thickness [198]. The discolouration was possibly due to the presence of an impurity, release agent or the matrix reacting with the oxygen dissolved in water. The intensity of the discolouration in Autoclave cured laminates on exposure to deionised water depended on the temperature of the liquid medium, and it possibly occurred due to reaction of the fire retardant additives with water molecules.

The discolouration in Autoclave cured laminates did not appear to have an impact on the mechanical strength. The absence of any significant degradation in the tensile properties of LCM and Autoclave laminates despite having over 0.75 matrix volume fraction, could be explained by the pseudo-crosslinking of water molecules with the epoxy resin as explained in Section 2.5. As the material absorbs moisture causing plasticisation and swelling, due to breaking of the Van der Waals forces and thereby increasing chain mobility in the resin, there may also be a tendency to form multiple hydrogen bonds with increasing exposure time, causing secondary crosslinking that does not contribute to plasticisation [151, 207]. Any possible fibre-matrix interface damage may have been masked by this secondary cross-linking. The development of microcracks that would further increase the fluid absorption and absorption of water into toughening additive particles was ruled out as possible damage mechanisms in carbon fibre/epoxy composites [198]. The damage mechanism could rather be attributed to the slow relaxation of the matrix polymer chains that would allow further absorption. The water ingress behaviour in SMC IM56R immersed in deionised water at 23°C and 50°C (much closer to its T_g) seem to agree with this explanation.

The failure modes of the tensile coupons for all aged rCF samples were not different from the unaged samples, giving a matrix dominated brittle fracture rather than fibre-matrix debonding and interface failures as reported in the literature [152, 203].

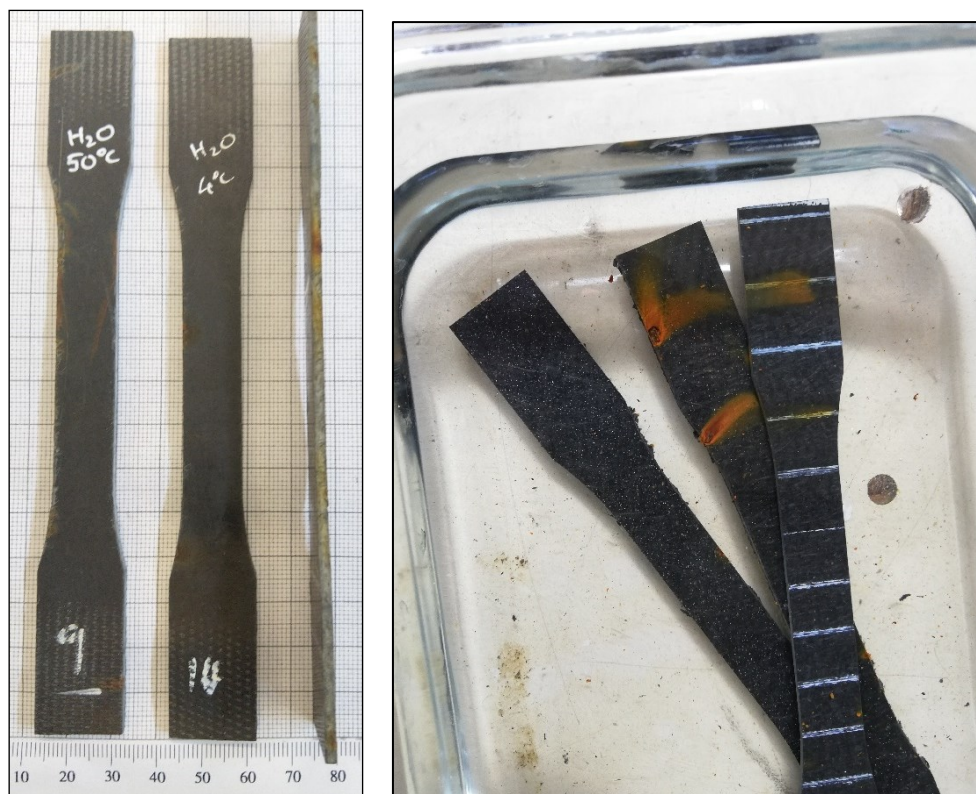


Figure 8.10: Discolouration of SMC laminates on exposure to deionised water

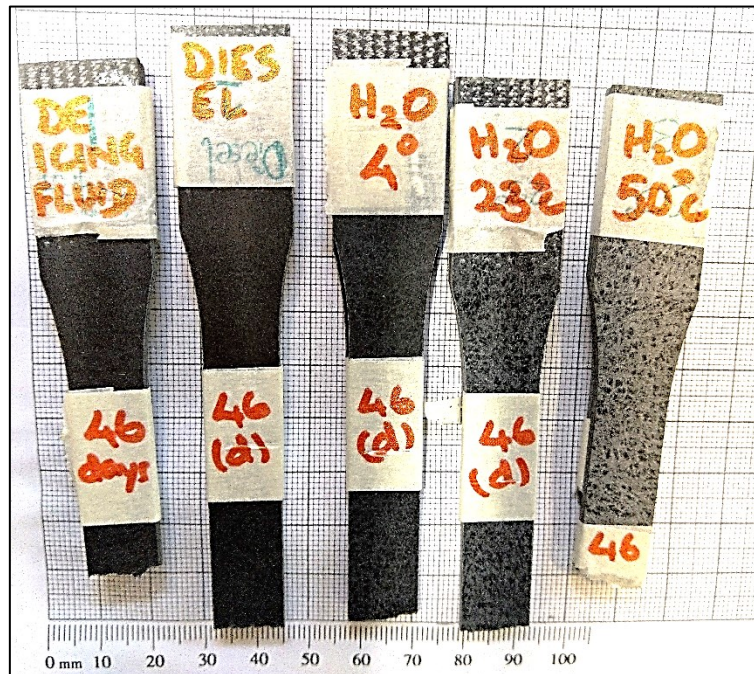


Figure 8.11: Discolouration of Autoclave cured laminates after 45 days

8.2.1 Arrhenius equation to predict long term performance

The long term durability of SMC composite in deionised water beyond 45 days can be predicted by using the Arrhenius Equation (8.1) using the dataset from 50°C, 23°C and 4°C respectively. Equation 8.1 was used to extrapolate data for the remaining temperatures and is plotted in Figure 8.12 for 95%, 90%, 80% and 70% retention in material strength. The Y axis depicts the degradation rate 'k', the natural logarithm of the time taken in hours to reach a particular tensile strength value and the X axis is the temperature in Celsius. The activation energy E_a and the Constant C are calculated from the linear equation of the plots of degradation in tensile strength at 50°C, 23°C and 4°C respectively.

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (8.1)$$

where E_a - Activation energy

R – Universal Gas Constant

T – Temperature in Kelvin

A – Constant relative to the material and degradation process

k – Degradation rate expressed as the inverse of time needed for tensile strength to reach a particular value

The degradation rate is applicable only for SMC composites here because LCM and Autoclave cured laminates did not exhibit any loss in strength over 45 days.

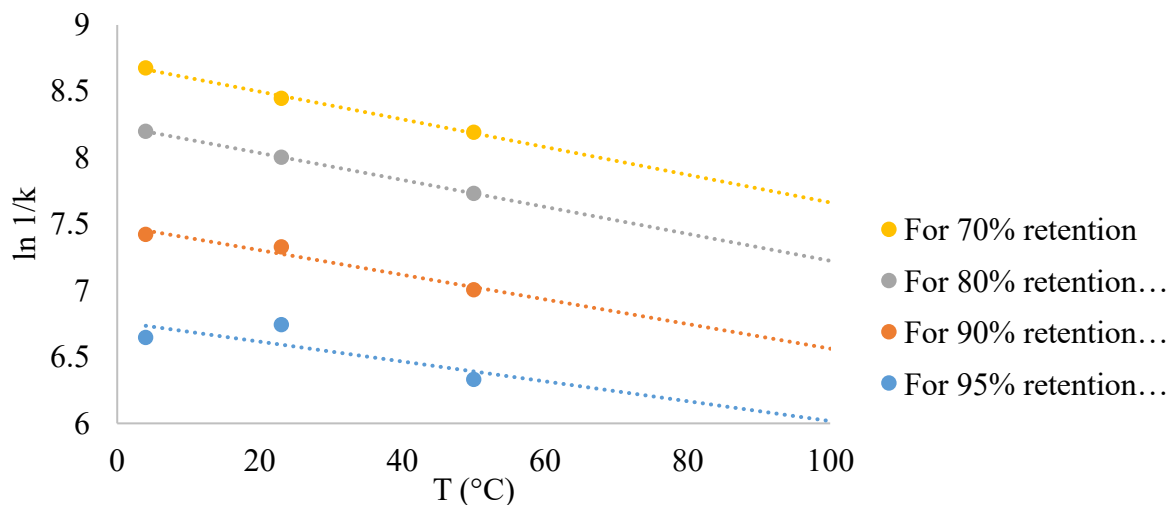


Figure 8.12: Long term durability of SMC laminates due to hygrothermal ageing in deionised water

8.3 Summary

The response to fluid immersion of rCF composites depended on the resin system and laminate processing methodology used, rather than the fibre type. This was reflected in the maximum percentage of absorption and changes in the laminate T_g . Non-woven rCF/epoxy laminates reinforced with pyrolysed/unsized fibres showed no particular worsening effects in comparison with those reinforced repurposed/virgin/sized fibres. From the mechanical properties of the aged laminates in this study, it could be said that the fibre-matrix interface was not greatly affected by the pyrolytic process.

The mechanical characteristics of aged rCF composites degraded with time of exposure and the temperature of the medium, particularly with respect to the T_g of the laminate, where the onset of T_g caused matrix relaxation. This was evidenced in the SMC laminates where laminate softening coincided with a drop in mechanical strength. Plasticisation was found to be minimal for LCM laminates and their physical appearance remained intact, unlike the discolouration observed in SMC and Autoclave cured laminates. The strengths of LCM and Autoclave cured laminates were largely unaffected by the various fluid media after 45 days of immersion. A probable explanation for their insensitivity to fluid ingress damage could be the dominance of the reinforcement architecture and pseudo-crosslinking of the resin system.

Chapter 9: Conclusions

The introduction of rCF composites into the market will support the increasing demand for composites at a reduced cost. It offers a route to more sustainable light-weight materials that exploit manufacturing waste from the established composites sector. The potential structural applications for rCF composites require reliable design allowables. The reinforcement structure of rCF composites is quite unlike continuous, long vCF composite systems, and it has been shown that they respond differently to mechanical loads within the bounds of this study. The basic hypothesis for this research was that rCF composite systems *may* require the development of a suite of specific test methods applicable to discontinuous, non-woven composites. This has been justified from comparisons of their mechanical behaviour with standard test methods traditionally used for conventional composite forms, in Chapters 4 to 7.

This research on particular materials extends our knowledge on the impact of waste source and laminate reprocessing parameters of rCF composites. The influence of fibre grades, laminate lay-up and moulding processes, fibre recovery methods, fabric packing efficiency and rCF composite environmental durability was assessed and analysed using specimens subjected to static and fatigue loading in Chapters 5, 7 and 8.

9.1 Mechanical Characterisation

9.1.1 Static characteristics

The mechanical behaviour of rCF composites was found to be highly dependent upon its discontinuous, needle-punched, non-woven reinforcement architecture. The coupon-level damage behaviour and stress transfer to the gauge length in both static tension and shear is different from that observed in standardised, continuous fibre reinforced composites.

- i. Non-woven rCF composites possess a certain degree of inherent variability due to the fibre distribution in its fabric. Although the fibres are randomly distributed, more fibres

align along the weft direction of the fabric due to the nature of the carding machine. The identification and standardisation of testing parameters that helps limit variability in the data and failure modes that arise due to differences in test schemes and configurations is critical to the reliable description and analysis of various non-woven rCF composite systems. In static tensile tests, the evidence presented in Chapter 5 supports the case of improved stress distribution in dogbone geometry coupons (over 80% gauge length failures) over traditionally used rectangular coupons (under 15% acceptable failures) in non-woven rCF composites.

- ii. Table 9.1 lists the tensile properties of the non-woven rCF composites along their dominant weft direction.

