MANUFACTURE AND CHARACTERISATION OF CARBON FIBRE PREPREG STACKS
CONTAINING RESIN RICH AND RESIN STARVED SLIP LAYERS

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SCHOOL OF MECHANICAL, AEROSPACE AND CIVIL ENGINEERING
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ABSTRACT

The cost of manufacturing high quality composite components can be significantly reduced by using Out of Autoclave (OOA) processes if they can achieve final parts with a finish quality as high as that obtained using an autoclave process. Much research has been carried out recognising that regardless of the reinforcement fibre orientation, manufacturing of preimpregnated (prepregs) carbon components is much affected during its forming stage by fibre deformation and failure modes.

This work sought to reduce wrinkling in the moulding of prepregs by introducing slip layers within the lay-up. Three types of slip layers were used: a dry fabric, a resin rich layer and a resin film. In order for the slip layers to be fully incorporated into the final laminate the resin content within the slip layer must be adjusted prior to crosslinking. In the case of dry fabric layer, additional resin must be introduced and in the case of a resin rich layer and resin film layer, excess resin has to be removed. The laminates used in the project were based on 2/2 twill and unidirectional carbon prepregs. These were manufactured by either Resin Infusion (RI) or Vacuum Bagging (VB). Resin adjustments were made at the same time.

The 2/2 twill and unidirectional carbon prepregs were first characterised by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) before RI and VB. Dry 2/2 twill and unidirectional carbon fabrics and/or Resin Film (for VB) or fabrics and Epoxy Resin (for RI) were introduced in several plybooks and then cured. Final parts were either made of 2/2 twill carbon or unidirectional carbon. The parts were used to investigate the relationship between individual plies during the consolidation of a plybook. The first characterisations were done on flat laminates. Also two moulds were manufactured and used to produce new parts for further characterisations. The first, an aluminium mould was machined using a Computer Numerical Control (CNC). The second mould was a fan blade, made using chopped strand mats. The final parts had 3, 4 or 6 plies. These parts were characterised using Optical Microscopy (OM), Scanning Electron Microscopy (SEM), and Torsion testing. The results provide a first step towards understanding how the friction at a ply/ply level can be influenced by the “starving” or the “enriching” of resin in a plybook during its consolidation.
The work showed that in OOA manufacturing, the friction at a ply/ply level can be controlled by introducing Resin Film, Dry or Resin Rich Fabrics in a prepreg plybook. It was demonstrated that introducing lubrication to control ply friction during forming can result in quality part as high as that obtained from a traditional composite forming process. As the final parts were made using a fixed die mould and a vacuum bag, most of the plies in the layups could deform individually and accommodate interply shear. Torsion testing on a number of a random selection of samples showed negligible effects on shear stresses, strengths and modulus within the parts were negligible. It is argued that the flexibility of the vacuum bag could have had an impact on the layups during forming. The plies could conform to the mould easier. This work has potential for other applications. For example in match die moulding, introducing wet lubrication could improve interply shear during forming and help in improving accuracy and geometrical conformity of final parts. Furthermore, developing techniques to control friction during forming in OOA can be attractive to industries which could not afford to invest in this OOA prepreg technology. OOA processing times have become very attractive to industries such as the sporting good, automotive, wind energy and transportation. These industries could explore the opportunity presented by the work in this EngD thesis.
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# ABBREVIATIONS

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<tr>
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<th>Description</th>
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<tr>
<td>4HS</td>
<td>Four harness satin</td>
</tr>
<tr>
<td>5HS</td>
<td>Five harness satin</td>
</tr>
<tr>
<td>8HS</td>
<td>Eight harness satin</td>
</tr>
<tr>
<td>APC-2</td>
<td>Advanced polymer composite</td>
</tr>
<tr>
<td>BSE</td>
<td>Back scatter</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CCC</td>
<td>Carbon carbon composite</td>
</tr>
<tr>
<td>CMC</td>
<td>Ceramic matrix composite</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer numerical control</td>
</tr>
<tr>
<td>Cp</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>DF</td>
<td>Dry film/fabric</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl ether of bisphenol-A epoxy</td>
</tr>
<tr>
<td>DGEBPA</td>
<td>Ether of bisphenol-A epoxy</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>EngD</td>
<td>Engineering doctorate</td>
</tr>
<tr>
<td>FRP</td>
<td>Fibre reinforced polymer</td>
</tr>
<tr>
<td>GMT</td>
<td>Glass matt filled thermoplastic</td>
</tr>
<tr>
<td>HTF</td>
<td>Heat transfer fluid</td>
</tr>
<tr>
<td>LVDT</td>
<td>Linear variable differential transform</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated differential scanning calorimeter</td>
</tr>
<tr>
<td>MEKTP</td>
<td>Methyl ethyl ketone peroxide</td>
</tr>
<tr>
<td>MMC</td>
<td>Metal matrix composite</td>
</tr>
<tr>
<td>-NCO</td>
<td>Isocyanate group</td>
</tr>
<tr>
<td>-OH</td>
<td>Alcohol group</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscope/microscopy</td>
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<tr>
<td>OMC</td>
<td>Organic matrix composite</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
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<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------------</td>
<td>-------------------------------------------</td>
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<tr>
<td>PGDip</td>
<td>Postgraduate diploma</td>
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<tr>
<td>PMC</td>
<td>Polymer matrix composite</td>
</tr>
<tr>
<td>R&amp;D</td>
<td>Research and development</td>
</tr>
<tr>
<td>RR</td>
<td>Resin rich</td>
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<tr>
<td>RS</td>
<td>Resin starved</td>
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<tr>
<td>RTM</td>
<td>Resin transfer moulding</td>
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<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Tc</td>
<td>Crystallisation temperature</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGGDM</td>
<td>Tetracycloxydyl 4, 4” – diaminodiphenylmethane</td>
</tr>
<tr>
<td>TGMDA</td>
<td>Tetracycloxydyl methylene dianiline</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>UAV</td>
<td>Unmanned aerial vehicle</td>
</tr>
<tr>
<td>UD</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>VBO</td>
<td>Vacuum bag only</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>RI</td>
<td>Resin infusion</td>
</tr>
<tr>
<td>VA</td>
<td>Vacuum bagging</td>
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<td>RF</td>
<td>Resin Film</td>
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<td>CarbonMC</td>
<td>Carbon Matrix composite</td>
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CHAPTER I

1 EngD COURSE STRUCTURE AND RESEARCH OUTLINE

1.1 EngD course
The Engineering Doctorate (EngD) is a four year doctoral level research degree in engineering, chemistry, physics and material sciences. The Engineering Doctorate program in "Engineering for Manufacture: Process and Product" comprised 3 main components: a doctoral level research project which was the core of the EngD (about 75%), a Postgraduate Diploma in Management (PGDip) and a professional development programme. The research project was supported by a short technical programme. The Postgraduate Diploma in Management (PGDip) was delivered in the form of lectures during the first two years of the program, this component was compulsory; it consisted of eight units or lectures of 15 credits each. As a compulsory component of the EngD, a pass mark or 50% or above was required in all units for the successful completion of the PGDip. The last main component of the EngD, the professional development programme runs over the four years of the project and comprises a series of courses and workshops aimed at developing professional and personal skills. Courses include leadership, management, negotiation skills and creative problem solving

1.1.1 Postgraduate Diploma
The Postgraduate Diploma (PGDip) in Enterprise Management was a mandatory component of the Engineering Doctorate. It was completed in the first two years of the degree. The course subject matter and materials were designed and delivered by tutors from the Manchester Enterprise Centre (MEC) to specifications set out by the EngD centre. MEC was part of the Manchester Business School. The PGDip in Enterprise Management consists of 120 credits all at level 4 (Masters Level). All course units had 15 credits each. The PGDip in Enterprise Management was assessed by a series of coursework assignments.
1.1.2 Professional development

The final element of the EngD was to develop personal and professional skills. This was achieved through a series of workshops and group activities on topics which included (but were not limited to) understanding teams and management styles, communication and negotiation skills, project management and industrial law.

There was a one-on-one mentoring and support scheme through the EngD Centre and through a personal professional mentor. The professional development mentor helped to prepare for professional membership to join the Institute of Mechanical Engineers (IMechE). Training was spread over four years with the aim of gaining a CEng qualification. Each quarter, a report was sent to the mentor summarising any knowledge acquired during that period, with a highlight on any strengths and weaknesses acquired or noticed.
1.2 Research Background

The use of prepreg materials in the manufacturing of aerospace composites has seen an exponential increase over the last two decades [1-5]. A prepreg consists of a reinforced material preimpregnated with a resin matrix in controlled quantities; the resin is partially cured to a B-stage point [6-10]. For each prepreg resin system, there is a range of options for curing temperatures. For a given cure temperature there is also a corresponding cure time. For highly reactive matrices and thick laminates, the heat up rate during curing is low and may incorporate an intermediate temperature soak in order to avoid exothermic reactions [11, 12]. In general, for manufacturing preimpregnated carbon fibre composites, unidirectional prepregs are mostly preferred to their woven pair as the primer can offer a possibility of increased drapability. This is due to the lack of fixed kinematic link between tows [13, 14]. Unidirectional prepregs have heavy yarns in the wrap direction and very light yarns in the weft direction; the light yarns in the weft direction hold the primary fibres in position. Up until the beginning of the 21st century, the conventional manufacturing process for prepregs (especially in the aerospace industry) was in an autoclave. Autoclave curing is a well-established process [15-17]; the final components had high fibre volume fractions and low void contents.

Manual lay-up of high-curvature products is complicated and time consuming. For complex parts, autoclave manufacturing costs can be high and the process is unsuitable for large parts. In order to build composite structures such as wings or a fuselage, smaller parts are manufactured independently and then assembled.

In a bid to reduce manufacturing costs of complex and/or large parts, vacuum pressured processes such as Resin Transfer Moulding (RTM), Resin Infusion (RI) or Vacuum Bagging (VB) have been adapted to prepreg composites manufacturing [18-22]. These manufacturing processes are referred to as Out of Autoclave processes (OOA).

The understanding of the physical mechanisms (friction, drape, interply shear, intraply shear) which takes place during the OOA process is essential for the production of high quality parts comparable to parts obtained using autoclave manufacturing. Friction between a ply/ply or ply/tool layup is essential to accommodate complex curvatures or/and angles.
This thesis presents an experimental method to characterise the impact of friction between prepreg plies during forming.
1.2.1 Research outline

Lack of parameters control in the manufacture of fibre reinforced composite parts can directly impact on the performance of the structure made. Arranging a fabric layup to conform to a complex shape can during forming, introduce fibre misalignments and voids. Although each ply will tend to remain “stuck” to one another, the fibres under stress will tend to stretch around corners and sharp edges in their attempt to drape. During forming, a layup drapes around a shape by a succession of dropping plies along the length of the mould surface to match varying in-plane and bending loads. The plies may slip with respect to one another or the tool surface as a result of consolidation. This occurs at the early stages of the cure, before the resin cures, when the resin modulus is low, causing a decay of tensile stresses away from the tool surface.

Figure 1-1: deformation of ply sequence under compaction forces
Therefore, the final quality part is a function of the variation in friction between ply/ply or ply/tool shear during forming. By adjusting the properties of this shear region, the amount of stress transferred between ply/ply and/or ply/tool can be tailored. Controlling interply shear will result in the control of the fibre slippage hence increasing the final quality part. The presence or lack of friction during forming is reflected by the control of lubrication between the plies. Different lubrication mechanics will have different impact on friction mainly dry or wet mechanisms.

A dry condition means that no lubrication is present between the plies, thus friction is high. This mechanism is generally used when the fabric formability is large enough to form a part with simple geometry without lubricants. If dry mechanisms imply that no lubrication is present between the plies, wet mechanisms are therefore defined as presence of lubrication. By correlation, it can be assumed that, when manufacturing complex shape parts, controlling fibre slippage can be done by introducing a wet lubricant between the plies and/or tool. A resulting parameter of the presence of lubricant during forming can be the reduction of void formation.

From these assumptions, using an OOA process, this project will introduce a novel method to control friction between ply/ply and/or ply/tool in a layup during forming of a prepreg part. The shear region is presumed to be under a wet lubricant mechanisms. The lubrication mechanics used are resin rich and/or resin starved fabrics. Final parts quality were evaluated quantitatively in terms of void percentage.

The two moulds used to manufacture the parts in the project were both made during the project. The first mould was made out of aluminium (section 11.1 Aluminium mould, page 188). The second mould was implemented using a split mould technique with chopped strand glass fibre for the primary mould and carbon fibre for the main mould. A description of the manufacturing of the mould is provided in section 7 (MOULD FABRICATION, page 133). The parts, once manufactured, were characterised using both optical- and electron-microscopy.
1.2.2 Aims of project investigation

The aim of the project was to test the hypothesis that introducing slip players within a prepreg layup could improve the final quality of manufacturing composite parts.

The project objectives are as set:

a) Carry a literature search on composite material, OOA processes and part quality manufacturing challenges.

b) Use slip layers in the design and manufacturing of composite parts

c) Characterised the quality of the manufactured part and access validity of hypothesis
1.3 Thesis structure summary

The next chapter to follow will be introducing composite materials. In this chapter composite materials are defined and classified. These have been classified in terms of their constituents and manufacturing processes. A review on the different weaves available with woven clothes is carried.

The following chapter introduces the main manufacturing processes used in industry in addition to autoclave moulding. Flow charts of the different processes provide details of all the steps required during manufacturing.

A literature review on composite deformation modes is carried out with an emphasis on friction and waviness and wrinkles formation during manufacturing processes of composite materials. Much research had been done recognising that regardless of the reinforcement fibre orientation, manufacturing of a carbon prepreg composite part is much affected during its forming process by its deformation and failure modes. Successful forming of the part depends on deformation modes taking place and undesired failure modes being suppressed. Characterisation of drape and interply shear on a woven fabric is conducted in chapters five and six.

Chapter seven describes the methods and analytical tools undertaken within this project. These include microscopy, image processing, calorimetry and torsion testing. The fabrication of a resin starved and resin rich part by vacuum bagging and resin infusion is explained in details. Most of the parts made during the project were composed of 2/2 twill prepregs dry carbon fabric. However, a few parts made from unidirectional carbon prepregs and unidirectional dry carbon fabrics were also fabricated.

The eighth chapter provides a full description of the chopped strand mat mould manufacturing. The component to be replicated, a blade from Siemens was used as a pattern to manufacture a four part split mould. The mould was post cured at 150°C for 4 hours, and used to make parts where the reinforcements were a combination of 2/2 twill prepregs and 2/2 dry carbon fabrics. A second mould was also used in this research to manufacture a unidirectional carbon prepreg combined with a unidirectional dry carbon fabric. The second mould was made from aluminum using a computer numerical control (CNC).
Chapter nine details the analysis carried out on data collected. DSC analysis established optimal curing cycles for the parts. The results from torsion testing were used to calculate the shear stress, strength and shear modulus of both resin rich and resin starved parts.

A conclusion chapter summarises the work done in this project. It is argued that the potential for obtaining further insights on the impact of introducing resin rich or resin starved plies within a layup to obtain better consolidation between a ply/ply or ply/tool surface can be greatly improved if some alterations to the fabrication processes were made. An alternative method is suggested in this chapter for reducing the formation of wrinkles during consolidation. A minor analysis of the commercial impact of composites in the market place is also carried out in this final chapter.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers
CHAPTER II

2 COMPOSITE MATERIALS – A REVIEW

The McGraw-Hill concise encyclopaedia of engineering defines a composite material as "a material system composed of a mixture or combination of two or more constituents that differ in form or material composition and are essentially insoluble in each other" [23]. In other terms, a composite material is a combination of two or more materials that complement each other with their respective properties. The individual components remain separate and distinct within the finished structure. That is, they do not dissolve or merge completely into one another, although they act in concert. Normally the components can be physically identified and exhibit an interface between each other. In principle, composites can be constructed from any combination of two or more materials: metallic, organic or inorganic. Combinations of different materials, which results in superior products, started in antiquity and have been in continuous use up until the present day. Some of the earliest forms of buildings were made of mud bricks. Dried mud has good compressive strength but poor tensile strength although straws have excellent tensile strength. Earlier builders realised that by embedding straws in a block of mud, the resulting brick would be resistant to both tearing and squeezing. Another example of a composite is wood, it is a natural composite made from long cellulose fibres held together by a substance called lignin.

Until the 19th century, materials such as gold, spider silk\(^1\), and ivory, had been man’s most valuable materials. At the beginning of the 20th century, Staudinger [24] proposed the concept of polymers as they are used nowadays. In 1953, Staudinger won a Nobel Prize for his work which is at the core of the science of macromolecules today. Deriving from Staudinger, substances made in laboratories can now have their properties engineered. They are referred as “Synthetic” composite materials, and are often just called composites in industries. Throughout this thesis, “synthetic” composite materials are referred to simply as composites.
Composites are classified either by their constituents or their shapes. If a composite is made of a combination of two materials, the constituent which gives bulk to its form is usually referred to as the "matrix". The matrix determines the composite’s internal structure [25]. The thermal and mechanical properties of a composite depend on a second constituent which is referred to as “reinforcement”. All the constituents of a composite are necessary for the system to function. Overall, the properties of a composite are determined by: The properties of the combined constituents, the constituents’ ratio with each other, and the constituents’ geometry.

Composites were traditionally used in the aerospace industry. They were ideal for structural applications where high strength to weight ratios were required. However, in the last two decades, they have found applications in myriad industries which also value such properties including boat manufacturing, sports equipment, racing cars, electronic packaging and medical equipment.

2.1 Composite materials classification in term of their constituents

Composites are classified at two distinct levels. The first level of classification is usually made with respect to the reinforcement constituent depending on their size. Reinforcements can be made of particles and/or whiskers, fibrous and/or powered materials. A particle is considered a reinforcement if its aspect ratio is 40 or above [26]. Generally, the reinforcements sizes are measured in microns and range from a few microns to several hundred microns [27].

In fibrous composites, the reinforcement is in the form of fibres in which the length of the fibre is much higher than the cross section dimension. The cross sectional dimensions are in the order of microns; also, depending on the length of fibres, the reinforcement can be short or continuous. Short reinforcements mixed with resins produce random orientation mat ². Continuous reinforcements can be unidirectional, multidirectional or tridimensionanal. Figure 2-1 illustrates a classification of composites with respect to their constituents.

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² Referred to as chopped strand mats in the industry
Figure 2-1: Classification of composite materials in term of the constituents

The second level of classification is with respect to the matrix. Matrices are categorised in three main groups: Metal-matrix composites (MMCs) are mainly found in the automotive industry, the ceramic-matrix composites (CMCs) are used in high temperature environments and organic-matrix composites (OMCs) which have not a particular target market.

The term “organic-matrix” is generally assumed to include two classes of composites: polymer-matrix composites (PMCs) and carbon-matrix composites (CarbonMCs). While MMC and (to some extent) CMCs are used in many technological applications, PMCs are by far the most significant matrix category. PMCs use a polymer based resin as a matrix and a variety of fibres such as aramid, carbon or glass as reinforcements. Carbon carbon Composites (CCCs) are made from PMCs original polymer matrix, where the PMCs are densifying and carbonising [28-30].
Polymer materials are used for their mechanical properties (strength and stiffness, toughness etc) and their ability to deform easily. These qualities are linked to the structure of the different atoms that form the polymer: the macromolecule. The word “polymer” is derived from two Greeks root: πολψ (many) and μερος (parts); polymers are molecules built up from numerous identical chemical units or monomer, in Greek μονο (single), spatially repeated to form a chain or macromolecules.

Another substance which is composed of large molecular chains of macromolecules is a “plastic”. Nowadays, the word “plastic” has become the generic name to describe polymers although strictly, plastic is an adjective that describes the way a material deforms under load [31, 32]. In engineering terms, a plastic contains hardeners, fillers (along with others elements in its solid finished state) and at some stage of its manufacturing process can be shaped by flow [33]. Plastics are divided into three main groups in analogy to their molecular structures, depending on the degree of crosslinking between the main macromolecular chains: thermoplastic polymers, elastomers and thermoset plastics (Figure 2-2).

![Figure 2-2: Plastics classification](image-url)
Depending on the method of production, or according to their properties, or structures, polymers can be classified into three groups (Figure 2-3) [34].

*Figure 2-3: classification of polymers*

*Polymers as a function of manufacturing processes, properties or structures*

Polymerisation, polycondensation and polyaddition are all syntheses in a chemical reaction.

Polymers are classified as thermoplastics when their heating and cooling may be repeated. They are thermosets when they can soften when heated by harden permanently.

Polymer chains are produced by different polyreaction which occur between monomers. In polyaddition, the monomers bond to each other without any loss of atoms. Polymers are classified as condensation polymers when to different monomers combined with the loss of water.

Polymers are amorphous when their molecules are randomly arranged in a long chains which are twisted around one another. When heated in a differential scanning calorimeter, they do not show crystallisation or melting points, only a glass transition point. The molecules in crystalline polymers are orderly.

[36]
2.1.1 Reinforcement

The first constituent of a composite material is referred to as a "fibre" or "reinforcement" which fortify the matrix by providing stiffness and strength. A fibre is characterised by its high length-to-diameter ratio. The strength-to-density and the stiffness-to-density ratios are generally used as indicators of the effectiveness of a fibre. Fibres make the most volume fraction in a composite laminate and share the main portion of the load acting on the structure [35, 36]. In general, the reinforcements can be classified in term of size, production or performance [37-39] (Figure 2-4).

![Figure 2-4: Reinforcement classification in term of size, production or performance](image)

In polymeric composite terms, fibrous reinforcements are referred to as fabrics. These are manufactured assemblies of long or chopped fibres of carbon, aramid or glass (or a combination of these) to produce a flat sheet of one or more layers of fibres.

These layers are held together either by mechanical interlocking of the fibres themselves or with a secondary material to bind them together and hold them in place, giving the assembly sufficient integrity to be handled.
Fabric types are categorised by the orientation of the fibres used and by the various construction methods used to hold the fibres together. Figure 2-5 shows a classification of fibre reinforcement in term of their fibrous nature.

Figure 2-5: General classification of fibre reinforcements in term of their fibrous nature

Examples of continuous reinforcements include unidirectional, woven cloth and helical wending while discontinuous reinforcements include chopped fibres and random mat. Continuous fibre composites are characterised by their laminates’ individual layers or plies to be oriented in directions that enhance the strength in the primary load direction [40-42].

In fibre reinforced polymers (FRP), reinforcing fibres have diameters ranging from 7 to 10μm; the fibres are long or short or chopped, with the length to diameter of the fibres being referred to as the aspect ratio. Properties of short fibre composites are very dependent on the aspect ratio; the greater the aspect ratio, the greater the strength and stiffness of the composite [43, 44].
By far the most widely used reinforcement form in high performance organic matrix composites (OMC) are fibre tows. These typically consist of thousands of fine filaments arranged in a single bundle. The tow is handled as a single unit or can be wrapped or woven using commercial equipment with different weaves available on the market [45].

2.1.1.1 Continuous fibres

Weaves

Weaving produces fabrics in a variety of shapes and weave configurations. Weaves are made on a loom by interlocking two orthogonal (mutually perpendicular) sets of yarns (warp and weft). The warp direction is always parallel to the length of the fabric while the weft is always perpendicular to the length of the fabric.

In composites, woven fabrics may be characterised in terms of the fabric crimp which is a measure of the yarn waviness. In general, a lower crimp improves drapability since it also means fewer wrap-weft crossovers that may resist shearing. Lower crimp also means straighter fibres, which translates into better composite mechanical proprieties [46, 47]. Most weaves contain a similar number of fibres and use the same material in both the wrap and weft directions [48, 49]. However, hybrid weaves using carbon and glass, and weaves dominated by wrap yarns are frequently used [50]. These hybrids weaves are used to obtain specific properties e.g. mixing carbon with aramid takes advantage of the heat resistance of aramid and the strength of carbon [51, 52]. The important parameters to consider when dealing with woven fabrics are the fibre type, the yarn type, the weave style, crimp, the yarn count (yarns / length unit) and the weight.

The size is also of great importance in the weaving operation where it should ideally eliminate any fibre damage. In woven fabrics, drape is the ability of a fabric to conform to a complex surface, surface smoothness and stability of a fabric. It is controlled primarily by the weave style. Basic fabric weaves are few in numbers, but combinations of different types and sizes of yarns with different warp/fill counts allow for hundreds of variations. Common weaves are plain, twill, satin and leno.
Plain weave

A plain weave fabric is a fabric where every wrap and weft yarn goes alternatively over and under successive warp and weft yarns respectively. This type of weave is extensively used by various industries, as it is the tightest possible weave available [53, 54]. It has the most interlaces per unit area than any other type of weave and therefore the tightest basic fabric design and the most resistant to in-plane shear movement. The essential construction requires only four weaving yarns: two warps and two wefts. This basic unit is called the pattern repeat [54] (Figure 2-6).

Although plain weaves resist distortion during handling, they are difficult to form (drape). Wetting out during impregnation, they frequently present issues related to the exchanges of position from top to bottom made by each yarn. This typical waviness drastically reduces the strength and stiffness of manufactured parts with the introductions of defects such as crimp.

A variant of the plain weave is the basket weave. The basket weave has two or more wrap and two or more wefts woven together. In this variation, the arrangement need not be symmetrical. Basket weaves are referred to as 2/2 basket, 8 x 2, or 5 x 4 variations [55]. The basket weave presents less crimp than the plain weave, making it stronger [56].

Twill weave

Twill weaves offer greater drapability than plain and basket weaves [57]. In this weave, one or more warp fibres alternately weave over and under two or more weft fibres in a regular repeated manner (Figure 2-7).
This produces the visual effect of a straight or broken diagonal ‘rib’ to the fabric. Superior wet out and drape is seen in the twill weave over the plain weave with only a small reduction in stability. With reduced crimp, the fabric also has a smoother surface and slightly higher mechanical properties.

Figure 2-7: Twill weaves

Here, the filling threads are woven over and under two or more warp yarns, producing a characteristic diagonal pattern.

Satin weave

The satin weaves are a family of weaves categorised by the number of yarns in the repeating unit (Figure 2-8). They produce a construction with low resistance to shear distortion and thus are easily draped over curved moulds [58]. Satin weaves allow fibres to be woven in the closest proximity and can produce fabrics with a close ‘tight’ weave. Common satin weaves are four-hardness satin weave (4HS) where the warp yarns skip over three fill yarns and then under one fill yarn; five-hardness satin weave (5HS), where the warp yarns skip over four fill yarns and then under one fill yarn; eight-hardness satin weave (8HS), where the warp yarns skip over seven fill yarns and then under one fill yarn. As the number of harnesses increase, so do the length and degree of looseness, making the fabric more difficult to control during handling operations.

The 8HS has the best drapability of this group. However, 5HS normally use a 6k carbon tow that is less expensive than the 3k carbon tow used in the 8HS. A ‘crowsfoot’ weave is a form of satin weave with a different stagger in the repeat pattern [59].
Leno and Mock Leno weaves

Leno and mock leno weaves are rarely used for structural composites. A leno weave is a form of plain weave in which the adjacent warp fibres are twisted around consecutive weft fibres to form a spiral pair, effectively locking each weft in place. A leno weave improves the stability in ‘open’ fabrics which have a low fibre count. Fabrics in leno weaves are normally used in conjunction with other weave styles because if used alone, their openness could not produce an effective composite component.

The leno weave is frequently found to be used to tie the edges of dry fabric together so that it will not unravel during handling. Another version is the mock leno weave where the fabrics form an open structure with small holes or gaps similar to leno weaves.

In Mock leno weaves, occasional warp fibres, at regular intervals but usually several fibres apart, deviate from the alternate under-over interlacing and instead interlace every two or more fibres Figure 2-9. This happens with similar frequency in the weft direction, and the overall effect is a fabric with increased thickness, rougher surface, and additional porosity.
In the leno weaves, the weave structure paired warp yarns are intertwined in a series of figure eights and filling yarn is passed through each of the intersections so formed, producing a firm, open mesh.

Unidirectional fabrics
A unidirectional fabric (UD) is one in which the majority of fibres run in one direction only. Their weave patterns are designed for directional strength in one direction only [60]. True unidirectional fabrics offer the ability to place fibres in the component exactly where it is required, and in optimal quantities. UD fibres are also straight and uncrimped. This results in the highest possible fibre properties from a fabric in composite component construction. For mechanical properties, unidirectional fabrics can only be improved on by pre-impregnated unidirectional tape, where there is no secondary material at all holding the unidirectional fibres in place. Prepreg materials have their fibres impregnated with resin under carefully controlled conditions. In these prepreg products only the resin system holds the fibres in place.