S. No.	Fibre Type	Remoulding Process	UTS (MPa)	Stiffness (GPa) Young's modulus between 0.05 % - 0.25 %)	Max. Tensile strain (%)
1	SM45D	LCM	189.20 +/- 69.2	26.64 +/- 3.5	0.73 +/- 0.3
2	IM56R	LCM	282.28 +/- 21.1	25.46 +/- 1.8	1.15 +/- 0.1
3	SM45D	SMC	297.23 +/- 20.1	35.86 +/- 2.5	0.87 +/- 0.1
4	IM56R	SMC	364.01 +/- 15.6	30.70 +/- 1.3	1.24 +/- 0.1
5	IM56D	SMC	317.80 +/- 15.2	23.23 +/- 1.7	1.42 +/- 0.1
6	IM56L	SMC	283.78 +/- 24.1	31.45 +/- 1.7	0.93 +/- 0.1
7	SM45D	Autoclave	240.26 +/- 7.3	26.75 +/- 1.4	0.94 +/- 0.1

Table 9.1: Tensile Properties of non-woven rCF composites along weft direction

- iii. The relevance of the selection of appropriate specimen geometry was further supported by the findings in cyclic loading too, where the poor stress transfer lead to premature failures, thereby resulting in high variability in cycles to failure in tension-tension loading.
- iv. A number of test methodologies exist in the case of shear testing but their scope is limited to conventional composite forms. Subjecting the material to a state of pure shear is rather challenging given the fibre distribution in rCF composites. The in-plane

mechanical properties of rCF composites benefit strongly from the fibre distribution in the XY plane but, like most 2D textile fabrics, the out-of-plane strength was expected to be poor. The manufacturing process can lead to the formation of a number of resin rich layers through the thickness of the laminate that cannot bear high shear stresses.

- v. The focus of this part of the research was to develop a methodology for characterising out-of-plane shear strength. Four interlaminar shear test methods were investigated, namely, Short Beam Shear, Double Notch Shear, Double Beam Shear and Iosipescu Shear. The Iosipescu test seemed to be the most successful for interlaminar shear but the specimen geometry needed to be remanufactured and redesigned with thick laminates so as to observe pure shear failure in the material, introducing load into the weakest planes of the material. The very same test method was unable to subject rCF composites to a pure shear stress state in their XY plane. The interlaminar shear strength of an SMC SM45D non-woven rCF laminate was measured to be 47.1 ± 4.0 MPa and its corresponding shear modulus was 2.81 ± 0.52 GPa.

9.1.2 Fatigue

The current study developed a family of S-N curves for non-woven rCF composite systems, for which there is no previously published work. Significant findings were that:

- i. rCF fatigue sensitivity was generally low. The endurance limit was attained at 50% of the material ultimate strength (refer Table 7.1), which generally corresponds to strain levels $\sim 0.5\%$ that is higher than the normal allowable working strain of 0.45%
- ii. the fatigue damage phenomena in the non-woven rCF composites and final failure was primarily attributed to the accumulation of matrix damage. Fibre breakage or fibre-matrix debonding was not evidently widespread across the laminate

- iii. the dynamic stiffness does not uniformly decrease for all rCF composite systems and casts doubts over the use of modulus as a composite damage metric.

9.2 Environmental Durability

The environmental durability of rCF composite systems was examined by immersion in organic and inorganic liquid media. The results of this investigation show that:

- i. the degradation in material strength did not extend beyond 18%
- ii. a decrease in the glass transition temperature was observed after fluid immersion. The sensitivity of rCF composites to glass transition depended on time of exposure and temperature of the medium
- iii. SMC cured laminates underwent greatest mechanical strength degradation. Autoclave cured laminates showed physical degradation phenomena such as discolouration and reduction in glass transition temperature. LCM cured laminates generally absorbed the least amount of fluids and did not degrade as much as SMC or Autoclave cured laminates. The processing methodology, which dictates the resin formulation (LCM vs SMC vs Autoclave) - and thus the glass transition temperature, appeared to strongly influence the durability of the rCF composites. SMC laminates had lower T_g than LCM and Autoclave and when exposed to fluid media at temperatures close to its T_g , their physical and mechanical behaviour was affected.
- iv. the pyrolysis process did not appear to have any effect on the durability of the rCF composites.

9.3 Effect of rCF manufacturing techniques

The research analysed the effect of various manufacturing processes on the rCF composite laminates. Significant findings were that:

- i. the fibre grade (Standard Modulus/ Intermediate Modulus) and type (Repurposed/ Pyrolysed) played an important role in defining the static strength of rCF composites, which was not found to be the case for fatigue sensitivity and environmental durability.
- ii. the random fibre distribution of the reinforcement carries an element of variability, which must be considered when analysing the results. The presence of fibre agglomerations and resin rich areas within the panels could be major contributors to this variability.
- iii. the material moulding process had the most significant impact on the tensile strength limits of the material with SMC cured laminates exhibiting the highest strength. This could be attributed to the high compaction pressure employed in the SMC process (2000 psi), as opposed to LCM (750 psi) and Autoclave (85 psi) processes.
- iv. the use of fire-retardant additives in the epoxy resin was thought to be the reason for the poor consolidation of the autoclave cured laminates. Although the static and fatigue strength values remained unaffected, the nature of failure modes were quite different. Furthermore, these laminates were found to be more susceptible to plasticisation when submerged in environmental media. The SMC laminates were found to have good consolidation whereas LCM laminates achieved good consolidation only at fibre volume fractions below 0.23.
- v. SMC pressed laminates may have a higher degree of in-plane anisotropy due to the realignment of fibres along the resin flow direction during the manufacture of non-woven, pre-impregnated sheets. The LCM pressed laminates may have a higher variability due to the multi-directional resin flow during compression moulding.
- vi. increasing fibre volume fraction increases the materials' static strength and fatigue endurance limit but at the cost of increased variability and fibre breakage, which are likely to be due to the high compression pressures.

- vii. Generally, carbon fibres recovered from the modified pyrolysis process described here, were believed to be devoid of residual chars on their surface. Nevertheless, any possible presence of residual char or impurities after pyrolysis did not reflect on the mechanical performance of non-woven rCF/epoxy laminates.

9.4 Test Methods for rCF composites

The methods used for the evaluation of a new composite system should not be directly adapted from the testing practices used to evaluate conventional composite forms, in order to avoid unreliable datasets. The difficulty lies in the identification, and perhaps modification, of an appropriate test methodology from a vast array of available standard test methods. The characterisation of composites are often complex and widely acceptable test standards would be difficult to establish considering that they are not homogeneous and isotropic materials. The introduction of rCF composites merely increases the complexity of characterisation and experience with these materials is very limited. This research highlights the importance and the necessity for the development of a suite of dedicated specification for the development of reliable datasets of discontinuous, non-woven rCF composite systems (Refer Section 2.6.2).

9.5 Overall Summary

The research acknowledges the differences and issues of material selection of new composite systems in the form of recycled carbon fibre, which potentially finds its application in the automotive, wind energy and sports industries. The recycling process could only be commercially feasible by converting pyrolysed carbon fibres into a non-woven textile fabric, such as the CARBISO™. This research identifies a link between the material processing parameters and the quality of the end-product, which are briefly summarised in Section 9.3. The pyrolysis process itself did not seem to severely degrade the material performance of non-woven rCF/epoxy composites. The assessment of material process parameters, tensile, and

shear behaviour was accomplished by developing appropriate testing practices for non-woven rCF composites.

This thesis should bridge the gap in knowledge in the long-term mechanical characteristics and shed further light on the durability of rCF/epoxy composites that currently impede its useful application across various sectors. At low strain levels, the results of this research indicate that rCF composites have long fatigue life and largely retain much of their strength and stiffness upon immersion in different fluid media. The composite material achieves its fatigue endurance limit at strain levels corresponding to $\sim 0.5\%$. Hence, the fatigue and durability performance of rCF composites are not a primary concern.

The CARBISO™ non-woven rCF composites offer a material to design engineers who seek an economical option without compromising on light-weighting. This material supports the sustainable use of the energy intensive carbon fibres, reducing environmental impact of their primary waste and also aid in efficient management of fuel and overall costs. Although their performance is limited by a lower fibre volume fraction, they outperform several short fibre composites available in the market and offer improved mechanical properties over random glass fibre composites. The static performance of non-woven rCF composites is a step down from that of woven CF composites, but that is compensated by their superior cost-savings and reduced environmental footprint. In fact, non-woven rCF/epoxy composites have similar stiffness to non-crimp CF/epoxy composites, but are half as expensive. Furthermore, design engineers can take advantage of their long fatigue life, relatively stable fatigue stiffness and improved durability to environmental media.

Chapter 10: Recommendations for future work

The outcomes of the research inevitably raised more questions regarding the behaviour of the composite systems assessed and, as such, recommendations for future research are suggested below:

- The development of a reliable in-plane shear test methodology remains an important challenge. The plate twist method (ASTM D3044) and rail in-plane shear tests (ASTM D 4255) are possible suggestions as Iosipescu Test or the related V-notch rail shear test and Arcan Shear test would be unsuitable.
- The stiffness of laminates due to fatigue cycling used in this study was monitored after subjecting the material to a pre-load. Hence, the effect of pre-load on the composite stiffness, and its effect on fatigue cycling need to be explored.
- Investigation of fatigue behaviour and stiffness evolution at other stress ratios and in a bending set-up, including in depth analysis of fatigue damage phenomena, possibly by acoustic emission.
- Development of a suitable remoulding process in which the fire-retardant epoxy system could be utilised without causing inter-ply voids
- Investigation of fatigue behaviour of fluid immersed rCF laminates: Fatigue loading may be more sensitive to degradation mechanisms.
- Assessment of fatigue life and durability of thermoplastic non-woven rCF composites to investigate the difference in behaviour from epoxy-based laminates.
- The influence of other processing parameters such as the needle-punching density, needle thickness, fabric areal weight, resin additives, fibre length and possible fibre surface treatment procedures need to be assessed for an optimal end product. Future work related to optimal resin systems for pyrolysed CF, taking the fibre-matrix adhesion into account is important.

- Investigation of techniques to reduce fibre agglomerations in the fabrics to reduce product variability.
- Development of textile fabrics with increased skewness to one of the principal directions so as to address the issue of fibre re-alignment with discontinuous fibres.
- Investigation of the impact characteristics of non-woven rCF composites to give an assessment of their suitability for impact based application parts. Future datasheets must prioritise the development of test methods to evaluate impact characteristics.
- Modelling of the rCF reinforcement architecture for damage prediction
- Investigation on the impact of a 2nd and subsequent recycling cycles would provide an indication of the longevity of rCF composites.

A Note on CARBISO™ rCF composites:

The data developed in this research is consistent and robust for non-woven rCF/epoxy composites assessed. Future work should focus on the impact resistance and holed strength of non-woven rCF composites. The product is suitable as an economic, alternative material option for a number of possible applications. However, the issues of needle-punching and relatively low fibre volume fractions should be addressed to achieve a closed loop recycling system. Future research should focus on improving the compaction of the textile fabrics by possibly minimising the impact of the needle-punching process and the z-direction fibres. More effort needs to be paid to either increasing the disparity of fibre dispersion between the warp and the weft directions, or developing a commercially feasible process focussing on aligned, pyrolysed carbon fibre composites.

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Appendices

Appendix 1

Journal Article Submissions by the Author:

- Krishna Kumar, K., et al. (2020). "Static shear response of recycled carbon fibre composites for structural applications." *Composite structures* 246: 112358.
- Fatigue Behaviour of Recycled Carbon Fibre Composites [*In Progress*] – Submitted to *Composites Part B* on 18 Mar 2019; Reworked submission to *Polymer Testing* by early 2020.

List of Conference Papers by the Author:

- Fatigue Resistance of Recycled Carbon Fibre Composites
Karthik Krishna Kumar, Allan Hutchinson, James Broughton, Richard Offer
SAMPE Europe Conference 2019 Nantes, 17 Sept 2019 – 19 Sept 2019
- Development of Design Data for Discontinuous Carbon Fibre Composites
Karthik K. Kumar, David Heath, Allan Hutchinson
SAMPE Europe Conference 2018 Southampton, 11 Sept 2018 – 13 Sept 2018
- Approaches to determine the constituent elements of discontinuous fibre-reinforced polymer composites
Karthik Krishna Kumar
TDE Student Conference 2018, Oxford Brookes University, 17 May 2017

Magazine Article:

- The Challenge of Identifying Test Procedures for Recycled Carbon Fiber Composites
Karthik Krishna Kumar
CompositesWorld, November 2019. Pgs. 8-9.