The surface quality of a unidirectional fabric is determined by two main factors: the combination of “Tex” and “thread count” of the primary fibre and the amount and type of the secondary fibre [61]. A Tex is a unit for expressing linear density equal to the mass or weight in grams of 1000 metres of filament, fibre or yarn. The drape surface smoothness and stability of a fabric are controlled primarily by the construction style; while the area weight, porosity and (to a lesser degree) wet out are determined by selecting the appropriate combination of fibre tex and number of fibres per metre square.
2.1.1.2 Discontinuous fibres

Discontinuous fibres are mainly associated with sheet moulding compound\(^3\) or wet layup. Discontinuous reinforcements are versatile in their properties and they have relatively low manufacturing costs [62, 63]. Low mechanical performance typically restricts discontinuous fibre reinforcements to cosmetic or non-structural applications. The aims of the discontinuous fibre group are to refine processes for non-woven textiles, focusing on improved mechanical properties, better repeatability, and accurate computational modelling.

2.1.2 Matrix materials

During the manufacturing process, the matrix undergoes a series of complex physical and chemical processes with the reinforced material forming a body with a predetermined shape. The matrix is the essential homogeneous material in which a fibre system or reinforcement particles/whiskers of a composite are embedded.

Although the high strength of composites is due to the fibre reinforcement, the matrix material provides support for the fibres and assists them in carrying the loads. The matrix causes the stress during the various manufacturing steps to be distributed more evenly between all fibres by causing the fibres to undergo the same strain in both the fibres and matrix [64, 65].

The stress is transmitted by shear process, which requires good bonding between fibre and matrix and also high shear strength and modulus for the matrix itself [66]. When too much resin is used, the layup process is classified as “resin rich”. On the other hand, if there is too little resin, the lay is referred to as “resin starved”. A resin rich final part is more susceptible to cracking due to lack of fibre support, whereas a resin starved part is weaker because of void areas and the fact that fibres are not held together, hence not well supported.

\(^3\) moulding compound often used for larger parts where mechanical strength higher than parts made from Bulk moulding compound is required
One of the important properties of cured matrix systems is their glass transition temperature ($T_g$) at which point the matrix begins to soften and exhibits a reduction in mechanical properties.

This property will be extensively described in section 2.1.2.1; Page 48.

A matrix material fulfils several functions in a composite structure including low moisture absorption, low shrinkage, a low coefficient of thermal expansion (CTE)\(^4\), providing good flow characteristics (for the reinforcements to be wetted throughout and eliminate voids during the compacting/curing process), providing a good surface finish, elastic quality to transfer load to fibres (which provides rigidity and shape to the structure), strength at high/low temperatures, providing protection to reinforcing materials against chemical attacks and mechanical damages. Matrix materials come in different forms, with polymeric resins being the ones most widely used. There are two types of reactions that can be used to create all modern polymers: poly-condensation and poly-addition.

In poly-condensation, the polymer molecules are formed by reaction between monomers which each have two or more reactive groups. It is a characteristic of polycondensation reactions that low molecular weight compounds are eliminated during polymerisation [68]. Poly-addition is marked by a gradual process involving monomers having at least two reactive groups. An example of polyaddition is the formation of polyurethane plastics from a monomer having at least two isocyanate ($-\text{NCO}$) groups and a monomer having at least two alcohol groups ($-\text{OH}$) [69].

Polymeric resins exist in two forms: thermoplastics and thermosets. Thermosets undergo an irreversible chemical change when they are heated, this is their most characteristic property. At room temperature, the resin starts as a viscous liquid, which changes to a rigid solid molecular network once a hardener is applied to it. When cooled to its original temperature, the resin is a completely modified material which remains solid. The reactions are irreversible.

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\(^4\) Polymers are generally considered to have a nearly constant thermal expansion rate as a function of temperature over their entire usable temperature range. This allows for an approximation of a single value rate of polymers expansion rate as a function of temperature 67. Daniels, C.A., *Polymers: structure and properties*. 1989, Lancaster (Pa.): Technomic.
Resin thermosets have been used for many years as matrices for composite materials. They have excellent mechanical properties and good chemical resistance. They also have fairly good impregnation, excellent processing temperatures and low melt viscosity. Their mechanical properties depend on the molecular units making up the network, the length and density of the cross links. Thermosets are normally regarded as brittle solids. Their brittleness in uniaxial tensile tests is due in part to their manufacturing processes.

Table 2-1, page 47 shows a classification of thermosets, thermoplastics and elastomers.

Thermoplastics are either amorphous (without a regular structure) or semi-crystalline (amorphous with regular substructures), (Figure 2-10). In general, an amorphous polymer is transparent and less resistant to a semi-crystalline polymer. A thermoplastic becomes a homogeneous liquid when heated which hardens when cooled, making it an accessible material to manufacture parts into any given shape. When frozen, a thermoplastic becomes glass-like and subject to fracture. Thermoplastics can therefore be reheated, reshaped and frozen repeatedly. This quality makes thermoplastics recyclable [70-72].

![Discontinuous](image)

**Figure 2-10: Schematic of the molecular structure of thermoplastics.**

*An amorphous thermoplastic is represented on the left and a semi-crystalline thermoplastic is represented on the right*
<table>
<thead>
<tr>
<th>Derivatives of natural products</th>
<th>Polyaddition resins</th>
<th>Polycondensation resins</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Naturally occurring resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Rosin</td>
<td>- Polyethylene (PE)</td>
<td>- Phenol-formaldehyde</td>
</tr>
<tr>
<td>- Shellac</td>
<td>- Polypropylene (PP)</td>
<td>- Resorcinol-formaldehyde</td>
</tr>
<tr>
<td>- Lignin</td>
<td>- Polybutylene (PB)</td>
<td></td>
</tr>
<tr>
<td>Derivative of cellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Cellulose esters</td>
<td>5. Polyvinyls</td>
<td>13. Aminoplastics</td>
</tr>
<tr>
<td>- Cellulose acetate (CA)</td>
<td>- Polyvinyl ethers</td>
<td>- Urea-formaldehyde</td>
</tr>
<tr>
<td>- Cellulose propionate (CP)</td>
<td>- Dipolyvinyls</td>
<td>- Melamine-formaldehyde</td>
</tr>
<tr>
<td>- Cellulose acetobutyrate (CAB)</td>
<td>- Polyvinyl chloride (PVC)</td>
<td>- Melamine-phenolics</td>
</tr>
<tr>
<td>- Cellulose acetopropionate (CAP)</td>
<td>- Polyvinyl fluoride (PVF)</td>
<td></td>
</tr>
<tr>
<td>- Cellulose nitrate (CN)</td>
<td>- Chlorinated polyvinyl chloride (CPVC)</td>
<td>- Phenol-furfural</td>
</tr>
<tr>
<td>2.2 Cellulose ethers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Methyl cellulose (MC)</td>
<td>6. Polyvinylidene</td>
<td>15. Polymers</td>
</tr>
<tr>
<td>- Ethyl cellulose (EC)</td>
<td>- Polyvinylidene chloride (PVDC)</td>
<td>- Alkyd resins</td>
</tr>
<tr>
<td>- Carboxymethyl cellulose (CMC)</td>
<td>- Polyvinylidene fluoride (PVDF)</td>
<td>- Polycarbonates (PC)</td>
</tr>
<tr>
<td>2.3 Regenerated cellulose</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>- Polyvinyl alcohol (PVA)</td>
<td>- Polyformaldehydes</td>
</tr>
<tr>
<td></td>
<td>- Polyacetal (PAc)</td>
<td>- Polyglycols</td>
</tr>
<tr>
<td>3. Derivatives of vegetal proteins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Caseine-formaldehyde</td>
<td>8. Styrenes</td>
<td>17. Polyurethanes (PU)</td>
</tr>
<tr>
<td>- Zein-formaldehyde</td>
<td>- Polystyrene (PS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Acrylonitrile-butadiene-styrene (ABS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Styrene-acrylonitrile (SAN)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Styrene-butadiene</td>
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<tr>
<td></td>
<td>- Polytetrafluoroethylene (PTFE)</td>
<td>19. Polymers (PI)</td>
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<tr>
<td></td>
<td>- Polytrichlorofluorooxyethylene (PTCFE)</td>
<td>20. Polyanides (PAR)</td>
</tr>
<tr>
<td></td>
<td>- Fluorinated ethylene propylene (FEP)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Perfluorooctoxy (PFA)</td>
<td></td>
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<tr>
<td></td>
<td>- Ethyleneetrafluorooxyethylene (ETFE)</td>
<td></td>
</tr>
<tr>
<td>10. Acrylics</td>
<td>11. Coumarone-Indenes</td>
<td>22. Epoxy resins</td>
</tr>
<tr>
<td></td>
<td>- Polymethylmethacrylate (PMMA)</td>
<td></td>
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<tr>
<td>12. Phenolics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. Aminoplastics</td>
<td></td>
<td></td>
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<tr>
<td>14. Furan resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. Polymers</td>
<td></td>
<td></td>
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<tr>
<td>16. Polyethers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17. Polyurethanes (PU)</td>
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<td></td>
</tr>
</tbody>
</table>
2.1.2.1 Glass transition temperature

The glass transition temperature is a transition which happens to the amorphous portion of a semi-crystalline solid. That is, polymers whose chains are not arranged in ordered crystals, but have random directions, even though they are in a solid state (Figure 2-10). The crystalline portion remains crystalline during the glass transition. At this point the mechanical properties of the polymer change from those of a rubber (elastic) to those of a glass (brittle, hard, rigid) [70]. The Young’s modulus (E) is a fundamental measure of the stiffness of a material [71]. The higher the value, the more resistant the material will be.

Melting is a transition which occurs in crystalline polymers. The melting point temperature (Tm) is the temperature at which crystalline order is completely destroyed on heating. At the melting point, Tm, there occurs a thermodynamic phase transformation and the material assumes an orderly crystalline structure [72]. Polymers show a range of temperatures over which crystallinity vanishes. By decreasing the temperature of a polymer which is in its molten state, the polymer reaches the glass transition temperature (Tg). A decrease in thermal vibration leads the molecules in the polymer to contract, which leads to a reduction in free space. Molecular movement is too sluggish or the geometry too awkward to take up a crystalline conformation. Therefore the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. Figure 2-11 shows the relationship between temperature and E for a polymer.
Figure 2-11: Behaviour of polymers as a function of temperature

A given polymer sample does not have a unique value of $T_g$ because the glass phase is not at equilibrium. The measured value of $T_g$ will depend on the molecular weight of the polymer, on its thermal history, age and on the rate of heating or cooling [73, 74].

Figure 2-12 shows specific volume (volume/unit mass) vs. Temperature curves for amorphous semi-crystalline, crystalline and liquid polymers [75].

Young’s modulus $E$ is written as:

$$\Sigma = E \varepsilon$$

$\Sigma$ = Tensile stress, $\varepsilon$ = Tensile strain
When temperature is applied to semi crystalline polymers, their molecular structure do not gradually soften with increasing temperature. Their molecules remain ordered in fixed position before rapidly starting to move in the material. Semi-crystalline materials remain solid until a given quantity of heat is absorbed and then rapidly change into a low viscosity liquid. The following physical properties undergo a drastic change at the glass transition temperature of any polymer: hardness, volume, modulus (Young’s module), elongation-to-break percentage.

2.1.2.2 Matrix resins of composites
Matrix materials come in different forms. Polymeric resins are found to be the ones that are most widely used. There are two types of reactions that can be used to create all modern polymers: poly-condensation and poly-addition. Polymeric resins exist in two forms: thermoplastics and thermoplastics. Thermosetting resins include epoxy resin, unsaturated polyester resin, phenolic resin, and thermoplastic resins include polyamide, polyimide, polyester and others.
2.1.2.2.1 Epoxy

As mentioned above (section 2.1.2; Matrix materials; page 44), thermoset composites matrix materials belong to a vast family which include polyesters, vinyl esters, epoxies, bismaleimides, cyanates esters, polyamides and phenolics. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation [76]. They are the most common matrix material for high performance composites and adhesives. They present excellent combinations of strength, adhesion, low shrinkage and processing versatility. They are now widely used as high-performance thermosetting resins in several industrial applications.

An epoxide group (oxirene ring) consists of one oxygen and two carbon atoms arranged in a ring Figure 2-13. Often, the epoxide group contain another carbon atom and is then referred to as a glycidyl group.

![Figure 2-13: Epoxide network structure](image)

![Figure 2-14: Epoxy and Glycidyl groups](image)
The most common epoxy is based on the condensation polymerisation of epichlorohydrin (Figure 2-15) and bisphenol-A (Figure 2-16), creating diglycidyl ether of bisphenol-A epoxy (DGEBA or BADGE) Figure 2-17.

![Figure 2-15: Epichlorohydrin](image)

![Figure 2-16: Bisphenol-A](image)

![Figure 2-17: Diglycidyl ether of bisphenol-A epoxy](image)

DGEBA is a difunctional epoxy (two epoxy end-groups that can react) that can be either a solid or a liquid and is available as a liquid at several viscosities. The properties of the DGEBA resins depend on the value of $n$, which is the number of repeating units commonly known as degree of polymerisation. The number of repeating units depends on the stoichiometry of synthesis reaction. In a stoichiometry system, the ratio of resin: hardener is in the range 1:0.01 - 1:1 by volume, and depends on the particular chemical groups involved. Typically, $n$ ranges from 0 to 25 in many commercial products [77-79].
If the repeat unit \( n \) is between 0.1 and 0.2, DGEBA is a liquid with a viscosity in the range of 6000 to 16000 cP. As \( n \) approaches 2, it becomes a solid [80]. For \( n \) values greater than 2, it is not useful as a matrix because the cross-link density becomes low. Crosslinking is accompanied by evolution of heat "exotherm" of between 200\( \text{J/g} \) and 500\( \text{J/g} \) and volume shrinkage of up to 15% [81].

The other most common epoxy found in industry is known as tetracyclic 4, 4" -diaminodiphenylmethane (TGGDM) also known as tetracyclic methylene dianiline (TGMDA). It is the base resin used in the majority of commercial epoxy matrix systems. Its high functionality provides highly cross-linked structures that exhibit strength, rigidity and elevated temperature resistance. It is important to note that functionality has got nothing to do with reactivity. Functionality is a simple description of what a chain looks like.

Under certain circumstances, an epoxide group will react with various agent groups. These are known as curing agents or hardeners. In order to convert epoxy resins into hard, infusible, and rigid materials, it is necessary to cure the resin with a hardener. The result is a highly cross-linked three dimensional network, Figure 2-18.

*Figure 2-18: A typical epoxy molecule (top) and amine hardeners (bottom)*
Epoxy resins cure rapidly from 5-150°C depending on the choice of curing agents. These are frequently added to improve processability (by reducing viscosity), elevated temperature performance or other properties of the cured resin system. Amine-based phenols and novalacs (containing multiple epoxide groups) are widely used for curing of epoxy resins. The former are highly reactive with epoxides and are generally used as catalysts, commonly known as accelerators for cure reactions; the latter give excellent adhesion, strength, chemical and flame resistance. The degree of cross linking is measured in $(\alpha)$. If $\alpha = 1$, all the groups have reacted. If $\alpha < 1$, there are some functional groups that remain.