Technical Presentations:

- Evaluation of Test Protocols for Recycled Carbon Fibre (rCF) Composites
SAMPE IOM3 Competition, London, 18 July 2019
- Recycling Carbon Fibre Composites
iMechE lecture 2019, Oxford Brookes University, 12 Mar 2019
- Development of design data for rCF/epoxy composites
ELG Carbon Fibre Technical Workshop 2018, 3 July 2018 – 4 July 2018

Appendix 2

Tensile Test Coupons

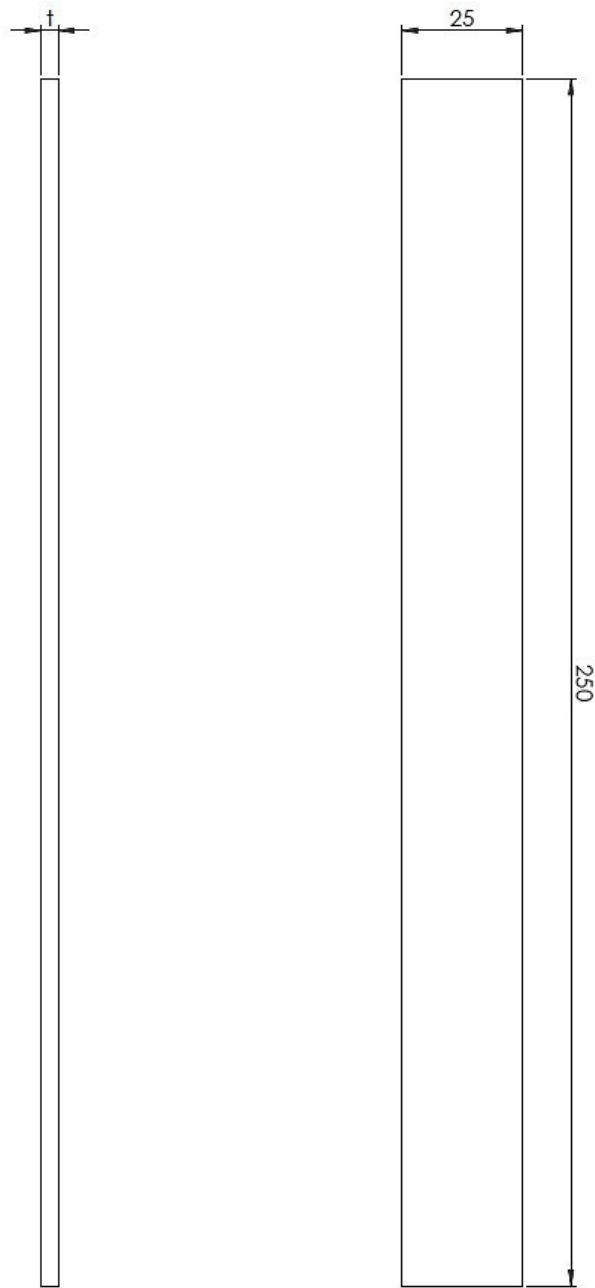


Figure A2.1: Geometry of Straight-sided, untabbed tensile coupon from ASTM D3039 (All dimensions in mm)

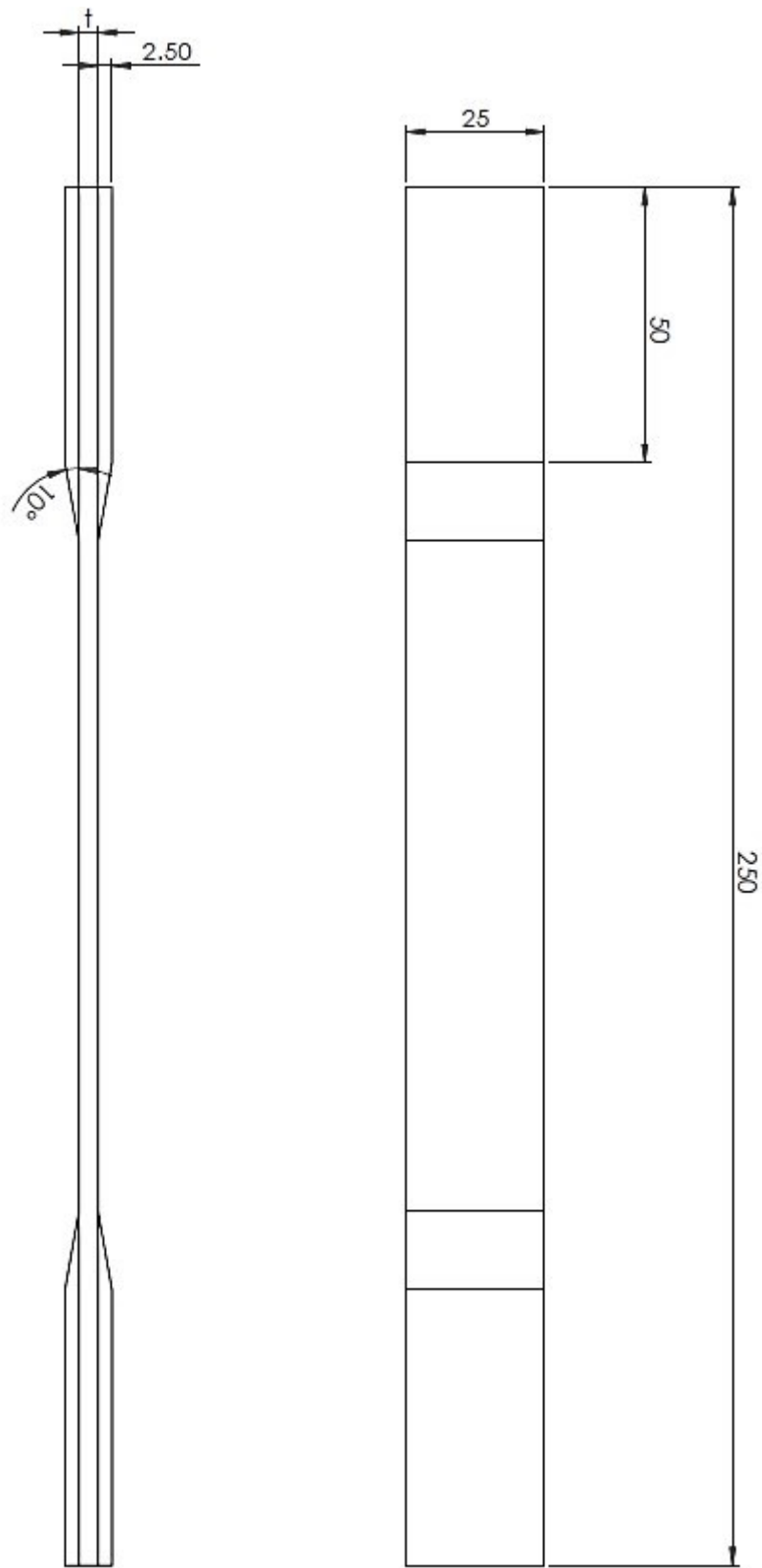


Figure A2.2: Geometry of Straight-sided, tabbed tensile coupon from ASTM D3039 (All dimensions in mm)

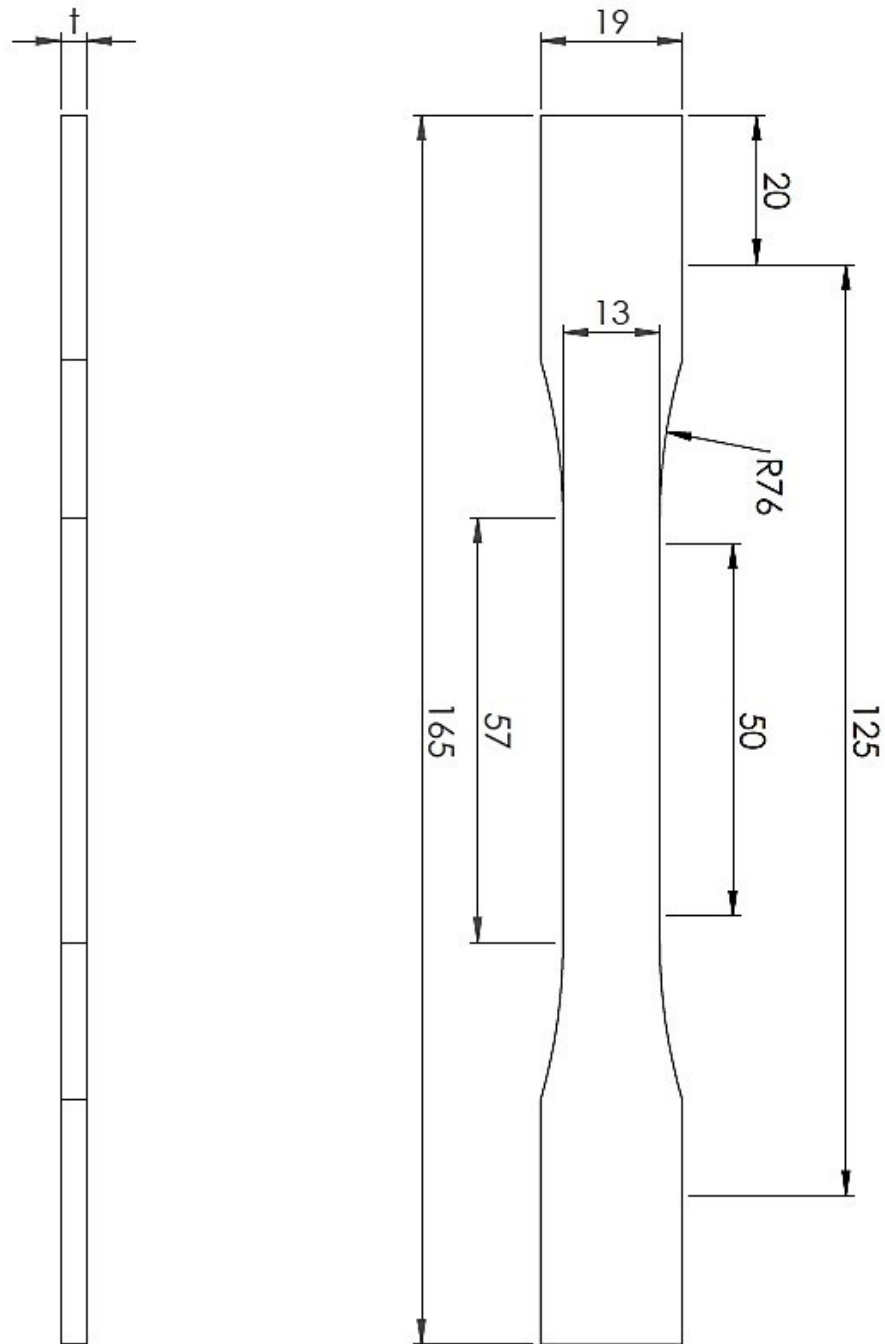


Figure A2.3: Geometry of Dogbone tensile coupon from ASTM D638 (All dimensions in mm)

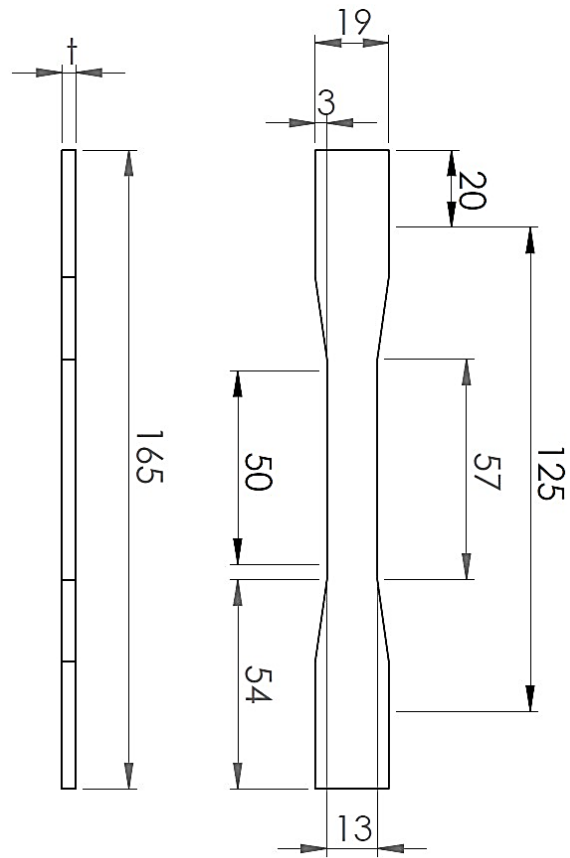


Figure A2.4: Geometry of 'Bowtie' tensile coupon (All dimensions in mm)