2.2 Preimpregnated fabrics

Prepregs are reinforcement fibres or fabrics into which a pre-catalysed resin system has been impregnated by a machine. One of the most important aspects of composite manufacturing concerns impregnation of the reinforcement. This can present further complications if the matrix is highly viscous. The resin systems in these materials react only very slowly at room temperature, giving rise to working times of many days to several months. The prepreg resins can only be fully cured by heating them to the prescribed cure temperature. The manufacturing of prepreg is schematised in Figure 2-19.

![Schematic of a prepreg material](image)
Dry lamina or plies to which resin mixed with its hardener is applied, (wetting) are partially cooked in an autoclave at high temperature. The resin is slightly cross-linked by going through a heat cure for a short period of time, and then cooled to prevent complete polymerisation of the system [82].

The resin at this stage is in a solid form, partially cured (typically less 10%) but still available for bonding parts together. This is referred to as a B-stage resin.

Prepregs are available in several forms depending on reinforcements and matrices. Commercially, they are available in a range of widths from 20 mm (tape) to 300 mm. They are supplied on rolls in lengths of up to 250 m between moisture films (typically aluminium foil). Prepreg rowings and tapes are normally used in automated processes such as filament winding, while unidirectional tape and prepregs fabrics are used for both autoclave and OOA processes. Unidirectional prepreg tapes offer improved structural proprieties over woven fabrics due to the absence of fibre crimp and the ability to more easily tailor the designs. However, woven prepregs offer increased drapability. Prepregs are labelled according to the convention outlined below (Figure 2-20) is an example of prepreg labelling

![Prepreg labelling diagram](image)

**Figure 2-20: Prepreg labelling**

Trade name: Fibredux

Fibre type C=Carbon; G=Glass; K=Kevlar (aramid)

Fibre Grade
- E = E-glass; R = R-glass; 49 = Kevlar (aramid)
- T= high tensile strength carbon
- M = high modulus carbon

Cured ply thickness in thousands of an inch (mil). 1 mil = 6

Surface treated fibre = S - applies only to carbon

Nominal resin content (% by weight) = 44
During design stages (lay-up), unidirectional prepregs generally require placement of more individual plies. Indeed, to design a simple cloth for instance, for each 0° ply in the layup, a 90° ply must be placed onto the design tool. To prevent the resin from curing, prepregs are generally stored at temperatures below (-18°C) which give them a shelf life between 6-12 months. At room temperature, the shelf life of a B-staged prepreg is in the order of days and the desirable stickiness or tack is gradually lost as crosslinking continues.

Prepregs are supplied with either a net resin (prepreg resin content = final part resin content) or excess resin (prepreg resin content > final part resin content).

Using an excess resin prepreg during design improves the removal of entrapped air when the matrix flows through the plies (during manufacturing, moderate heating of prepregs results in the B-staged resin melting before further heating results in complete crosslinking) while the extra resin is removed by impregnating bleeder plies on top of the lay-up. The amount of bleeder used in the lay-up will dictate the final fibre and resin content. A major advantage of using prepregs with net resin content during design is the ability offered to designers to easily control the fibre and resin volumes; however, void contents may be higher due to the fact that excess does not flow through the part, removing the entrapped air. Prepreg manufacturing using machinery under well controlled conditions has resulted in prepregs having low void content and reasonably uniform fibre distribution. These significant advantages require higher costs.

One of the best known thermoplastic prepregs is made from the combination of polyether ether ketone (PEEK) containing 65% by volume of continuous unidirectional carbon fibre known as Advanced Polymer Composite (APC-2). APC-2 is manufactured continuously by a modified pultrusion process [83]. Another type of thermoplastic prepreg is known generically as Glass Mat filled Thermoplastic (GMT) and consists of a chopped strand glass mat wetted by and sandwiched between layers of thermoplastics such as polypropylene or nylon-6 [84, 85]. APC-2 type materials are intended for aerospace use, while GMT and discrete fibre prepregs are directed towards the automotive industry for the manufacture of various load bearing components by hot stamping [86]. The main market for GMT is automotive body panels and other large area mouldings for the automotive industry.
The most recent thermoplastics based materials are known as discrete fibre prepregs which are manufactured by a proprietary paper-making process. Discrete fibre prepregs provide a greater degree of flow in moulding than GMT prepregs.

The benefits of OOA prepregs are their potential to reduce high capital and operating costs. Earlier prepregs were cheaper because they cure at lower temperatures under vacuum pressure, but they had neither the mechanical properties nor the sufficiently short cycle times necessary for production parts. The first generation of OOA VBO materials included Advanced Composites Group’s LTM series. By 2005-2006, the properties of two OOA prepreg systems: ACG’s MTM45 and Cytec Engineered Materials’ CYCOM 5215, were approaching those of autoclave-cured prepregs. Both prepregs feature flexible cure cycles, requiring longer cure times between 66°C to 79°C but providing shorter cycles at 121°C [87, 88]
CHAPTER III

3 MANUFACTURING PROCESSES OF ADVANCED COMPOSITES

3.1 Autoclave manufacturing

Autoclave manufacturing has been used for decades in the design of advanced composites materials. It is the exclusive preserve of high performance composites based on prepregs. High performance composites are designed to the limit of performance of the resins and fibres used in their construction. Autoclave manufacturing process is based on the principle of differential gas pressure. For large components, autoclave moulding is almost universal where double curvatures and the highest quality moulding are specified [89, 90].

An autoclave consists of a cylindrical chamber which can be evacuated and/or pressurised and through which heated gas can be passed. It is also equipped with the means of producing a vacuum within any airtight membranes placed within the vessel, so that volatile matter such as solvents or water vapour can be removed, (Figure 3-1) page 59. The device may also incorporate radiative heat sources which can be controlled externally.

The process of manufacture starts with the cutting of the fabric (e.g., prepreg, woven glass etc) to fit the required mould. For individual fabrics, this is done with a scalpel or a sharp 'pastry cutter' die of the appropriate shape. When greater productivity is required a series of shapes can be cut from stacks of fabrics. Various techniques for cutting fabrics have been evaluated; water jet cutting provides clean edges but since many fabrics absorb water, this is not commonly used. Laser cutting can cause premature crosslinking along the cut edge and tends to be used only for 'rough cutting' of blanks which are subsequently trimmed. Jigsaws are used only if adequate dust extraction is provided.
Once the layup has been done, it is placed against a mould surface and backed with a porous film, parting agent and a "bleeder layer" of glass fibre cloth or glass fibre paper. This allows excess resin which escapes from the moulding to be absorbed. Outside the "bleeder layer" is the pressure blanket which transfers pressure from the interior of the autoclave to the lay up within.

![Figure 3-1: Schematic of an autoclave](image)

A typical moulding cycle would be as follow [91]:

1. the vacuum is applied and the temperature is allowed to rise
2. a lapse of time is allowed at constant temperature to allow resin flow with little cure
3. pressure is applied and the temperature allowed to rise, gelation occurs within the hour
4. temperature and pressure are maintained constant to the end of the cure, usually 2-3 hours
5. heating is turned off and the moulding is allowed to cool to room temperature, some pressure is maintained during the cooling phase

Because of the expense of autoclave moulding and the slow cycle times imposed by indirect heating (up to 36 hours), efforts have been made to simplify the procedure and various alternative methods have been designed which, depending on the end products, have their own advantages.
3.2 Out of autoclave manufacturing

In the aerospace industry, most of the manufacturing processes involve autoclave moulding. A manufacturing process requires high capital investment, a lot of space as well as long turn around and long cycle times. Trying to find a solution to the many issues autoclave manufacturing present, engineers and designers have developed alternatives such as quickstep and tape laying. These processes are still expensive and are still only used to manufacture large advanced composites using materials such as carbon fibre. Traditional manufacturing processes such as Resin Transfer Moulding (RTM) or Vacuum Forming can be re-designed to allow for the manufacture of small advanced composites components.

Recently, a new generation of out-of-autoclave prepregs has been introduced. Experience with these prepregs has demonstrated that it is possible to produce autoclave-quality parts using vacuum bag-only (VBO) consolidation.

The first and most important steps in the design process are to define clearly the purpose of the resulting product and to identify the service environment, and then the identification of suitable materials can be carried out. The following are generally regarded as the most important characteristics requiring consideration for most engineering components: mechanical proprieties (strength, stiffness, fatigue and toughness, specific strength and stiffness and temperature), corrosion susceptibility and degradation, special properties (thermal, electrical etc), wear resistance and friction properties, methods of fabrication and total cost.

There are still real constraints inhibiting the application of composites to more sensitive components. One problem is the difficulty in the analysis of composite components. The methodology lacks the maturity of that for conventional metal structures. Some of the more sensitive components, particularly those in rotating systems, will require an understanding of fatigue. A modern engine can be expected to remain in service for more than 30 years, thus ageing of both the material and the adhesives must be understood. Aspects such as fire containment and impact tolerance still require further study.
Manufacturing and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

Early-generation of composite parts made from prepregs were designed for low-temperature initial cure (below 80°C) followed by high-temperature postcure, and intended for low quality load-limited structures [92, 93].

For the past decade, advanced composite parts, made from carbon fibre and epoxy or polyimide resins have been used for elements of aircraft construction. This has followed decades of intensive modelling, analysis and experimental measurements, all of which have established robust design data for these materials. In addition, manufacture of these materials has been predicated on the elimination of voids and the minimisation of residual stresses both of which criteria are implicit in the design data.

These manufacturing requirements impose the use of prepregs. Prepregs ensure that each ply in a lay-up is free from voids; their manufacturing process ensures elimination of inter-ply voids, and minimises residual stresses by reducing temperature excursions, and hence crosslink density variations within the material as a result of the crosslinking isotherm. These criteria are met by using an autoclave process which incorporates carefully prescribed temperature and pressure ramps, as well as holding periods during the cure cycle. The penalty for this rigour is cycle times in the range 24-36 hours. For large components and relatively small production runs this is acceptable given the acknowledged value of the product.

As the aerospace timescale requirements are shortening, an increase in production rates is required; this is difficult to achieve with traditional autoclave manufacturing. Also, high capital expenditure, infrastructure requirements and time to commission has made autoclave processing increasingly undesirable. These limitations for autoclave processing provide the motivation to research more economical and/or quicker alternative fabrication routes for composites. Several processing methods have been reported in the past and out of them Resin Transfer Moulding (RTM), Resin Infusion (RI), Quickstep and many more are constantly being investigated and improved. Among them, traditional processes such as hand layup, vacuum forming and pultrusion are also being scrutinised by engineers and designers in the industry.
Over the past few years, the aircraft industry has had to trim costs consistent with market forces. In addition, the prospect of making unmanned aerial vehicles (UAVs) has posed the challenge that these will be made in quantities that far exceed the current demand for conventional aircrafts. Taken together, the industry is seeking to make aircraft components including those made from fibre reinforced composites considerably faster than before. In fact, the aim is to make an advanced composite in a cycle time closer to 20 minutes than 24 hours [94-97].

This has resulted in the industry examining a range of so-called "Out-of-Autoclave" (OOA) processes that include variants of resin transfer moulding (RTM), resin infusion (RI) and the Quickstep process.

3.2.1 Quick step

The Quickstep Process involves a unique fluid-filled, balanced pressure, heated floating mould technology for the curing, partial curing and joining of composite materials. It works by rapidly applying heat to the laminate which is trapped between a free floating rigid (or semi-rigid) mould that floats in a Heat Transfer Fluid (HTF). The mould and laminate are separated from the circulating HTF by a flexible membrane or bladder. The temperature and pressure of the HTF behind the mould and flexible membrane stay the same Figure 3-2.
The quickstep process uses balanced pressure, combined with vibration within the HTF and vacuum on the laminate, to remove the air and then compact and heat the laminate to cure the part. A flexible membrane beneath the mould is bonded into a pressure chamber creating the lower half of a ‘clam-shell’ like mould set. A second flexible membrane is bonded to a separate pressure chamber creating the upper half of the clam-shell. These HTF filled pressure chambers are clamped together during processing. This permits the laminate to be compressed while the mould is not subject to any distortion or stress as it is floating in a balanced pressure/force environment within the HTF. The use of fluid to control temperature offers several advantages, including:

- Up to 25 times the heat transfer rate of gas systems like autoclave, resulting in shorter cycle times
- Improved control of component temperature
- Rapid decrease in fabric (e.g. prepreg) resin viscosity, resulting in improved fibre wetting and laminate consolidation without high pressures
- The ability to change temperature quickly, permitting more accurate injection temperatures
- Reduced exotherm risk as liquid carries away the heat of reaction more efficiently than air or nitrogen
The Quickstep Process can use thermoset and certain thermoplastic prepregs as well as wet resin/dry fibre to produce superior composite parts [98].

3.2.2 Tape laying

Tape laying is a manufacturing process commonly used in the aerospace industry to make large flat parts such as wing skins. A typical tape layer machine consist of a large floor mounted with parallel rails, a cross feed bar that moves on precision ground ways, a ram bar that raises and lowers to the delivery head, and the delivery head that is attached to the lower end of the ram bar.

Optical sensors are present on the head and these detect flaws during the tape laying process and send appropriate signals to the operator. The head usually contains a hot air system that will preheat the tape to a certain temperature to improve the tack and tape to tape adhesion. Computer controlled valves maintain the temperature in proportion to the machine speed. Modern machines are programmed offline, with systems that automatically compute the path for tape laying over a contoured surface [99].

Prepregs have found extensive usage in tape laying. A tape laying process generally consists of laying down three, six or twelve inch unidirectional tapes, depending on whether the application is for flat structure or mildly contoured structure. Processes such as hand layup, or filament winding are normally used to make more highly contoured parts depending on the geometry and complexity of the part.

The materials required for tape laying come in large diameter spools, some containing almost 1K linear of material. The tape contains a backing paper that must be removed during the tape laying operation. The spool of material is loaded onto the delivery head and threaded through the upper tape guide shoot and paste cutters. The material then passes though the lower tape guides under the compaction shoe and onto a backing tape. Backing paper is separated from the material and wound onto a take up roller. The compaction shoe makes contact with the tool surface and the material is laid onto the tool with compaction pressure.
To insure uniform pressure, the shoe is segmented so that it follows the contour of the layup. The segmented compaction shoe is a series of plates that are air pressurised and conform to lay up surface deviations, maintaining a uniform compaction pressure.

3.2.3 Resin infusion

Resin infusion (also referred to in the industry as vacuum infusion) is a manufacturing process where dry reinforcement is stacked in a mould under a vacuum bag that draws resin into the stack. One of the most difficult aspects of resin infusion is maintaining a vacuum within the assembly before the resin is introduced. Once a complete vacuum is achieved, resin is literally sucked into the laminate via carefully placed tubing.