Shear Test Coupons

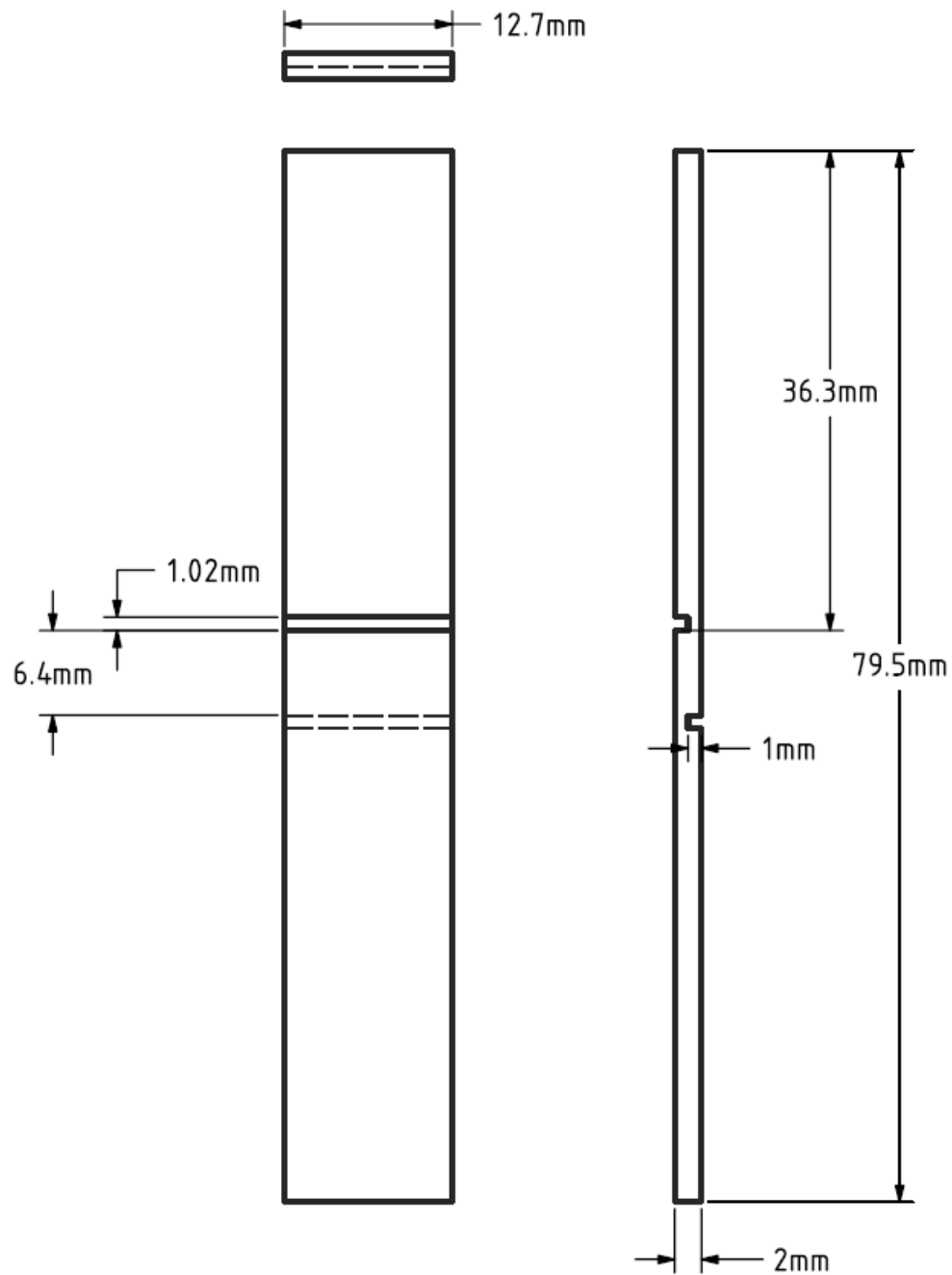
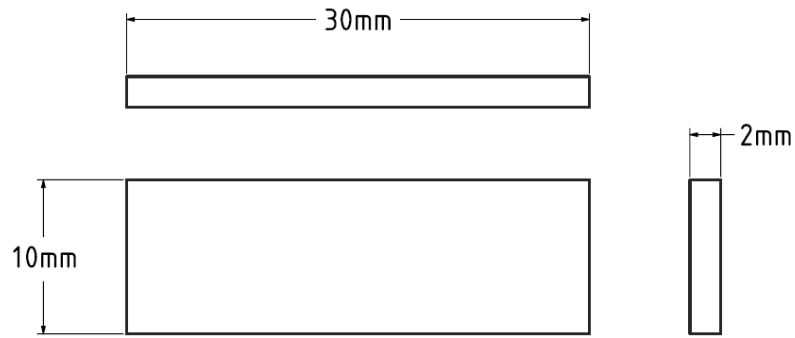
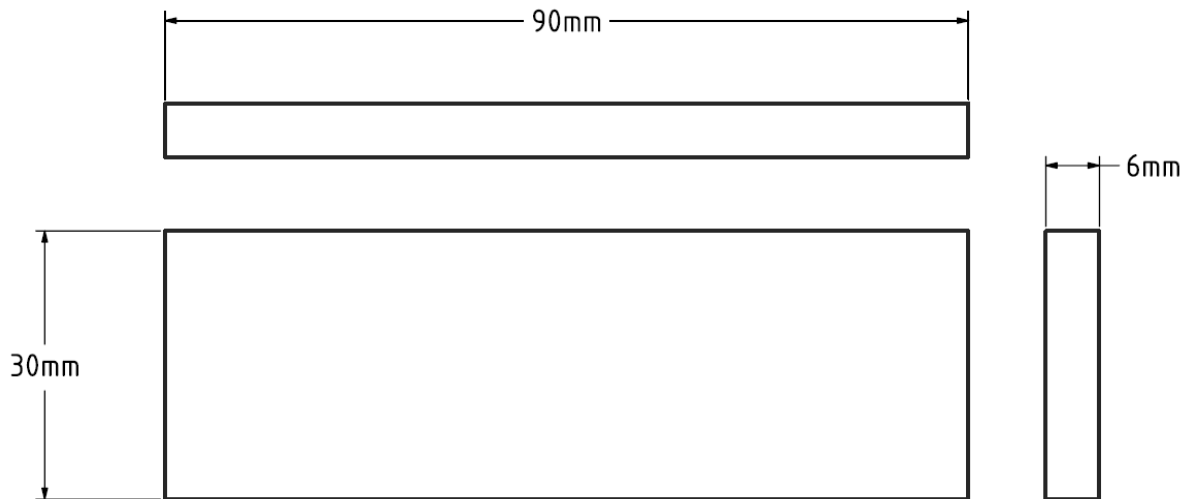


Figure A2.5: Standard geometry of DNS test specimen for autoclave laminate

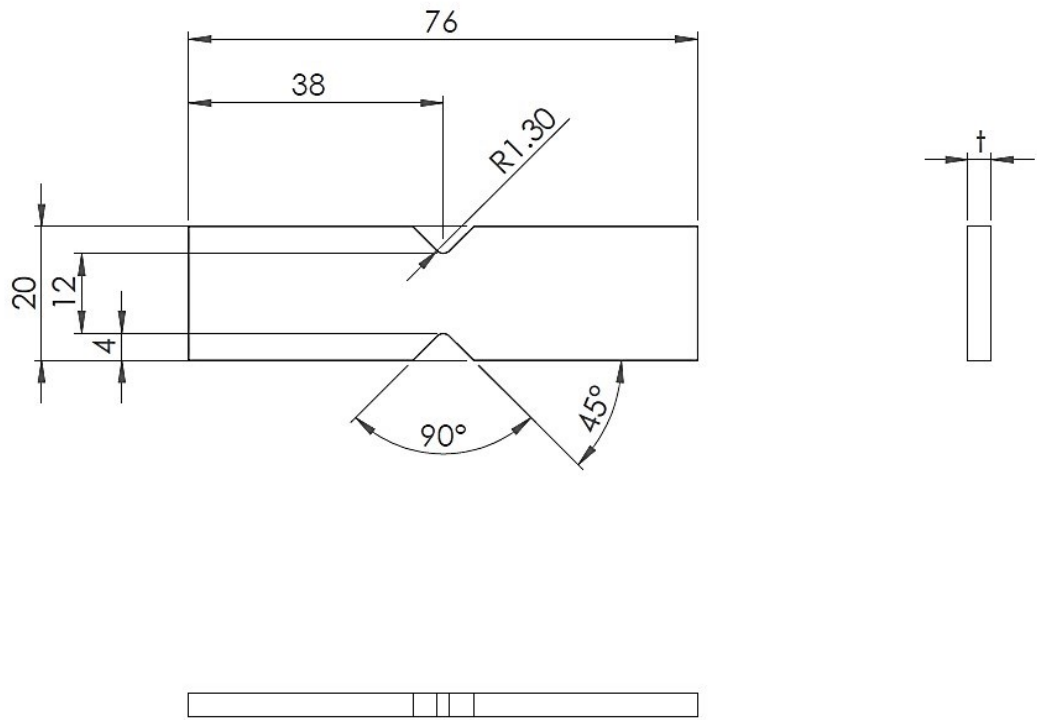


(a)

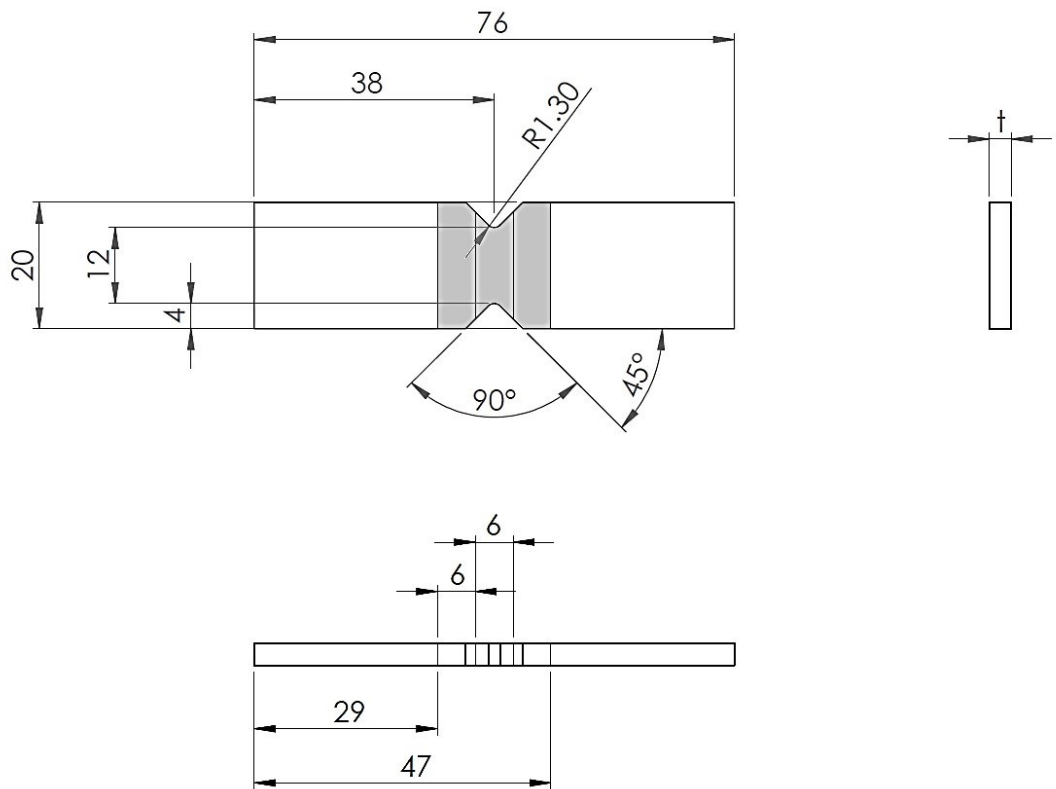


(b)

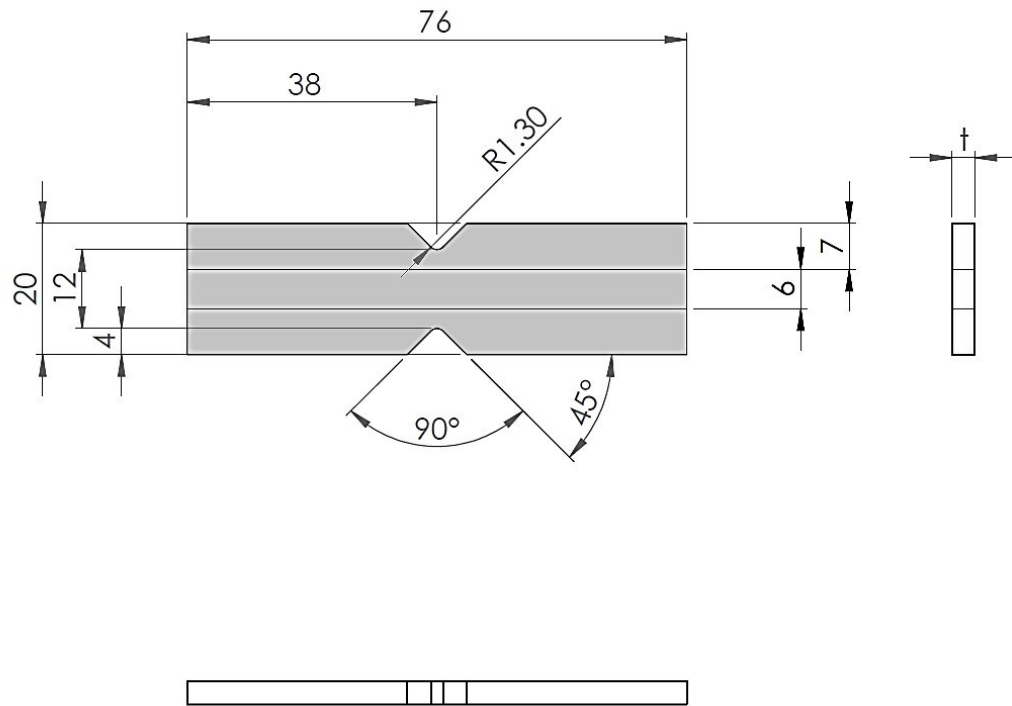
Figure A2.6: Geometry of DBS test specimen for a (a) 2mm thick Autoclave laminate and (b) 6mm thick SMC laminate



(a)



(b)



(c)

Figure A2.7: Geometry of Iosipescu test specimen for (a) XY/YX plane, (b) ZX/ZY plane and (c) XZ/YZ plane (All dimensions in mm)

Appendix 3

Typical Tensile Stress-Strain curve in dogbone rCF composite coupons

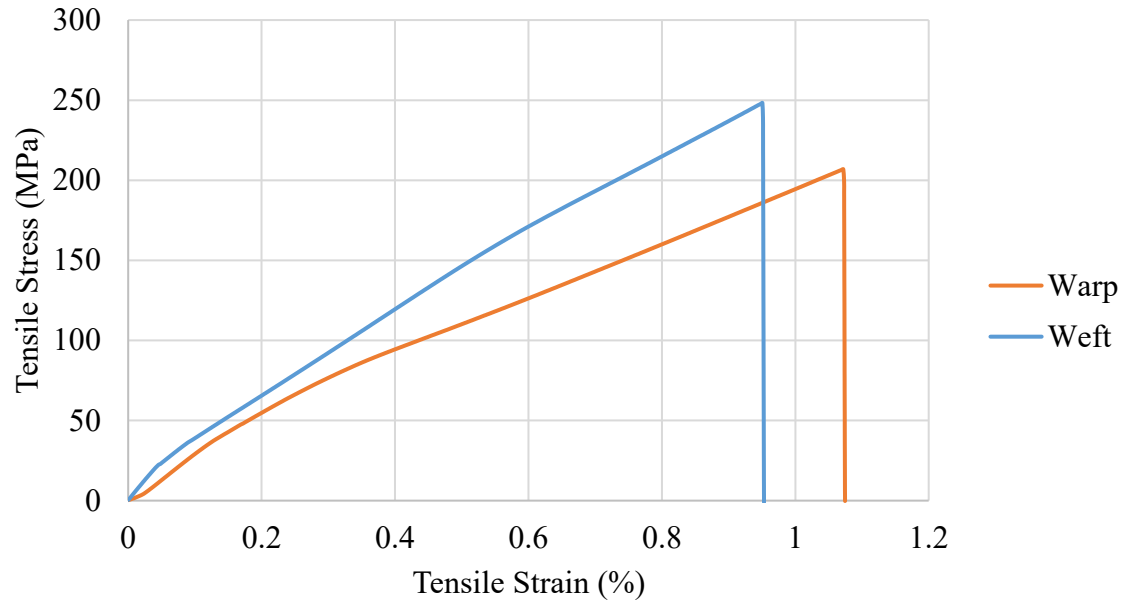


Figure A3.1: Representative tensile stress/strain curve until fracture in the warp and weft directions of an SMC IM56L laminate