High quality composite parts made from a wide range of fibre and resin combinations can be utilised to infuse laminates up to 150 mm thick [100, 101]. The resin distribution over the whole laminate is aided by resin flowing easily through the non-structural fabric, and wetting the fabric out from above. Moulds used for infusion need to have larger flange areas to accommodate sealing of the vacuum bag perimeter. The keys to a resin infusion process are to understand the compaction and permeability of the material to be infused and the kinetics and viscosity of the resin system.

Resin infusion provides a number of improvements over traditionally vacuum bagged parts. A typical hand lay-up usually results in excess of 100% fabric weight by resin; resin alone is very brittle, so any excess will actually weaken the part. With resin infusion this number is significantly reduced.

Other improvements over traditional manufacturing processes (e.g. hand layup) include decrease in wasted resin, consistency in resin usage, unlimited set-up time and a cleaner process. Typical resins used are polyester, vinyl ester, and epoxy with many being UV cure initiated. This process can routinely produce parts as large as 186 m$^2$ such as boat hulls, bus bodies, and railcar panels. This process adds benefits, such as eliminating weaker secondary bonds and reducing volatile organic compounds (VOC) emissions. A resin infusion set up is illustrated in Figure 3-3; see page 66.
Figure 3.3: Typical resin infusion layup.

Figure 3.3 shows a schematic view of the process as a whole and the bottom image gives a detailed account of the materials used in the mould layup process.
3.2.4 Vacuum bagging

Vacuum bagging is typically used for manufacturing prepreg parts. Prepregs are already B-staged, therefore not requiring additional resin in the form of an infusion.

The steps required for vacuum bagging are:

- Cut the prepreg plies in the required shaped by machining or by hand, this depends on the design requirements
- Clean the chosen mould with a mould cleaner\(^5\), and a release agent\(^6\)
- Place the prepreg plies on top of the mould following the chosen layup or plybook
- Apply a release film on top of the layup. For prepregs, the release film is perforated to allow entrapped air, excess resin and volatiles to escape.
- Apply a peel ply on the top of release film. The peel ply absorbs moisture and excess resin from the layup
- At this stage, a barrier film can be applied on top of the peel ply. It’s role is similar to a release film except that it is not perforated or porous
- Apply a breather cloth on top of peel ply or the barrier depending of the layup. A barrier film between the peel ply and the breather cloth, any absorbs moisture and excess resin are contained. The breather cloth is porous. It creates even pressure around the part and also allow air and volatiles to escape
- Place a hose connector onto the breather cloth, preferably not on top the layup
- Apply vacuum bag and seal all sides of the mould by using a seal tape. The seal tape sticks to both the mould and the vacuum bag. A small hole is made on the vacuum bag, to accommodate the hose connector’s head, which is connected to a vacuum
- Connect a vacuum tubing between the bag hose connector and the vacuum hose
- Place a two way shut-off valve onto the vacuum tubing, to control vacuum pressure by limiting air flow; also place a vacuum gauge on the tubing to measure vacuum pressure

\(^5\) Blend of solvents, designed to dissolve and clean mould surface contamination such as wax, dirt, oil and grease
\(^6\) Blend of semi-permanent release agents; provides exceptional sealing and release properties over a huge range of resins and mould materials
According to different pressure methods, the cure process of vacuum bagging is done either in an oven or an autoclave. Figure 3-5, page 68, shows the process flow chart of pressure bag moulding.
3.2.4.1 Resin transfer moulding

Resin transfer moulding (RTM) is a low pressure closed moulding process for moderate volume production quantities. In RTM, continuous strand mats and woven reinforcements are laid up as a dry stack of materials. These fabrics are sometimes pre-pressed to the mould shape, and held together by a binder, these 'Preforms' are then more easily laid onto the mould tool. Preformed glass reinforcements are often used for complex mould shapes. A second mould tool is then clamped over the first, and a low viscosity catalysed resin is pumped in, displacing the air through strategically located vents [102].

Metered mixing equipment is used to control resin/catalyst ratios that are mixed through a motionless/static mixer and injected into the mould port; common matrix resins include polyester, vinyl ester, epoxy, and phenolics. Vacuum can also be applied to the mould cavity to assist resin in being drawn into the fabrics; this is known as Vacuum Assisted Resin Injection (VARI) [103]. Once all the fabric is wet out, the resin inlets are closed, and the laminate is allowed to cure. Both injection and cure can take place at either ambient or elevated temperature.

For optimum surface finish, a gel coat can be applied to the mould surface prior to moulding. High quality parts produced by this method include automotive body parts, bathtubs, and containers.

3.2.5 Pultrusion

Pultrusion is the only continuous process for the manufacture of a profile such as an I-beam, channel section, tube, etc., from a fibre reinforced thermosetting resin. Glass reinforcements, such as unidirectional rowings or multi-directional glass fibre mat, are guided through a liquid resin bath to thoroughly wet every fibre. The reinforcements are then guided and formed, or shaped, into the profile to be produced before entering a die. Profiles must have a constant cross section along their length. Profile sizes ranges from 5mm$^2$ to 0.5m$^2$ [104, 105]. As the material progresses through the heated die, which is shaped to match the design profile, the resin changes from a liquid to a gel, and finally, into a cured, rigid plastic. A pulling device grips the cured material and literally pulls the material through the die, hence the name pultrusion.
3.3 Defects in composite during manufacturing

Composites forming processes are divided into three stages [106]: the first stage is the preparation of semi-product materials such as prepregs; the second stage is that of the preforming of reinforced materials which gets a preform to the shape of the mould and finally the last stage is concerned with curing of composites. As long as compounding of resin and fibre, impregnation, curing and moulding are well accomplished during the manufacturing process all stages can be done together or separately according to different techniques. The forming processes can be carried out using a wet or dry method.

![Figure 3-6: typical technical flow chart of composites processing](image)

The advantages of using a dry method over a wet method process are:

- Low void content
- Control of fibre volume fraction
- Control of laminate thickness
- Better conformity and quality
- Cleaner process
For curved complex parts, autoclave manufacturing costs can be high and the process is unsuitable for large parts. In the aerospace industry for example, in order to build large composite structures, such as wings or fuselage, smaller parts are manufactured independently and then assembled. OOA processes used to manufacture prepreg composites are many but only a few are closing the gap necessary to make final quality parts as high than those seen in autoclave manufacturing. Successful OOA processes require understanding of all the manufacturing parameters to achieve high quality parts finish.

G. Fernlund [107] proposed the concept that there were two distinctive parameters to consider during a forming process. The first parameter is an intrinsic parameter, related to the resin’s cure cycle, the resin’s shrinkage, and thermal expansions. The second parameter is referred to as an extrinsic parameter where the mould material, the mould surface and the bagging arrangement are important. Both intrinsic and extrinsic parameters act in parallel and superpose each other. However, depending on the part’s shape, one effect is dominant. For example, the fabrication of flat laminates using metallic moulds is mainly affected by the mould-part interaction which is an extrinsic effect while the intrinsic effects (mainly warpage deformations) are negligible. Conversely, deformations of curved shapes are mostly driven by intrinsic effects which are induced by the resin’s high coefficient of thermal expansion (CTE) and the shrinkage due to the ongoing curing process. Besides, the parameters to consider during forming processes, factors such as sharp corners, thickness variations and highly viscous matrices all contribute to the mechanics of the part being manufactured.

Although the deformation behaviour of unidirectional prepregs exhibit a similar global deformation behaviour to woven prepregs, their local deformation is very different from the latter. Unidirectional prepregs are mostly preferred to their woven pair as the primer can offer a possibility of increased drapability; this is due to the lack of fixed kinematic link between tow. Unidirectional prepregs have heavy yarns in the wrap direction and very light yarns in the weft direction. The light yarns in the weft direction hold the primary fibres in position, whilst other fibres may also offer some structural support.
Over the years, initial work on out-of-autoclave prepregs deformation on complex moulds has been performed by prepreg manufacturers and their industrial partners. However, research in an industrial context is often only selectively published because of intellectual property considerations. Much research has been carried out recognising that regardless of the reinforcement fibre orientation, manufacturing of a carbon prepreg composite part is much affected during its forming process by its deformation and failure modes. Successful forming of the part depends on deformation modes taking place and undesired failure modes being suppressed. These modes are derived from thermoplastic sheet forming. From the literature; the same modes are likely to occur when forming thermoset prepreg parts [108-110].

To measure intraply and interply shear, two types of tests are frequently used, the picture frame test for the former and the pull-out test for the latter. The picture frame test is based on a method where a square frame deformed into a parallelogram, thus imposing a shear deformation on the material. The shear deformation allow for the determination of four critical material parameters known as the pre- and post-locking shear modulus, the locking angle and the intraply shear viscosity of the fabric. They are measured above the melt temperature of the polymer matrix and during cooling. The picture frame method has been extensively used to characterise intraply shear. In the picture frame, two diagonally opposite corners of the picture frame with a fabric mounted on it are pulled apart at a constant rate in a tensile testing machine. If it is assumed that the fabric is inextensible in the two fibre directions, there is only in-plane shear before wrinkling starts.
Characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

Figure 3-7: Schematic deformation of a woven fabric

In the picture frame experiment: initial configuration (a), imposing left shear (b), imposing right shear (c)

Displacement of the tensile testing machine causes the frame to shear. The frame deforms at a constant velocity. The fabric displacement can be expressed in terms of the frame deformation displacement and velocity, Figure 3-8.

Before deformation

After deformation

Figure 3-8: Schematic view on half of a mounted fabric on a picture frame.

Fabric on a picture frame before and after deformation. Where $\alpha_0$ is the initial frame angle $l_f$ a side length of the frame, $\Delta u_r$ the shear right displacement and $v_r$ the right shear velocity
During manufacturing (lay-up), unidirectional prepregs generally require placement of more individual plies. To design a simple laminate for instance, for each 0 ply in the layup, a 0 ply must be placed onto the design tool. For each prepreg resin system, there is a range of options for cure temperature. For a given cure temperature there is a corresponding cure time. For highly reactive matrices and thick laminates the heat up rate is low, and may incorporate an intermediate temperature soak in order to avoid exothermic reactions.

The cost to manufacture high quality composite parts will be significantly reduced if OOA processes can achieve final parts with a finish quality as high as that of autoclave [111-113]. In practice, failure rates of commercially manufactured composites is relatively high due to the formation of defects such as voids, wrinkles and in-plane fibre waviness [114]. H.M.Hsiao investigated the effect of fibre waviness under compressive loading, and found that when testing UD composites, both major Young’s modulus and compressive strength degraded and fibre waviness increased. Also, interlaminar shear was the main failure mechanism for wavy fibres under axial compression. Under a local interlaminar shear, failure was initiated then followed by delamination and buckling [115].

A. Raouf used an analytical method to predict the effects of layer waviness on interlaminar stresses in thick plates. He concluded that the presence of waviness increased interlaminar and shear stresses during the manufacturing process [116].

M.P.F Sutcliffe concluded in his paper “Measurement of fibre waviness in industrial composite components” that when a prepreg component consolidated under vacuum is compared with a dry preform which is manufactured using RTM, the fibre mis-orientastion angles for out-of-plane waviness of the prepreg components are considerably smaller than that of the preform. He suggested that the fabric’s geometry and consolidation processes might have an impact on the results [117].

T.J.Dodwell and R.Butler investigated the out-of-plane ply wrinkling of a plybook during consolidation over an external radius. They identified that there was a gap for models used to identify
w wrinkling defects during prepreg consolidation as well as methods to extract the input parameters for such models [118].

K. Potter defined the out-of-plane fibre waviness as a function of the wavelength $\lambda$, the amplitude $\delta$ and misalignment angle $\theta$. The wavelength is defined as the maximum span of wavy fibres referred to the nominal fibre direction (length of the wavy region); the amplitude is defined as the maximum high of wavy fibres to the nominal fibre direction; the misalignment is defined as the angles of wavy fibres inclined to the nominal fibre direction [119, 120]. Out-of-plane fibre waviness can be represented as in Figure 3-9.

![Figure 3-9: edge view of out-of-plane fibre waviness](image)

For an L and T laminate, $\delta$ and $\lambda$ are respectively the gap between the two discontinuous layers and the length of the way region.

When layers become discontinuous, waviness is generated along the nominal fibre direction ((a) L laminates); and transverse to the nominal fibre direction ((b) T laminates).

In theory, when a plybook is consolidated with temperature and pressure, air trapped between the plies is removed. Dependant on the thickness of the plybook, a number of debulking steps are necessary to ensure that plies are correctly seated onto the mould part. Debulking also promotes adhesion between plies. When there are radiuses present on the mould part, friction between ply/plly or ply/tool necessary for the plybook to drape onto the geometry of the mould can present some issues. In these conditions, shear between layers should be higher to accommodate any
additional length required by the radiuses. Methods such as matched die moulding, deep drawing or press forming are available to encourage interply shear during forming [121-123].

If the plies cannot shear relative to one another, the plies are put into axial compression. Where the plies in the layup are parallel to the axial compression, stiffness increases; with an increase in stiffness, resistance increases and wrinkles formation starts. The formation of wrinkles not only disrupts the even distribution of fibre and resin, but most significantly can increase through-thickness stresses triggering failure at significantly reduced loads.

When consolidating a layup, the friction between ply/plies or ply/mould tool also have a major influence on the final geometry of components, especially if they are of complex components (presence of curves, radii on the mould). Sections in the plybook must slide with respect to one another, and deform individually to accommodate interply behaviour.

Successful forming of any part depends on the deformation modes taking place (interply shear, intraply shear, resin percolation, squeezing flow), and failure modes being suppressed (laminate wrinkling, in-plane fibre buckling, part thinning/thickening, fibre misalignment). For the deformation modes to take place and the failure modes to be suppressed, defects introduced during the processing cycles are to constantly reduce.

The defects as a results of manufacturing conditions are:

- **Ply misalignment introduced during layup.** This will alter the stiffness and strength of the final part and can cause warping during curing
- **Incomplete cure of the matrix when incorrect curing cycle are used**
- **Bonding defects during curing or compaction** (air entrapment, wrinkles created during lay-up). Dirt, cure conditions (rheology, dynamic and isothermal viscosity profiles, cure cycles, thermal characterisation), temperature (variation in room temperature, manufacturer’s suggested processing temperatures) or raw material contamination can introduce bonding defects
- **Fibre misalignment and waviness,** which is detrimental to the mechanical performance of manufactured parts.
• Delamination, which can be introduced during the layup
• Foreign body or wrong laminate weight. An example of a foreign body can be the backing paper when prepregs are used as raw materials
• Porosity, due to volatiles and trapped air bubbles in the layup
• Incorrect fibre volume fraction
• Ply cracking, caused by a difference in thermal expansion during cure
• Fibre defects. Faulty fibres have a huge impact in determining the strength of composite materials.