Appendix 4

S-N Curves of rCF composite systems subjected to T-T fatigue at R =0.1; f= 10 Hz

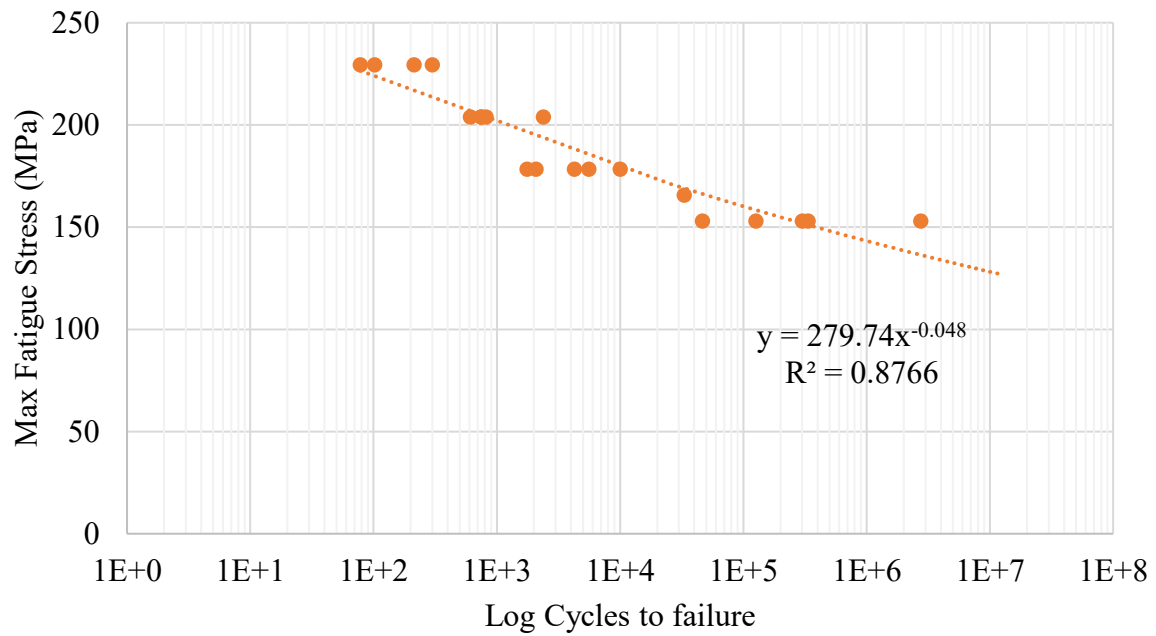


Figure A4.1: S-N curve of LCM IM56R cross-ply laminate

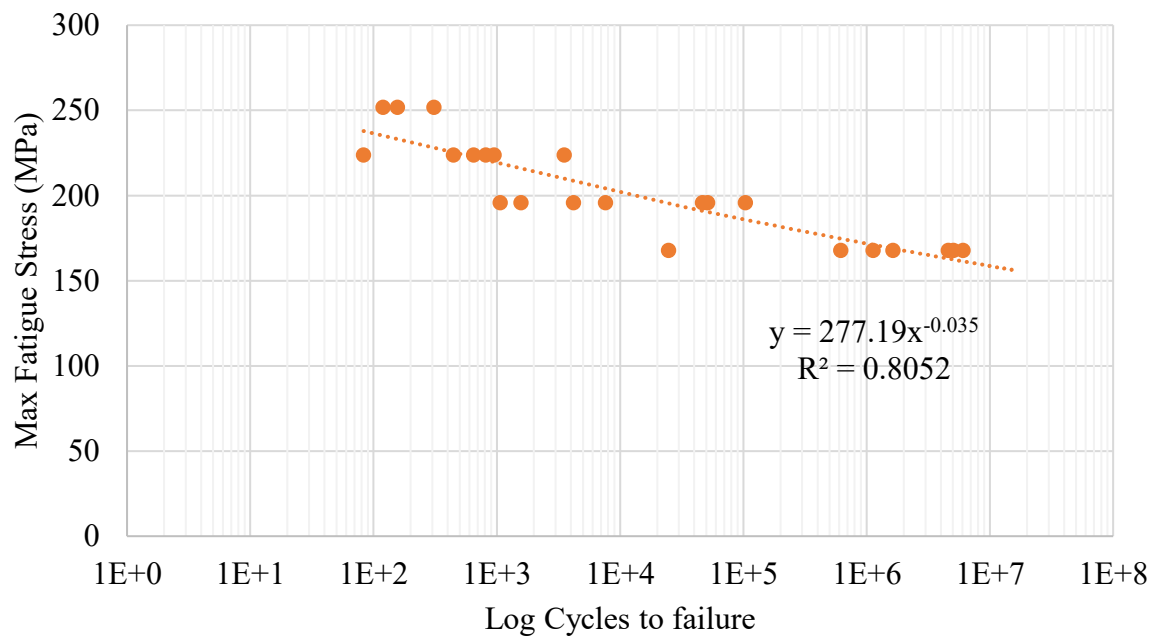


Figure A4.2: S-N curve of SMC IM56R cross-ply laminate

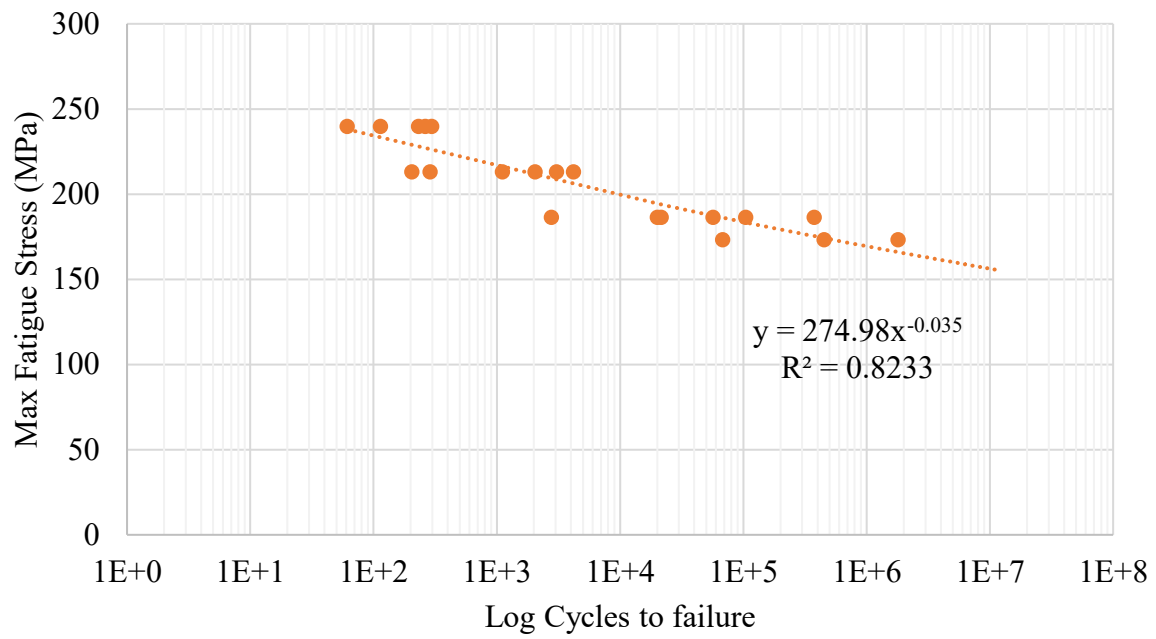


Figure A4.3: S-N curve of SMC SM45D cross-ply laminate

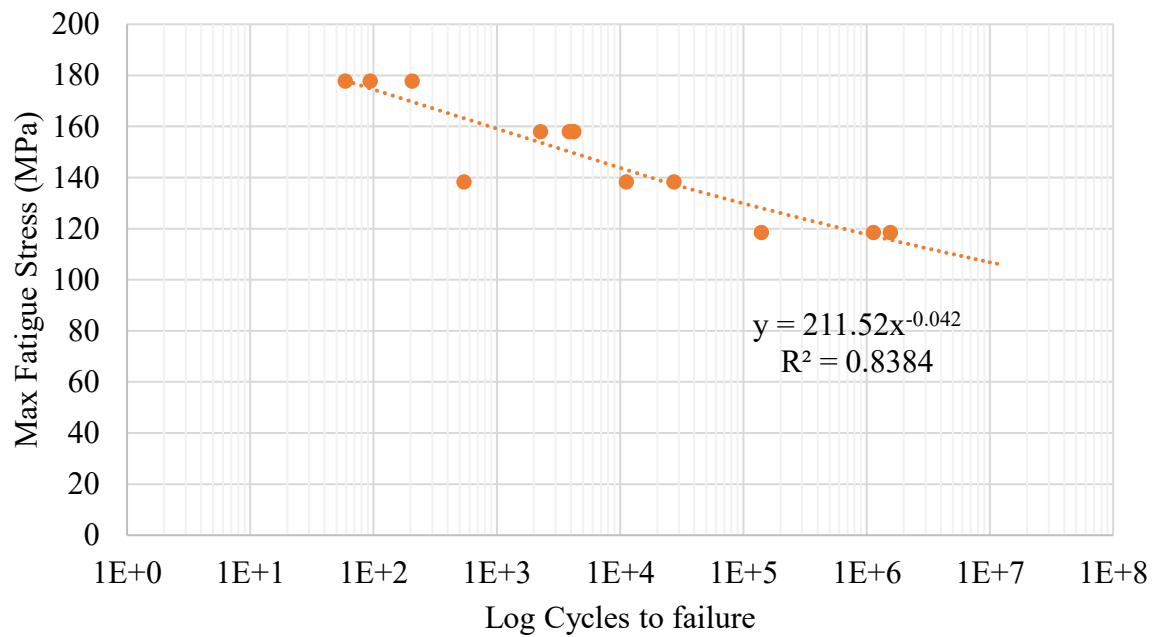


Figure A4.4: S-N curve of SMC IM56R warp laminate

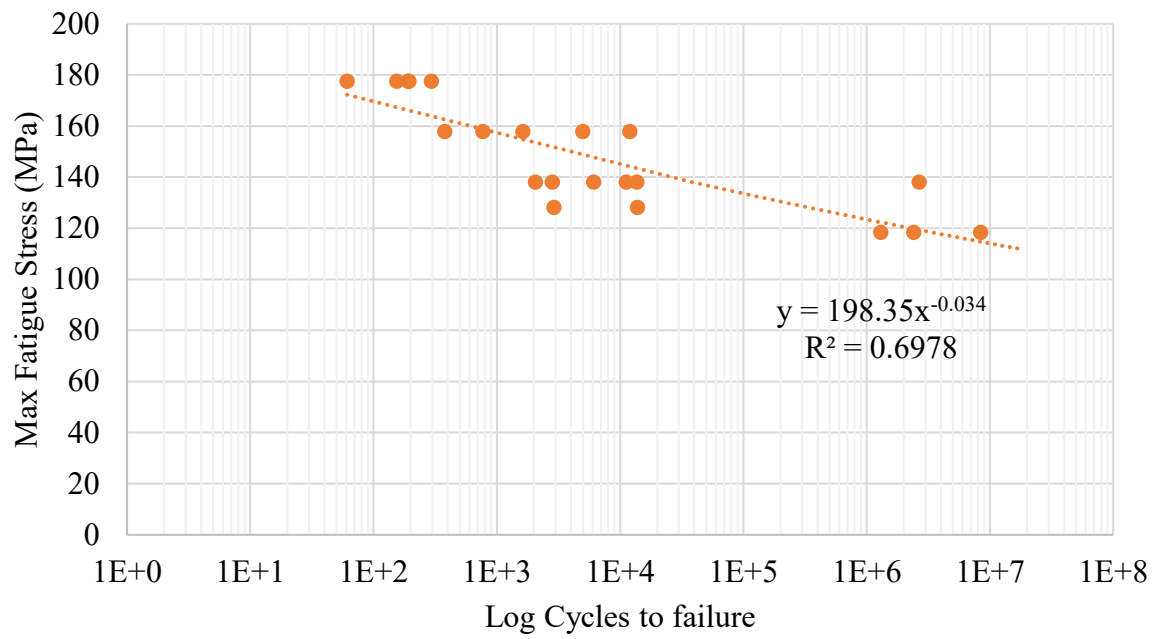


Figure A4.5: S-N curve of SMC IM56L warp laminate

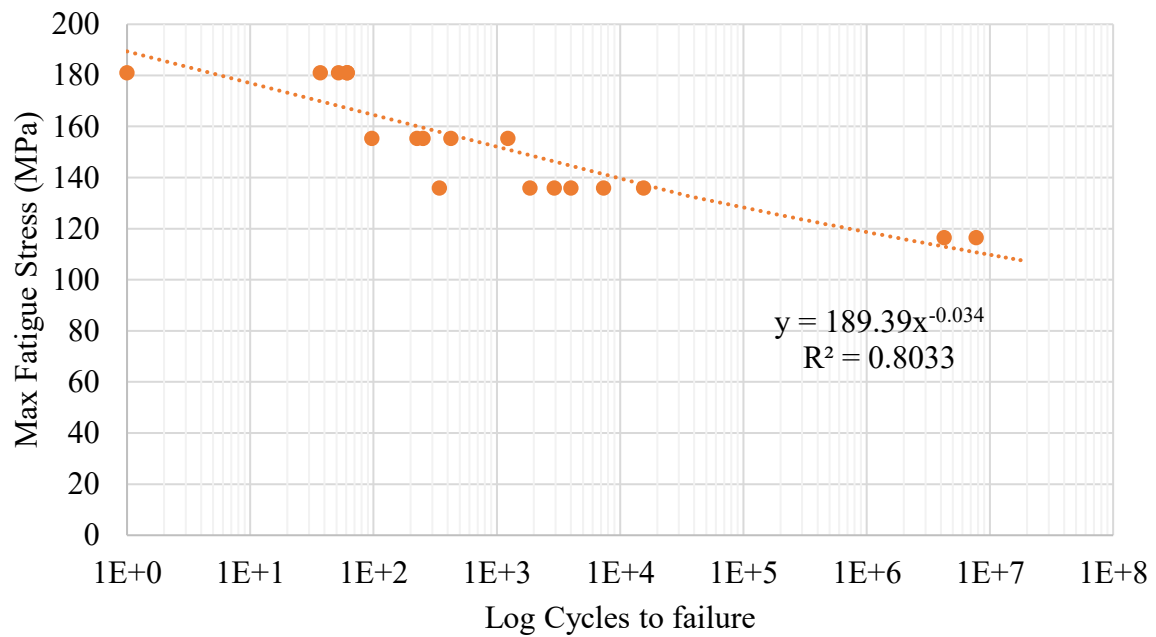


Figure A4.6: S-N curve of LCM SM45D warp laminate

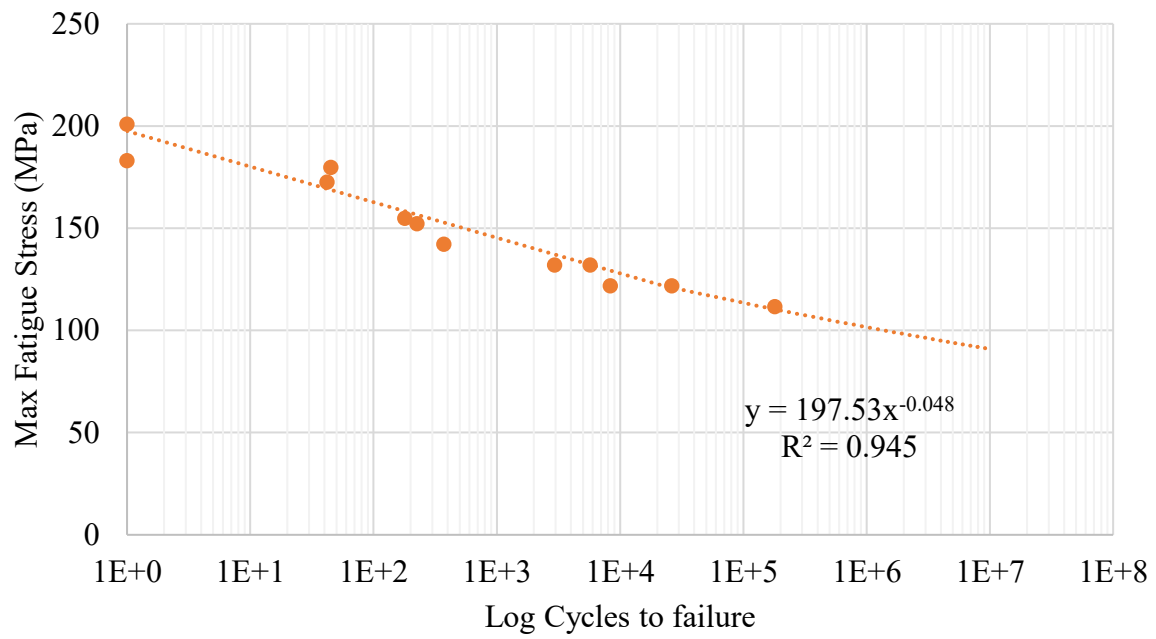


Figure A4.7: S-N curve of Autoclave SM45D warp laminate

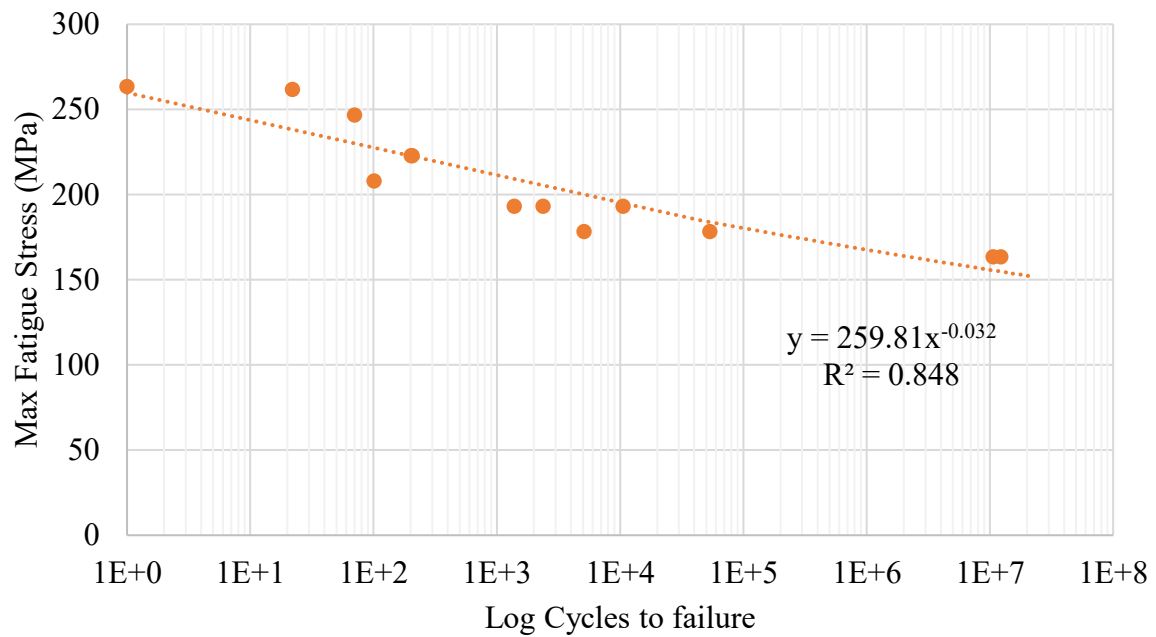


Figure A4.8: S-N curve of Autoclave SM45D weft laminate

Filtered stiffness curves

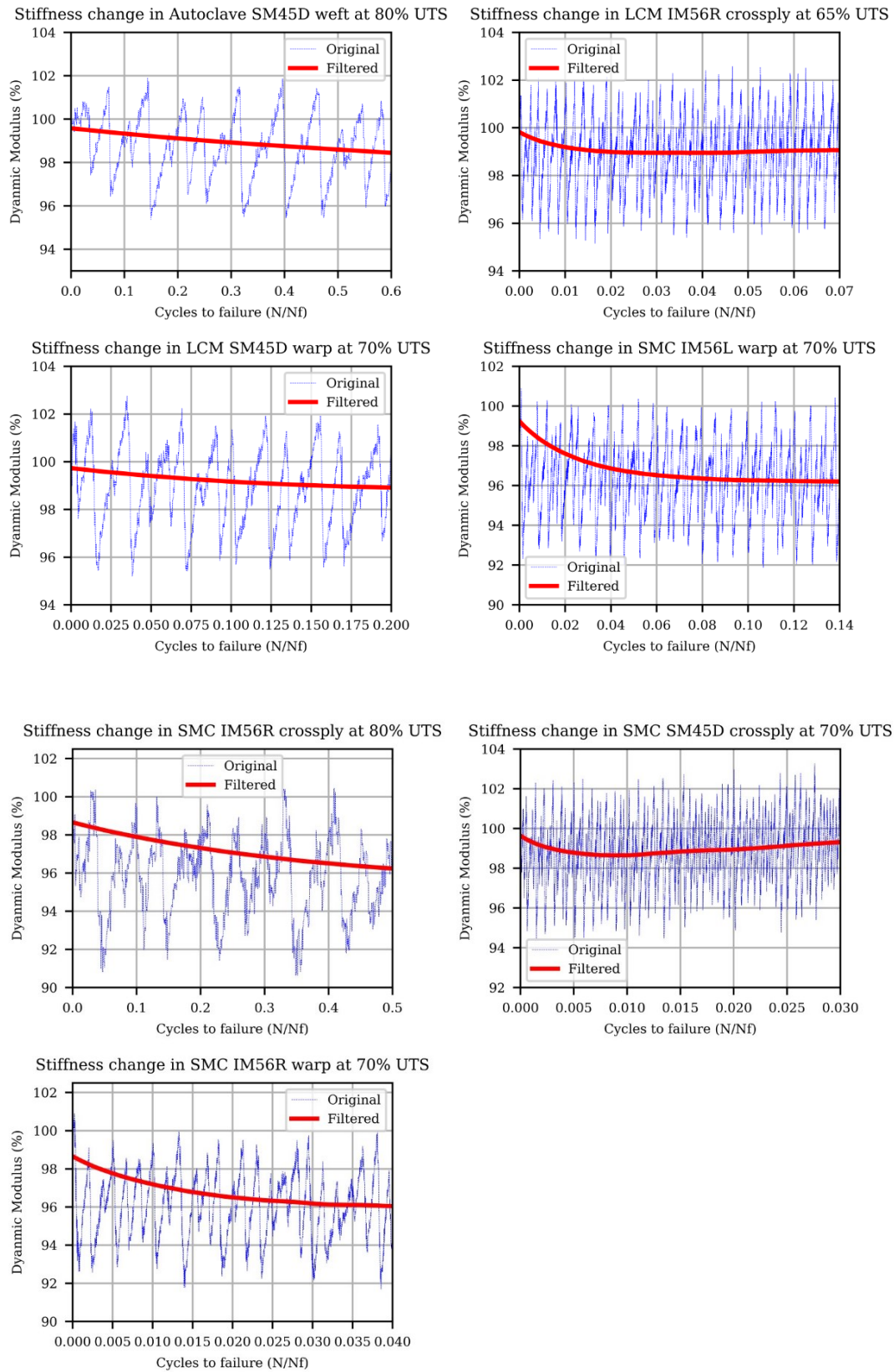


Figure A4.9: Skewed filtered stiffness curve in the initial fatigue cycles

Appendix 5

Tensile Strength and Stiffness changes in rCF composite systems due to fluid immersion

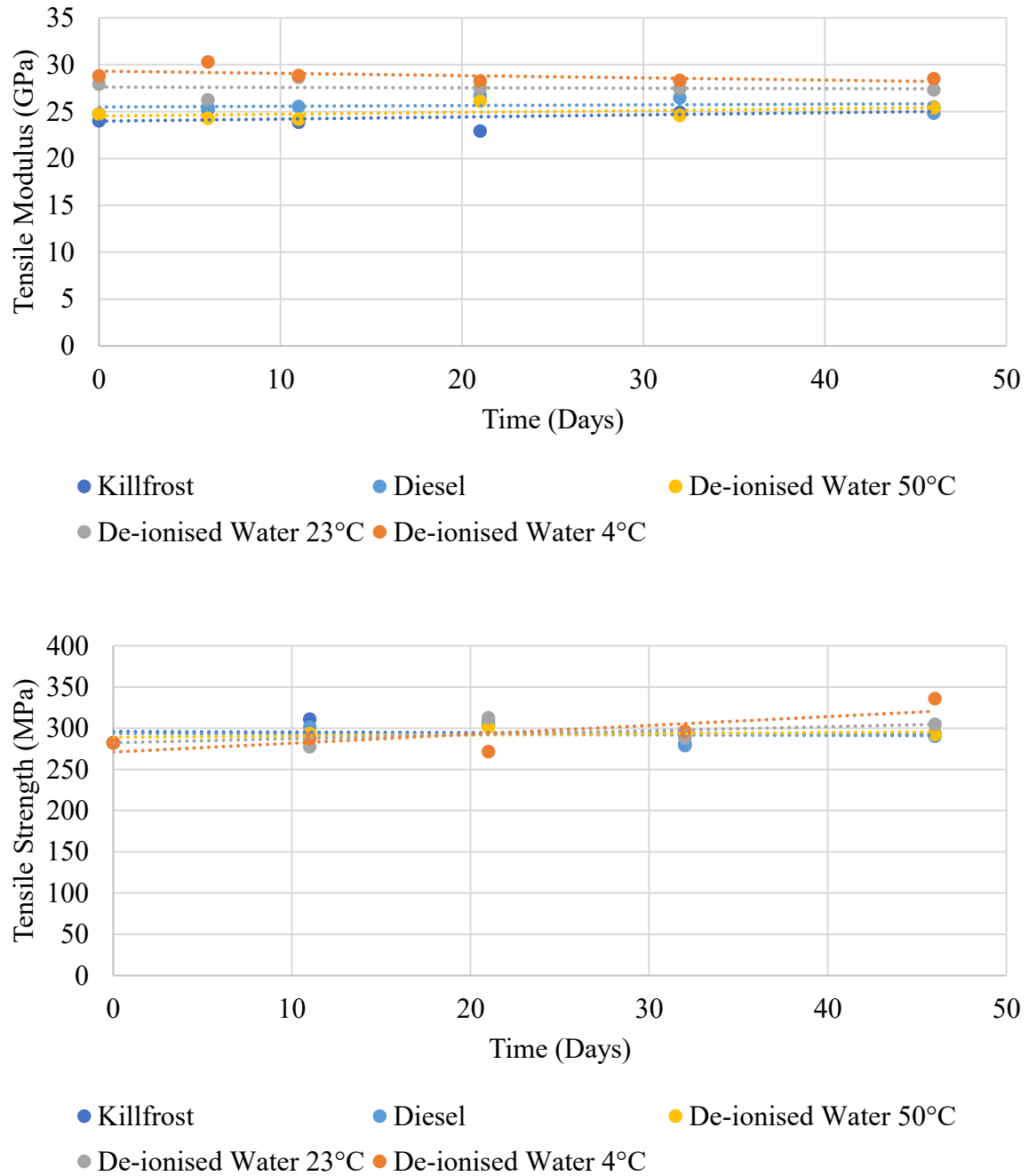


Figure A5.1: Modulus and UTS evolution in LCM laminates

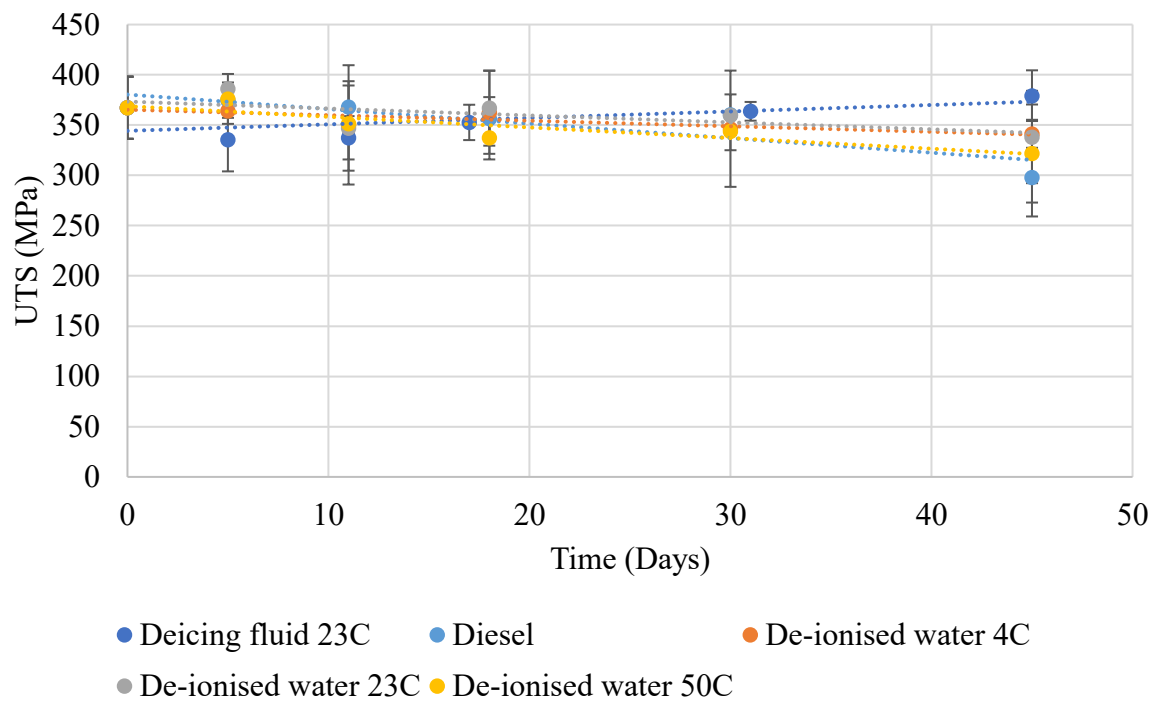
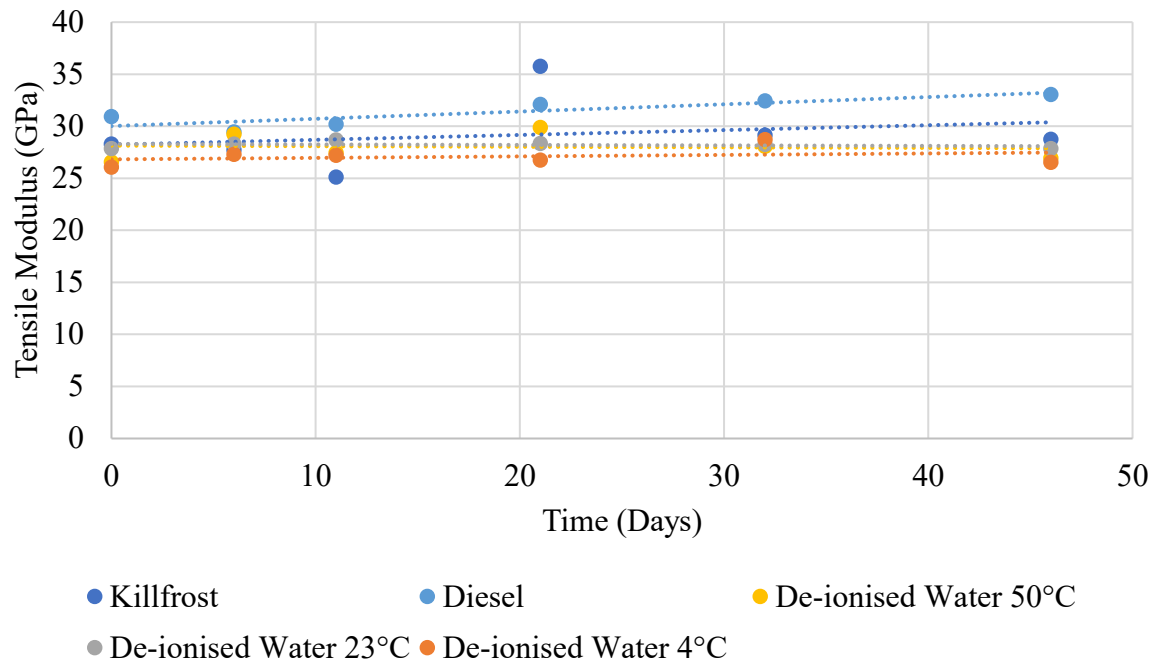