There has been extensive studies to predict deformations of composite material during manufacturing using numerical models based on finite element methods [124-131]. However, finite element analyses can be costly to set up and run, and often do not lead to any insight into the physics of the problem, thus making the interpretation of their results difficult.

Judd and Wright reviewed the effects of voids on the mechanical properties of composites and concluded that “regardless of resin, fibre type or fibre surface treatment, the interlaminar shear strength of a composite decreases by about 7% for each 1% void up to a total of about 4% (beyond which the rate of decrease of interlaminar shear strength diminishes)” [132]

Voids are one of the most significant defects found within composites. Extensive research has proven that they reduce the performance of composites structures [133-136]. The understanding of the impact of the size and distribution of voids on laminate properties is still limited because voids have proven difficult to deliberately control.

Dry spots can result in small voids that significantly degrade the mechanical properties of the manufactured components. Voids are undesirable within composite material parts due to their effect on their mechanical properties especially strength, and surface finish [137-140].

Ylva R. Larberg and Malin Åkermo in the their paper “on the interply friction of different generations of unidirectional prepreg materials” concluded that the friction coefficient of prepreg materials when at similar conditions (normalised with respect to matrix viscosity) shows an exponential dependency on prepreg surface roughness [141]. During consolidation the particles
into the fibre reinforcement seem to fuse the prepreg material at the same time as it become slightly resin starved, which influence the interply friction coefficient. The ply/ply friction in composite prepreg materials has previously been reported to influence the quality of the formed composite component by causing residual stresses and shape distortions [142, 143]. The final quality of a composite is always a depending factor of the defects incurred during manufacturing. These defects can be reduced but not completely eliminated. The presence of such defects is detrimental to the service life of the components as it can lead to a very significant reduction in mechanical performance [144-146].

The impact of the interaction between a mould tool and the surface of a ply layup have been investigated by Ferlung G and Al., Albert C and Al [147, 148]. They have concluded that within sharp corners during consolidation, the top surface tool interaction with the adjacent ply surface results in a ply length shortage at the outer edges of a layup up, almost forming a plybook.

![Diagram showing layer 1 and layer 2 shear](figure3-10.png)

*Figure 3-10: Exaggerated design of the impact ply/ply, ply/mould surface in sharp corners. Each adjacent “layers” would against one another to accommodate the mould shape. The shear will result in a gap.*

Figure 3-10 shows an exaggerated design of a blade and wedge to illustrate the layup of each ply in the book. Any plybook must take account of the curvature of the component, for example the plane width of any layer in the plybook for the wedge in (Figure 3-10) will in fact be its chord.
length. Given these chord lengths, the appropriate layer must still be shaped or conformed to the previous layer or to the mould. It is during this shaping operation that the ply can be deformed.

The aim of the research is to investigate the impact of introducing resin rich or resin starved plies within a prepreg layup, consolidate over a complex shaped mould and investigate the impact of the new stacks on the final parts. Before fabrication of the composite, its constituent materials’ cure kinetics are studied. Characterization of samples of the finished part is carried out by using optical and scanning electron microscopy.
4 VACUUM BAGGING OF 3 PLY LAYUP

In an effort to reduce defects (wrinkles, voids and delamination) typically introduced within a prepreg layup whilst using OOA processes, a 3 ply layup was attempted where the amount of resin within stacks was finely tuned (either resin rich or resin starved).

4.1 Vacuum bagging of plies

Two VaryPreg plies and one 2/2 twill dry fabric were placed on a flat aluminium plate. The dimensions of the plate were 300mm x 300mm with a thickness of 5mm and those of the laminates were 200mm x 200mm. A perforated film was then placed on top of the layup which was then covered by a peel ply. The peel ply was introduced to separate the breather from the laminate. A breather cloth was finally placed on the layup. The dimension of the cloth was 50 mm bigger than that of the layup. The extra cloth was then secured onto the laminate mould with flash tape. A tubing system provided air tight passage from the vacuum envelop to the vacuum pump (see Figure 3-4, page 68 ) allowing the vacuum to reduce air and increase pressure within the envelope.

For curing, the layup was placed in an oven at 150°C for 20 minutes, before the temperature of the oven was reduced to 80°C for a few hours. This post curing is necessary to insure that the layup has fully cure.
4.2 Adjusting the resin content of the dry slip layers

In order to adjust the resin content of the resin-starved slip layer, laminates such as those made in (Section 4) were cured and then vacuum impregnated. After the post curing of the resin starved laminates, two test experiments made of 2 clear acrylic plates and one plain woven glass fabric were resin infused. The matrix in the experiments was a glycerine based viscous liquid.

![Image of resin infusion experiment](image_url)

*Figure 4-1: Resin infusion of 2 acrylic plates and a plain woven glass fabric*

In these two experiments, acrylic plates were assumed the role of prepregs which had already been vacuum bagged and cured. In Figure 4-1 the resin inlet in placed along the nominal plane.

An ECVP 425, 185w pump was used for the infusion as well as a vacuum hose and gauge, a stop cock, resin catch pot, thermometer, stopwatch, C270 Logitech HD webcam, glue gun, sealant tapes and tubing (10-12 mm diameter). The vacuum pump was connected to the resin catch pot (Figure 4-3). The coefficient of friction on the inside face of the plate was not taken into account. Each C channel (200mm * 25.40mm) had a manifold inserted into it.
Two C channels were used to seal the glass plates/dry fabric lay up on each 200mm end. (Figure 4-2)

![Figure 4-2: C-channel manifold (see appendix for dimensions)](image)

Aluminium was used to manufacture the channel. A Computer Numerical Control (CNC) was used to manufacture the channel.

![Figure 4-3: Schematic of the resin infusion diagram](image)

In order to visualise the impregnation process a mesh was drowned onto the surface of the top plate, Figure 4-4.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

**Figure 4-4: Mesh on surface layup using Resin infusion**

In Figure 4-4, the image at the left is a magnification of the mesh drawn on the surface of the top plate. It was easier to track the impregnation of the glass fibre. In this experiment, the impregnation stopped after 300s.

**Figure 4-5: Rate of fill of glycerol in resin impregnation of acrylic plates and glass fabric**
The pictures were taken at an internal of 30s for 300s by a webcam (c270 Logitech HD). Above 300s, the glycerol did not continue to infuse the fabric. Although leak tests were conducted, the same results were recorded.

These experiments underlined the difficulty of this “second” impregnation since the predominant flow direction is through the thickness of the prepreg. This has an extremely narrow cross-sectional area and not all of it was available to the resin as it flowed into the laminate.

![Figure 4-6: Resin infusion of acrylic plates and glass fabric](image)

It can be argued that this resin flow rate would increase if the impregnation could be carried out normal to the plane of the prepreg. To pursue this, some experiments were carried out to infuse resin into the fabric layers between sheets of solid acrylic. Here the acrylic acted as an “impermeable” prepreg. Holes were made in the acrylic plates so that flow could start from the hole in the “top” layer and permeate through the next fabric layer to the next (set of) holes in the next layer of prepreg and so on. This is shown schematically in Figure 5-8.

The glass fabric used for the RI was cut to fit the polyester plates. The lay up for the experiment consisted of two glass fabrics and three polyester plates. The sequencing of the lay up was polyester – glass - polyester - glass – polyester (Figure 17). The top and bottom polyester plates each had one hole of 19mm diameter drilled into them; the mid plate had two holes instead (Figure 18). The woven glass fibre fabric was 0.3 mm thick.
Figure 4-7: Schematic of a polyester/glass fabric impregnation.
In this layup, the top and bottom polyester plates have each a hole drilled into them (hole 1 & 2). Hole 1 represents the resin inlet and hole 2 represents the pump inlet. Three more plates are used in the layup where the middle plate is drilled with two holes to encourage the resin infusing the layup.

Figure 4-8: Variant of polyester plate and plane woven glass fibre resin infusion schematic
The resin used in these experiments was a low viscosity unsaturated polyester (Table 4-1), and, while the results were disappointing, they were a considerable improvement over those based on solely transverse impregnation. By way of illustration, the impregnation of the glass/PS laminate is shown in Figure 4-9.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>CRYSTIC 701PAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Infusion temperature</td>
<td>°C</td>
<td>18 – 20</td>
</tr>
<tr>
<td>Gel time</td>
<td>Minutes</td>
<td>85 (at 25°C using 2% Catalyst M (or Butanox M50))</td>
</tr>
<tr>
<td>Volatile content</td>
<td>%</td>
<td>50</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td>Mauve</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Months</td>
<td>At 20°C, 3 months</td>
</tr>
<tr>
<td>Stability at 20</td>
<td>Months</td>
<td>24h at 23°C 10 (mg)</td>
</tr>
<tr>
<td>Shelf life</td>
<td>Months</td>
<td></td>
</tr>
<tr>
<td>Storage</td>
<td>°C</td>
<td>Less than 20, no more than 30</td>
</tr>
</tbody>
</table>

*Table 4-1: Polyester resin properties*
Figure 4-9: Polyester plate/glass fabric resin infusion experiment

This represented the initial experiment carried out to access resin infusion using polyester plates in which various holes have been drilled to encourage the resin to infuse the layup.

Figure 4-9 represents the infusion of the polyester/glass fabric. After 25 min, the part infused showed two distinctive colour gradients: a dark and light grey. The grey colour represented the resin percolating through the plates and fabrics. The light colour represented the impregnation of the first glass fibre fabric and the dark colour was the impregnation of the second glass fibre fabric.

The presence of bridging created paths of least resistance for the matrix system. This impregnation of the layup was not uniform.
Figure 4-10: Bridging formation during the resin infusion of polyester plate/glass fabric

Once the resin started permeating towards the edge walls of the plates, resistance started changing. At the edge walls of the part, there was no friction between the plates and the fabrics, therefore nearly nulling any resistance to the resin flow. With the resin reaching the edges of the part, the near absence of friction resulted in a decrease of resistance to flow and an increase to resin flow. Resin started to build up at the edge walls of the plates and moving along its ends; travelling from one corner to the opposite end corner without infusing the inner parts of the layup.

Once the resin reached all end corners of the plates, it then started permeating again through the part. With the increasing friction between the plates and the fabrics, the resistance to flow increased and the resin flow decreased. The pressure at the resin inlet was assumed to be the same as that in the vacuum; only the resistance variation was taken into consideration.

The final image of the impregnation is shown below highlighting a considerable build-up of resin under the infusion inlet connector.
The resin was seen to concentrate with the resin inlet region. The vacuum bag was leaking which created paths of least resistance for the resin to travel.

The flow within the vacuum was laminar, but the nature of the flow at the resin inlet was not taken into account. The size of the holes on the polyester plates would play an important role in the infusion process; indeed, the smaller the tubing diameter, the more energy would be required to drive resin through the tubing into the vacuum bag which in turn would disturb any laminar flow at the inlet region into a turbulent flow. By controlling the size of the tubing flow or introducing a stopcock between the resin pot and the resin inlet, the type of flow at the resin inlet could be controlled. Also, a turbulent flow would increase the pressure gradient required to drive a given resin.

With high resistance to flow, the resin flow decreased whilst low resistance to flow implies an increase in flow. The pressure gradient is the difference between the atmospheric pressure and the pressure in the vacuum bag (>800 mbar).
A second experiment using the same layup was carried out. Two plain weaves of 300g glass fibres and an IN-2 epoxy infusion resin was used. The aim was to try to reduce the formation of bridging and also better record the infusion process.

The resulting experiments did not have any bridging and vacuum was always over 800 mbar. The vacuum inlet was kept at 19 mm and the differences in infusion from that of the polyester plate/glass fabrics were already apparent:

![New resin infusion experiments using polyester plates as reinforcement](image)

The picture on the left showed the initial infusion carried out using polyester plates and plane woven glass fabric resin infusion process. The picture on the right showed the new infusion carried out after controlling paths of least resistance; this was achieved by securing the layup in a carefully sealed vacuum bag where vacuum at 1 bar was tested using a gauge.
The resulting laminates obtained from this infusion presented regions where the resin did not infuse the glass fabrics. This can be confirmed by eye inspection.

*Figure 4-14: Final part obtained from polyester/glass layup infusion*

The picture above showed that the edges of the layup were fully infused. This is due to the presence of bridges during infusion. The resin would follow the paths of least resistance during percolation.

This failed infusion was likely due to the fact that once the resin started permeating towards the edge walls of the plates, resistance started changing. At the edge walls of the part, there was no friction between the plates and the fabric, therefore nearly annulling any resistance to the resin flow. With the resin reaching the edges of the layup, the near absence of friction resulted in a decrease of resistance to flow and an increase to resin flow. Resin started to build up at the edge walls of the plates and moving along its ends; travelling from one corner to the opposite end corner without infusing the inner parts of the layup. Once the resin reached all end corners of the plates, it then started permeating again through the layup. With the increasing friction between the plates and the fabrics, the resistance to flow increased and the resin flow decreased. The pressure at the resin inlet was assumed to be the same as that in the vacuum; only the resistance variation was taken into consideration.

With the experiment where acrylic was used as a substitute to prepreg, the cure part had a larger infused area compare to the polyester plate experiment cure parts Table 4-2.
Table 4-2: Comparing polyester and acrylic plate layups

The wetted region for the polyester and acrylic experiments were represented by the blue colour. There is noticeable difference between the wetted regions when using acrylic or polyester plates. Resin percolation was much easier in layups where acrylic was used as reinforcement.

Resin percolation is the flow of a viscous polymer through or along the fibre bed that allows the plies to bond together. This definition was coined in “manufacturing processes of advanced composites” edited by Flake C Campbell Jr.

It is interesting to note that this technique may be better suited to resin injection rather than resin infusion since the “injection” pressure can be higher than one atmosphere. Of course in reality the holes through the prepreg plies will fill with resin (without fibres – (Figure 4-15)) and hence be a source of weakness in the laminate as a whole. Nonetheless this may be worth pursuing (hole size, spacing etc) in future work.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

4.3 Adjusting the resin content of dry slip layers by addition of resin film

For layups with dry fabrics, resin films were introduced during the vacuum bagging layup. In this case, a perforated release film was used between the peel ply and the breather cloth to encourage suction of extra resin. The plies were placed at (-45°/0°/+45°) angles. The figure below show a resin film placed onto a 2/2 twill prepreg.

The release film was an epoxy based resin (MTM54, Cytec Industries) which has the same characteristics as the resin used with unidirectional prepreg (see experimental procedures for more details). A part made of 4 unidirectional prepreg plies and 2 unidirectional dry fabric was moulded onto an aluminium mould. The resin films were placed around each side of the dry fabric. The resulting part is illustrated in the Figure 4-17 and Figure 4-19.
The optimal room temperature to lay the resin film is 19° C. at this temperature, a clean film can be spread over the prepreg (Figure 4-18). When the temperature is under or over 19° C, the resin is extremely brittle and rubbery.
Figure 4-19: Part moulded using vacuum bagging and resin rich stacks in the layup
CHAPTER V

5 CHARACTERISATION OF DRAPE AND SHEAR

5.1 Pull out test

During forming, the plies will need to slide against one another to accommodate curves and/or sharp edges. A pull out experiment was conducted on woven fabrics.

A woven carbon prepreg was used in this experiment. The weight of the plies used during the experiments was around 250g. The origin, weave type, modulus band, filament count and size content were not taken into account. First, a polyurethane resin was used as matrix. A second matrix for the experiments was a mixture of gelatine powder and water (viscosity at 20°C is $\eta = 1.002 \times 10^{-3}$ Pa.s). Compaction pressure was applied with a Bentley paint brush (75g, 50mm width), and an universal tensile testing machine with a servo-controlled speed was used. The breaking load of the tensile testing machine was between 15 and 85% of the machine capacity.

Two grip vises on each end of the Tensometer were used to mount the samples on the machine. The serrated grip inserts are designed to dig into samples and prevent them from slipping. The grip inserts are aligned so that the centreline of the grip assembly is aligned with the adhesive bond. Proper alignment was achieved with vice grips by adjusting the grip inserts from side to side so that the centre line of the upper and lower grips pass through the adhesive.

Two specimens were made: a polyurethane/woven carbon fibre layup and a gelatin/woven carbon fibre layup. Each specimen was made of two plies of carbon (300mm*50mm). Each ply had a strip grip (5mm * 50mm).

At room temperature, each grip was dipped entirely in a water/gelatine solution (one pack of Dr Oetker powered gelatine and 568.2 ml of warm water ~ 55°C) and left to cure for 24 h. After curing of the plies, a specimen was made by arranging the ply strips in single lap joint (70mm * 50mm). The strips were put under a manual compaction force for 5 minutes. A brush was used to apply the manual compaction force, Figure 5-1.
The specimen was then dipped either in a polyurethane resin or water/powered gelatin mixture. Concentration of water/powered gelatin mixture varies from 20-50% gelatin. The specimen was set to cure for 1, 2, 5 and 24 h. Once cured, the specimen was then loaded on the tensile tester using the grip vise on each end of the Tensometer. Forces from 5-250 N were applied.

*Figure 5-1: pull out test schematic*
The specimens were mounted on the tensile testing machine.
The lap-shear strength is given by:

\[ \tau = \frac{P}{WL} \]  

*(Equation 5-1: lap shear strength equation)*

Where \( P \) is the maximum load (N), \( W \) is the joint width (mm) and \( L \) is the joint length (mm).
For the first experiments, the matrix was set to cure at room temperature for 1h, 2h, and 5h. Initial slippage was recorded at 10.

Beyond this value, no slippage was recorded at the shear area. Throughout the experiments, both grips of the woven carbon fibre plies in contact with the Tensometer vises grip area were torn Figure 5-4.

[Figure 5-3: Lap shear test for gelatine/woven fabric. Specimen failed at 10N]

[Figure 5-4: woven carbon fibre strips at point of failure]
When the matrix was set to cure for 24 h, the load required to induce slippage increased drastically and was recorded at above 400 N. The extension on the shear area varied between 6 and 6.5 mm.

![Graph showing load vs. extension for 20% gelatine/woven carbon fibre at 24 hours](image)

**Figure 5-5**: Sample shear test after 24h

When the matrix viscosity was also increased, the load required to induce slippage increased. For the 20 specimens used throughout the experiment, the percentage of gelatine/water was consistently above 40%, the loads recorded varied between 260-270N, Figure 5-6.
During consolidation of part, the individual plies in the ply book must slide with respect to one another, and deform individually to accommodate interply behavior. These experiments showed that:

- When the matrix was cured for less than 5h, the force required to induce slippage on the tested specimens was less than 10N.
- When the matrix was cured for 24h, the force required to induce slippage increased drastically, higher than 400N

By extrapolating these two statements onto experiments were the matrix would be a resin, a simple correlation could be drawn.
Figure 5-7: Schematic of gelatine/water mixture findings

This figure shows that when the force required to inducing slippage increases, the time for curing the carbon strips is longer. This can be extrapolated in prepreg laminate that slippage will generally occur during the compaction step when the curing temperature of the matrix has not yet been reached.
5.2 Drape and inter-ply slip

A layup drapes around a shape by a succession of dropping plies along the length of the mould to match varying in-plane and bending loads. Each ply remains “stuck” to its immediate neighbor because of the tack present on its surface. The resulting stack or book remains “stuck together” because of cohesion between the layers.

Cohesion arises as a result of the “tack” on each ply from the excess resin. Tack is defined as a transient phenomenon related to the ratio of elastically stored energy to the dynamic loss factor at a particular high rate of deformation. It is also defined as an incomplete bonding formed with low contact pressure during a short contact time. Tack is also defined as a pull resistance of liquid to an oppositely directed force. Hence, since tack has different meanings in different applications, the definition of tack must be adopted according to the way a material system tack is utilised for a specific application.

The presence of fibres in a prepreg prevents intimate contact of the resin across the stack thickness. A potential consequence of this is the presence of rough and incomplete interfaces between adjacent plies during layup processes. Cohesion of prepgs during forming is therefore dependent on the presence of tack. From a practical point of view, prepreg tack is the property that allows individual plies to adhere to each other so that multiple plies can be stacked and maintained at a desired orientation. However, tack must not be so overwhelming that when a ply is misplaced during the layup procedure, the ply cannot be relocated easily. Each ply in a composite laminate without bending needs to carry the same amount of strain when a ply is dropped. There is a reduction in area that places the thinner section under a higher stress, transitioning via shear lag. This will affect the deformation during molding. Also, within the stack, the force of cohesion varies in the patches between different layers and in different regions of the stack; modelling this behavior can be challenging.
A simple concept is to assimilate the cohesion between two consecutive plies to that of two strips (layers) of an isotropic material. The cohesion between the strips interface is only friction. The “friction-only” idea was in fact pursued in a notionally simple model of a 3-point bend simulation of two steel plates, modelled in Abacus, Figure 5-8.

Figure 5-8: simulation of steel plate under 3 point bending test

Here, as expected, the upper plate slips relative to the lower one. It was intended to extend this approach to model the “cohesion” between plies in a stack of prepregs as the stack deforms during molding, but, unfortunately it proved impossible to generate a stable and realistic model. This will be pursued in future work. For prepregs there is a close relationship between drape and tack. Drape is the ability for fabrics or prepregs to conform to different curvatures. The concept of assimilating the behavioural deformation of a stack of plies to that of layers of an anisotropic material is an original approach, since little investigation has been carried out in the literatures.
CHAPTER VI

6 EXPERIMENTAL PROCEDURES

6.1 Materials

Originally, Cycom 977-2 prepreg and its virgin resin system 977-20 were the chosen materials for all the experiments. The sponsoring company Rolls Royce was proving both the prepreg and the resin system.

Cycom 977-2 is a unidirectional thermoset prepreg. It is formulated for autoclave or press moulding. The recommended lay-up procedure for this material is supplied by Cytec [149]. The recommended cure is 177°C. At room temperature, Cycom 977-2 has a tensile strength and modulus of 81.4 ± 11 MPa and 3.52 ± 0.14 GPa.

Unfortunately, it was not possible to get access to the materials. As such, it was necessary to use an alternative material throughout the research project.

Experiments were carried out using two different types of prepregs which were combined with two different types of carbon fibre fabrics and two different types of resins (infusion and film). Prepregs were either MTM57 unidirectional Carbon Fibre (Cytec Industries Inc, NJ, USA) or Vari Preg PrePreg Carbon Fibre 215g 2/2 Twill (Easycomposites Ltd, Cheshire, UK). Carbon fibre fabrics were either unidirectional 250g or 2/2 Twill 3k 240g (Easycomposites Ltd, Cheshire, UK). The infusion resin used was an Epoxy IN2 whose composition was unknown due to proprietary obligation of the manufacturer (Easycomposites Ltd, Cheshire, UK). The film resin used was MTM57 (Cytec Industries Inc, NJ, USA) and the same as that used in the prepreg of the same name. Twill was a multi-purpose prepreg carbon fibre specially developed to offer excellent mechanical performance combined with a long out-life (4-6 weeks) and a very wide range of cure temperatures [150].

[105]
MTM57 Unidirectional prepreg was an intermediate viscosity and tack carbon prepreg; it was a qualified for Federal Motor Vehicle standard no.302 when reinforced with 3k carbon fabrics [151]. MTM57 prepreg and its resin film cured between 80 to 120° C. Table 6-1, page 106 showed the manufacturer’s curing cycle for the resin system.

The Vari-Preg carbon Fibre 215g 2/2 Twill could be cured at variable temperatures from 80 to 150° C which was recommended to process in vacuum/oven. Curing down at 80° C was within the manufacturer’s recommendations. Table 6-2 shows the manufacturer’s specifications for this system. Alternatively, at 150°C the prepreg would reach full cure in a matter of minutes meaning that very high production volumes can be achieved off a single tool.

<table>
<thead>
<tr>
<th>Vacuum bag pressure</th>
<th>Minimum of 980 mbar (29”Hg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramp rate</td>
<td>1 to 3° C/ minute</td>
</tr>
<tr>
<td>Recommended cure cycle</td>
<td>1 hours at 120° C, +5/-0° C</td>
</tr>
<tr>
<td>Cool down</td>
<td>Maximum of 3° C/ minute</td>
</tr>
</tbody>
</table>

*Table 6-1: MTM57 cure cycle, Oven Vacuum bag cure.

*this is the ideal vacuum level, however, it is recognised that it is not always possible to attain.

Vari-Preg PrePreg Carbon Fibre 215g 2/2 Twill Specifications.

- Main properties

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Fibre areal weight</th>
<th>Weave</th>
<th>Resin ratio</th>
<th>Freezer life</th>
<th>Out-life Temp</th>
<th>Max cure Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafil TR30S 3k</td>
<td>215g</td>
<td>2/2 Twill</td>
<td>46%</td>
<td>12+ months at -18° C</td>
<td>80° C for 10 hours</td>
<td>150° C for 10 minutes</td>
</tr>
</tbody>
</table>
Additional properties (Resin)

<table>
<thead>
<tr>
<th>Elongation (ISO 527)</th>
<th>$T_g$ after 150º C cure</th>
<th>$T_g$ after 120º C cure</th>
<th>Flexural strength (ISO 178)</th>
<th>Modulus (ISO 178)</th>
<th>Tensile strength (ISO 527)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170º C</td>
<td>120º C</td>
<td>148 – 170 MPa</td>
<td>3500 – 4000 MPa</td>
<td>68 – 78 MPa</td>
<td></td>
</tr>
</tbody>
</table>

*Table 6-2: Vari-Preg PrePreg Carbon Fibre 215g 2/2 Twill Specifications*

Figure 6-1, shows a schematic representation of a UD prepreg and Figure 6-2 shows a schematic representation of a 2/2 Twill prepreg.

*Figure 6-1: Schematic of a UD prepreg*
For brevity the materials used in this research will be referred to as follows:
MTM57 Unidirectional Carbon Fibre prepreg will be referred to as Up, Carbon Fibre Unidirectional 250g 1m wide as Ud, Carbon Fibre 2/2 Twill 3k 240g 1.25m wide as 2/2d, Vari-Preg Carbon Fibre 215g 2/2 Twill as 2/2p.

Where p and d indicate the material resin structure; the subscript p indicates that the carbon fibre is a prepreg; while d indicates that the carbon fibre is a fabric. The infusion resin IN2 Epoxy Infusion Resin will be referred to as ri; the resin film MTM57 resin film is referred to as rf, where the subscripts i and f indicate the resin form; liquid or film respectively. The parts geometries used for characterisation are shown in chapter 5: MOULD FABRICATION, page 133. Figure 6-3 shows a generic layup of the plies with their orientations. Here, the resin film is represented by a black rectangle, the prepreg is represented by a coral rectangle and the dry fabric by the blue rectangle. All the layup in the experiments are a combination of one of these arrangements.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

Figure 6-3: Generic layup sequence
6.2 Microscopy

Microscopy analysis allowed important individual void characteristics to be assessed. To limit the effects of section-bias, three cross-sections were analysed per part layup, making a total of twenty-four cross-sections. This large number made the analysis process very time consuming, with each surface requiring careful preparation to a mirror like finish. The microscopy was used to determine the void content, ply counts, fibre orientations, fibre morphology and the effects of the processing parameters.

The voids observed within a single cross section of a laminate were not consistent, but had variable shapes and distributions due to the sections cutting through pores at different orientations. The samples were sectioned through the z-axis and viewed normal to the zx or zy angle. For crystallinity and microcracks, the samples were viewed in the xy plane.

![Figure 6-4: Specimen cutting method](image)

The samples were cut using a diamond blade cutter. Water was used as a coolant during sectioning. After cutting the samples, they were documented and labelled before polishing.
Rough polishing was carried out first using 400, 800 and 1200 silicon carbide (SiC) grit paper, then an automated polishing system was used to obtain the mirror finish required for high quality characterisation.

The part laminate orientation codes were slightly amended to accommodate notation for the type of inserts: prepreg, fabric or film. The laminates orientation was layed up as described:

Twill carbon:
- \((-45/0/+45)(p/d/p)^2\)
- \((-45/0/+45)(p/d/p)^2\) resin infused
- \((p/f/d/f/p)[-45/(\alpha^7)/0/(\alpha)/+45]^2\)

UD carbon:
- \((-45/0/+45)(p/d/p)\)
- \((p/f/d/f/p)[-45/(\alpha)/0/(\alpha)/+45]\)

3 ply prepreg
- \((-45/0/+45)(p/p/p)\)

Where p is for prepreg
- d is for dry fabric (either UD or 2/2 twill)
- RI stands for resin infused

\((\alpha^7)\) represented MTM57 resin film
6.3 Differential Scanning Calorimetry and Dynamic Mechanical Thermal Analysis

6.3.1 DSC measuring principle
A DSC Q100 (TA Instrument, TX, USA) was used to study the cure kinetics for the prepreg composites and the resin film during processing. To design a manufacturing process, it was a prerequisite to characterise the cure kinetics of the chosen resin system. It has been demonstrated that the cure process during manufacturing is the most crucial stage to produce high quality composite parts [152-154]. Manufacturers often provide recommendations on the resin system cure cycles, but generally the recommendations cannot be accurately followed. This was due to the fact that the parameters during the moulding processes often diverge from the recommendations. Hence, it is essential to study the curing characterisation of a resin system before fabricating a composite part.