Figure A5.2: Modulus and UTS evolution in SMC laminates

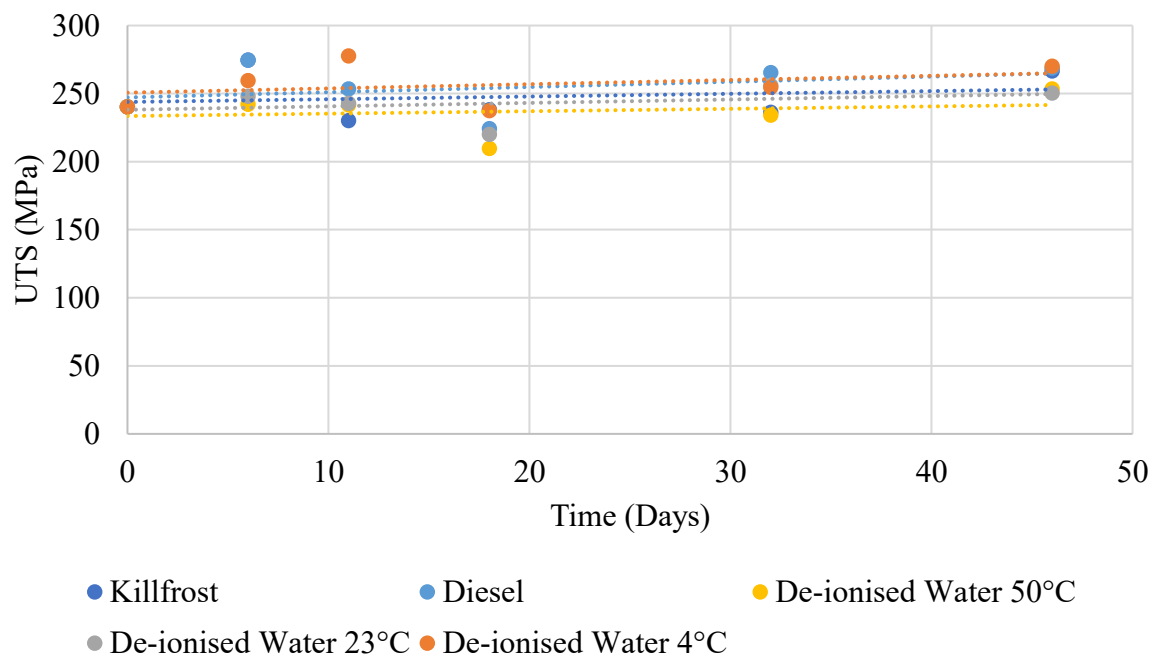
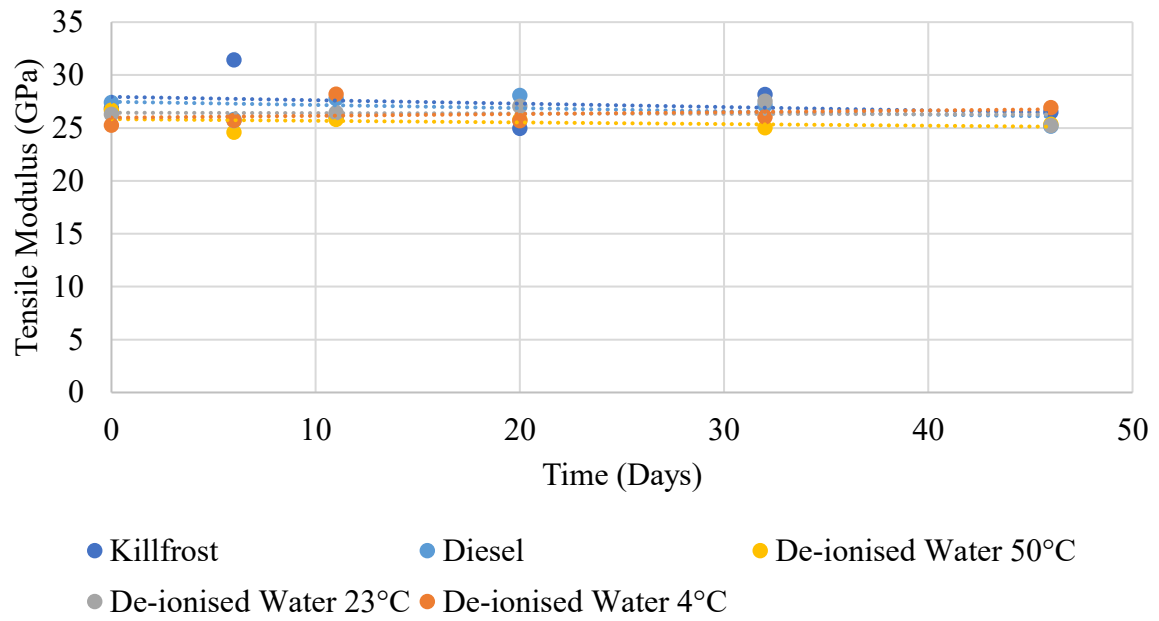


Figure A5.3: Modulus and UTS evolution in Autoclave cured laminates

Appendix 6

Quantifying fibre dispersion by Linear Thermal Expansion

The processing nature of the carding process is such that even though the carbon fibres are randomly dispersed in the conveyor belts, a favourable number of fibres and tows align themselves perpendicularly to the machine direction during the initial web formation stage. The movement of the conveyor belts could further aid to this ‘fibre reorientation’. The fibre dispersion and partial fibre alignment may have an effect on the strength and mechanical properties of the laminate but one that cannot be quantified accurately or is uniform across all rCF laminates. The disparity in the fibre alignments along the XY plane was also assessed by measuring the coefficient of linear thermal expansions (CTE) in the warp and weft directions. The linear thermal expansion of the material along the two principal directions was evaluated for 0° laid non-woven laminates of LCM, SMC and Autoclave processed samples with the help of dedicated resistance strain gauges.

Experimental Procedure:

The measurement of CTE, α_x , by the strain gauge method involves bonding the rCF composite test sample and a reference specimen of known CTE with two identical strain gauges from the same manufacturing lot to minimize error due to resistivity of the constantan grid material. This method is independent of the dimensions of the reference and test material. One of the two strain gauges is bonded to a stress-free test specimen and the second to the reference material at room temperature conditions. The strain gauges used were EA-06-125PC-350 manufactured by Vishay Precision Group. The reference material used was a flat prismatic nickel-iron alloy - INVAR 36, which is a low expansion metal chosen for its known, repeatable, stability with time, and relatively low CTE ($\alpha_r = (0.5 \text{ to } 1.1) \mu\text{strain between } 25^\circ\text{C and } 93^\circ\text{C}$) up to 200°C [208]. The specimen surfaces were thoroughly cleaned and the strain gauges were

bonded onto the test specimens with a thin bond line of M-bond 200 adhesive. As the temperature of the test specimen changes, the resistance of the strain gauge changes due to variation in the resistivity of the grid alloy due to the differential thermal expansions of the alloy and the test material they are bonded to, giving a thermal output that was measured on a P3500 strain indicator device. The difference in the thermal outputs from the rCF material (ϵ_x) and the INVAR alloy (ϵ_r) was calculated over a temperature range ΔT between 20°C and 60°C. The differential thermal output over a certain temperature range gives the unit expansion (mm/mm) under stress free conditions [209]. The strain gauges were wired to the P3500 that is connected in a quarter bridge Wheatstone bridge configuration as shown in Figure A6.1. The temperature changes in the test materials were achieved in an enclosed oven and the temperature changes of both the reference and the rCF material were monitored with thermocouples attached to the specimens. The thermal outputs of both the rCF and the reference material were calibrated to zero at 23°C and the changes were measured at temperature increments of 5°C from 30°C to 60°C. The test materials were left to thermally stabilize at a particular temperature for 15 minutes and the heating rate was set at 1°C per minute.

The CTE of the rCF composite, α_x , was calculated using Equation A6.1:

$$\alpha_x = \alpha_r + \frac{\epsilon_x - \epsilon_r}{\Delta T} \quad (A6.1)$$

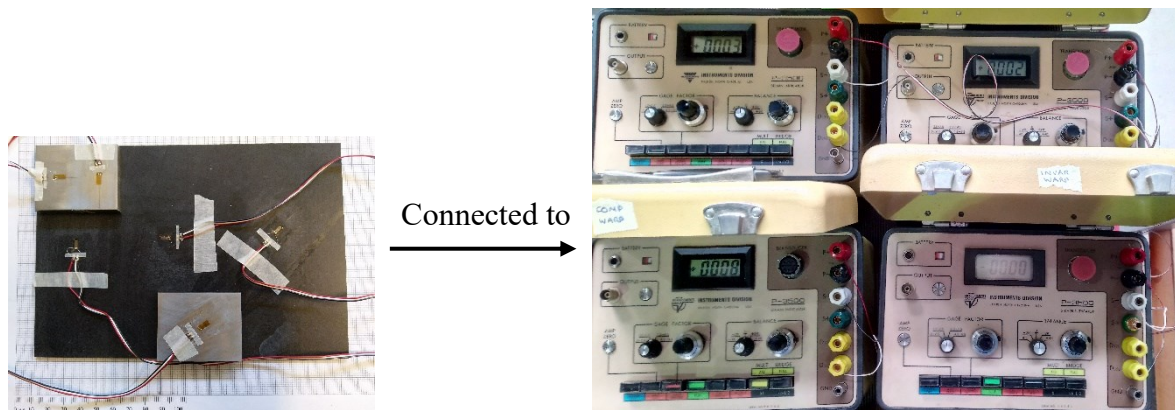


Figure A6.1 – Representative CTE experimental set-up depicting strain gauges connected to P3500 in quarter-bridge Wheatstone network

The linear thermal expansion of the rCF composite was measured along three directions – along the warp, weft and at 45° for IM56R reinforced LCM and SMC laminates and SM45D reinforced Autoclave cured laminate.

Results:

Table A6.1 depicts the average CTE by strain gauge method between 23° to 60°C for rCF composites where the non-woven mats are laid in the same direction. The mismatch in the thermal expansions in the warp and weft directions exemplifies the degree of anisotropy in rCF composites due to the preferential fibre alignments in the non-woven fabric. The CTE of cured epoxy resins is generally around 55 $\mu\text{strain}/^{\circ}\text{C}$, whereas for a UD CF/epoxy the CTE measured by strain gauge method was reported to be -0.9 and 27 $\mu\text{strain}/^{\circ}\text{C}$ along [0°] and [90°] directions respectively [210, 211]. For a plain weave T-300 CF/epoxy composite, CTE is 5.68 and 8.33 $\mu\text{strain}/^{\circ}\text{C}$ along the longitudinal and transverse directions [212].

<i>Remoulding Process</i>	Warp ($\mu\text{strain}/^{\circ}\text{C}$)	Weft ($\mu\text{strain}/^{\circ}\text{C}$)	+/-45° ($\mu\text{strain}/^{\circ}\text{C}$)
<i>LCM (IM56R), $V_f = 0.21$</i>	12.27	5.34	-
<i>SMC (IM56R), $V_f = 0.24$</i>	10.61	4.91	6.92
<i>Autoclave (SM45D), $V_f = 0.21$</i>	11.75	6.34	9.30

Table A6.1: Average CTE in rCF laminates

Appendix 7

Archimedes Test

Experimental Procedure:

A section of the composite weighing between 1 to 5g is taken and its density is calculated by the Archimedes principle as per ASTM D792-13 (A) [213]. The specimen weight in air at 23°C is measured using an analytical balance following which the specimen is completely immersed into distilled water at 23°C in a beaker with the help of a sample holder, as shown in Figure A7.1. It is made sure that bubbles do not appear on the surface of the composite when submerged. The specimen mass in distilled water is measured. This procedure is repeated for 5 different sections of (30 x 30) mm² of the composite laminate. All weight measurements are taken to an accuracy of 0.1 mg. The density of the specimen at 23°C is calculated from Equation A7.1.

$$\rho_{exp} = \frac{M_a}{(M_a - M_w)} \times \rho_w \quad (A7.1)$$

where ρ_{exp} – experimental density of the composite (g/cm³)

M_a – mass of the specimen in air (g)

ρ_w – density of distilled water at 23°C (g/cm³)

M_w – mass of the specimen when immersed in distilled water (g)

Theoretical density is calculated by rule of mixtures equation with the knowledge of the materials used in the manufacturing stage of the composite.

$$\rho_{th} = V_f \times \rho_f + (1 - V_f) \times \rho_m \quad (A7.2)$$

where ρ_{th} – theoretical density of the composite (g/cm³)

V_f – fibre volume fraction

ρ_f – fibre density (g/cm³)

ρ_m – density of resin (g/cm³)

The void content in the composite is given as the ratio of the difference in the theoretical and experimental values to that of the theoretical value.

$$\text{Void \%} = \frac{\rho_{th} - \rho_{exp}}{\rho_{th}} \times 100 \quad (\text{A7.3})$$

where ρ_{th} – theoretical density of the composite (g/cm^3)
 ρ_{exp} – experimental density of the composite (g/cm^3)

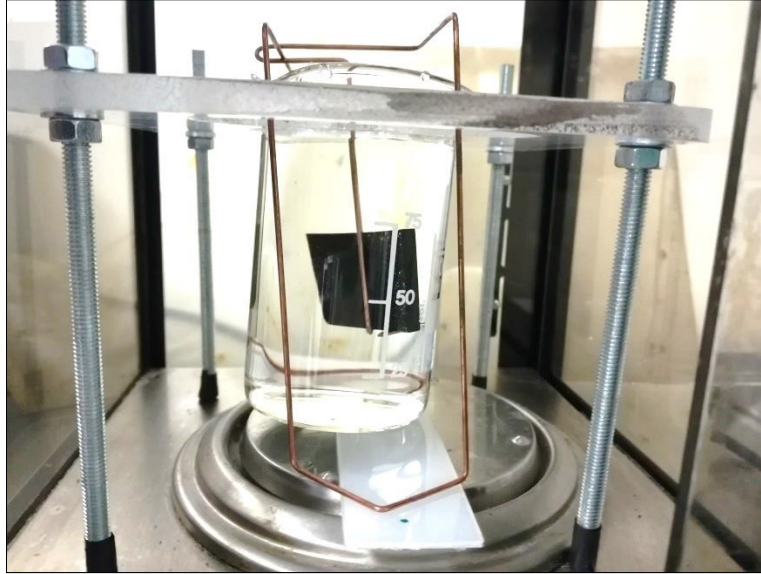


Figure A6.1: Archimedes test apparatus to measure density and void fraction of rCF composites

Results:

<i>Property/ Material</i>	LCM laminate	SMC laminate	Autoclave laminate
<i>Archimedes Density (g/cm^3)</i>	1.34 +/- 0.01	1.31 +/- 0.01	1.51 +/- 0.01
<i>Void Fraction (%)</i>	1.18 +/- 0.84	0.54 +/- 0.81	13.75 +/- 0.84

Table A7.1: Density and Void Fraction in rCF laminates