Calorimetry is a universal method for investigating the chemical reactions and physical transitions occurring during the generation or consumption of heat [155]. The term DSC implies that during a linear temperature ramp, quantitative calorimetric information can be obtain from a specimen.

According to the British Standards BS EN ISO 11357-1:2009, EN ISO 11357-1:2009 (E), DSC was a technique which measured the difference in the heat flow from a sample to a reference sample as a direct function of time or temperature under heating, cooling or isothermal conditions [156].

[112]
DSC was also used to characterise melting, crystallisation, resin curing, loss of solvents, and other processes involving an energy change. For analysis, the sample is placed in a pan (aluminium, gold or copper). The sample and an empty reference pan are placed on small platforms within the DSC chamber between thermocouple sensors (Figure 6-5).

![Figure 6-5: Schematic of the interior of a Differential Scanning Calorimeter DSC [157]](image)

There are two types of DSC instruments: a power compensation DSC and a heat flux DSC. A power compensation DSC has two separate heaters for the reference and the sample, and the temperature difference between them is compensated by supplying a differential power to the heaters. In a heat flux DSC, the sample and reference positions are subjected to the same temperature control, programmed by a single heater [158]. The DSC ultimately outputs the differential heat flow (heat/time) between the sample and the empty reference pan. So the heat absorbed by the polymer matrix is plotted against temperature as given in Figure 6-6 [159].
The heat flow $q$ is supplied per unit time. The heat flow rate is written as in Equation 6-1.

$$\varphi = \frac{dq}{dt}$$  \hspace{1cm} (6-1)

**Equation 6-1: heat flow rate**

The heating rate, $\beta$, is the time rate of change of temperature, $T$ [160]; Equation 6-2, below

$$\beta = \frac{dT}{dt}$$  \hspace{1cm} (6-2)

**Equation 6-2: heating rate**

The heat capacity, $C_p$, may be determined by taking the ratio of the heat flow to the heating rate, thus Equation 6-3.

$$C_p = \frac{dq/dt}{dT/dt} = \frac{\varphi}{\beta}$$  \hspace{1cm} (6-3)

**Equation 6-3: heat capacity**
A schematic of a DSC thermogram is shown in Figure 6-7, [161]

*Figure 6-7: Schematic of a DSC thermogram*

The baseline is obtained during the calibration of the DSC. Materials which are often used for calibration are but not limited to gallium, indium, tin, mercury as their purity can be obtained 99.9999% + pure.
There are four critical points on the thermogram: the glass transition temperature $T_g$, the crystallisation temperature $T_c$, the melting temperature $T_m$ and the curing temperature.

Their interpretation are [162-164]

a) In amorphous and semi crystalline polymers, the glass transition is a result of the reduction in motion of the large segments of molecular chains as a consequence of decreasing temperature. Upon cooling, the glass transition correspond to the gradual transformation from a liquid to a rubbery material and finally into a rigid solid. The temperature at which the polymer experiences the transition from a rubbery into a rigid state is called the glass transition temperature, $T_g$

b) Crystallisation occurs when a polymer loses its random chain arrangement, intermolecular bonds form and the polymer molecules become more regular or ordered

c) During melting of a polymer, there is a rearrangement of the molecules in the transformation from disordered to ordered. It is an exothermic reaction.

d) Curing is similar to crystallisation in the fact that it is exothermic. At this stage, the individual chains of a polymer form strong bonds between them.

Isothermal measurements and dynamic measurements are the two different approaches that can be used to obtain the cure kinetics of a resin system. Isothermal measurements involve maintaining the sample at a fixed temperature for various time intervals, whereas dynamic measurements involve heating the sample at a constant rate over a temperature range. In the measurements, the degree of cure $\alpha$ ranges from 0 (completely uncured) to 1 (completely cured) [165].

In order to obtain the time dependent degree of cure (DOC) profile for the cure cycles, the ultimate heat of reaction $H_u$ at $T_{cure}$ must be known. Both isothermal and dynamics measurements are frequently use to obtained $H_u$ and $T_{cure}$. TA instruments offer three analytical approaches for DSC kinetics studies: Borchardt and Daniels, ASTM E-698 and Isothermal, see Table 6-3, page 120.
The chart shown in Figure 6-8 provides broad guidelines for deciding which DSC method was most appropriate. The Borchardt and Daniels approach assumes that the sample’s reaction follows a nth order kinetics and obeys the general rate equation

\[
\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n
\]

(Equation 6-4: Reaction rate equation as following the Borchardt and Daniels approach)

Where \(\frac{d\alpha}{dt}\) is the reaction rate in (1/sec), \(\alpha\) the fractional conversion, \(k(T)\) the specific rate constant at temperature \(T\) and \(n\) the reaction order.

The isothermal approach requires three or more isothermal experiments to generate kinetic parameters (\(E_a, Z, n, m\) and \(k\)). \(E_a\) is the activation energy expressed in (J/mol); \(Z\) is the pre-exponential factor or Arrhenius; \(n\) and \(m\) are reaction orders; \(k\) is the specific rate constant at temperature \(T\).

The final approach, the ASTM E698 thermal stability approach is based on the variable program rate method of Ozawa [166].

Besides these models, a proposed model for the kinetics of isothermal cure, published in 1973 from the University of Manchester is considered as one of the standard model used for to characterize the cure of a general-purpose polyester during isothermal and scanning experiments [167].
Figure 6-8: selecting a DSC method

Isothermal, ASTM and B/D are respectively the isothermal kinetics, ASTM E-698, and Borchart and Daniels DSC methods for obtaining kinetic information of a material.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Borchardt and Daniels</th>
<th>ASTM E-698</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (s)</td>
<td>( t )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat (J)</td>
<td>( q )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>( T )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat flow ( \beta )</td>
<td>( \frac{dq}{dt} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating rate ( \alpha )</td>
<td>( \frac{dT}{dt} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat capacity ( C_p ) (J/g)</td>
<td>( \frac{dq}{dT} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fractional conversion</td>
<td>( \alpha ), when the ASTM E-698 method is used, the fractional conversion is represented by ( \alpha ); hence ( \alpha = a )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction nth order</td>
<td>( n )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction mth order</td>
<td>( m )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor (1/sec)</td>
<td>( Z )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation energy (J/mol)</td>
<td>( E_a )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fractional conversion</td>
<td>( \alpha ), when the Borchardt and Daniels method is used, the fractional conversion is represented by ( a ), hence ( \alpha = a )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas constant (J/mol K)</td>
<td>( 8.314 )</td>
<td></td>
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</table>
## Methods

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Borchardt and Daniels</th>
<th>ASTM E-698</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific rate constant at temperature T</td>
<td>$k(T) = (Ze)^{-Ea/RT}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction rate (1/sec)</td>
<td>$\frac{d\alpha}{dt} k(T)[1 - \alpha]^n$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{d\alpha}{dt} = (Ze)^{-Ea/RT} (1 - \alpha)^n
\]

*Table 6-3: DSC kinetics study methods suggested by TA instruments*
6.3.2 Sample preparation

Two specimen types were used with the Q100 DSC. The steps involved in conducting a DSC experiment are:

1. Prepare the specimen.
2. Weigh out the specimen into a pan.
3. Seal the pan with the aid of a press.
4. Place the specimen and reference pans into the test chamber.
5. Set the temperature program.

![30 μl aluminium pan](image)

*Figure 6-9: Hermetic Aluminium sample holder with prepared sample*

Five specimens were made using 2/2p. From these, three were used for dynamic measurements and two for isothermal measurements. The uncured 2/2 twill prepreg samples weighed around 5 mg. They were each placed in a hermetic aluminium pan which were sealed using a manual press, before being placed opposite to the empty reference pan in the Q100 chamber. For the dynamic measurements, the DSC was set to temperature ranging [-50°C – 300°C], with 3 different heating rates: 5°C/min, 10°C/min, 15°C/min. For isothermal measurements, the samples were cured at 80°C and 120°C for 600 minutes. The heat flow generated from and to the samples was recorded constantly.
6.3.3 Dynamic Mechanical Analysis measuring principle

Dynamic Mechanical Analysis (DMA) is a technique for the characterisation of the viscoelastic properties of materials, in particular polymers and composites. It gives a quantitative assessment of materials’ properties such as stiffness and damping, but also provides important structural information. DMA as the DSC gives thermal transitions values. e.g. typical output of tanδ versus temperature will display a peak at glass transition temperature (Tg). Above Tg, peaks correspond to the crystalline regions and eventually melting temperature (Tm).

Samples were subjected to tension on the DMA. Tension is a simple mode of deformation in which the load is applied along the specimen axis and the stress distributed uniformly across the cross section. Also tension measurements return the most appropriate modulus values. Here, prepreg samples were subjected to a periodically changing force; by means of either stretching or torsioning samples. When a certain stress is applied to a sample, it reacts elastically by building a strain directly proportional to the applied stress [168, 169]. The same sample, can also react elastically. Polymeric behaviour is somewhat in between; the behaviour is referred to as viscoelastic behaviour.

Dynamic mechanical properties refer to the response of a sample/material as it is subjected to a periodic force. These properties may be expressed in terms of a dynamic modulus E′, a dynamic loss modulus E′′, and a mechanical damping term tanδ [170]. Typical values of dynamic moduli for polymers range from $10^6$ - $10^{12}$ N/cm$^2$ depending upon the type of polymer, temperature, and frequency [171, 172].
Figure 6-10 shows a schematic drawing of a DMA instrument. Courtesy of the School of Chemical Engineering, department of Physical and Engineering Sciences, The University of Manchester. Copyright 2015.

Figure 6-10: Schematic drawing of a DMA instrument

A viscoelastic material will respond with a sinusoidal strain if the applied stress is sinusoidal with time. The sinusoidal variation in time is described as a rate specified by the frequency (f in Hz; \( \omega \) in rad/sec). Therefore, when the stress is periodical, a phase difference is said to be between the applied stress and the resulting strain. This difference is caused by the internal damping of the material referred to as \( \tan \delta \), where \( \delta \) represents the phase shift angle.

The strain of a viscoelastic material is out of phase with the stress applied, by the phase angle, \( \delta \). This phase lag is due to the excess time necessary for molecular motions and relaxations to occur. The modulus and compliance functions are obtained through mathematical operations on the relationship between the dynamic stress, \( \sigma \), and strain, \( \varepsilon \) \([173, 174]\). The equations are given as:

\[
\sigma = \sigma_0 \sin(\omega t + \delta)
\]

*Equation 6-5: Dynamic stress*
\[ \varepsilon = \varepsilon_0 \sin \omega t \]  \hspace{1cm} (6-6)

*Equation 6-6: Dynamic strain*

Where \( \omega \) is the angular frequency in rad/sec.

By decomposing the associated stress vector into two vectors forming a phase angle of 90° with respect to each other, the dynamic stress (Equation 6-5) can be rewritten as:

\[ \sigma = \sigma_o \sin(\omega t) \cos \delta + \sigma_o \cos(\omega t) \sin \delta \]  \hspace{1cm} (6-7)

*Equation 6-7: Dynamic stress expressed as function of in-phase and out-of-phase components*

Dividing the stress and the strain gives the modulus (dynamic modulus and loss modulus); where the in-phase component is \( E' \) and real, and the out-of-phase component is \( E'' \) and imaginary. A new equation is obtained where the dynamic stress is expressed as:

\[ \sigma = \varepsilon_o E' \sin(\omega t) + \varepsilon_o E'' \cos(\omega t) \]  \hspace{1cm} (6-8)

*Equation 6-8: Dynamic stress expressed in dynamic modulus and loss modulus*

In Equation 6-8, \( E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \) and \( E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \)

\[ \varepsilon = \varepsilon_0 e^{i\omega t} \text{ And } \sigma = \sigma_o e^{(\omega t+\delta)i} \]  \hspace{1cm} (6-9)

*Equation 6-9: Dynamic and loss modulus expressions*

\[ \varepsilon = \varepsilon_0 e^{i\omega t} \text{ And } \sigma = \sigma_o e^{(\omega t+\delta)i} \]  \hspace{1cm} (6-10)

*Equation 6-10: Stress and strain expressed in complex numbers*
The complex modulus $E^*$ can then be expressed as:

$$E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_o e^{i\delta}}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} (\cos \delta + i \sin \delta) = E' + i E''$$ \hspace{1cm} (6-11)

*Equation 6-11: Complex modulus as a function of dynamic and loss modulus*

The real portion of the complex modulus expression describes the ability of the material to store potential energy and release it upon deformation. The imaginary portion is associated with energy dissipation in the form of heat upon deformation. Equation 6-11 is rewritten for shear modulus as:

$$G^* = G' + i G''$$ \hspace{1cm} (6-12)

*Equation 6-12: Shear modulus expressed in a complex number*

Where $G'$ is the storage modulus and $G''$ the loss modulus.

The phase angle is given by

$$\tan \delta = \frac{G''}{G'}$$ \hspace{1cm} (6-13)

*Equation 6-13: Phase angle as a function of dynamic and loss shear modulus.*

Tensile testing was used for experiments. It is a mode ideal for examining thin specimens. Clamped at top and bottom, the specimen is subjected to an underlying tensile stress to prevent it from buckling during dynamic loading.
6.3.4 Sample preparation

For dynamic mechanical analysis, both unidirectional and 2/2p samples were cut with dimensions of 40 mm × 10 mm (length and width). A Q800 DMTA (TA Instruments, TX, USA) operating in tension measuring system was used to evaluate the specimens. The DMTA equipment was calibrated using a metallic standard. The experimental conditions used were: 1 Hz frequency, heating rate (2.5, 3 and 5° C/min for up; and 5, 10,15° C for 2/2p) with temperatures ranging from 25° C to 200° C. Before the start of each experiment, the equipment was stabilised at 25° C for 5 minutes.

6.4 Scanning Electron Microscopy

6.4.1 Equipment description

A FEI quanta 200 (E) SEM +EDX (FEI Company, OR, USA) was used for all the experiments. A simple schematic showing the principle of scanning electron microscopy is shown in Figure 6-11 [175].

![Figure 6-11: Principle of SEM diagram](image-url)

[126]
The quanta simultaneously provides a secondary electron (SE) and back-scattered electron (BSE) imaging in low vacuum mode. The Quanta 200 has a 50 mm motorised stage (x/y travel), with a motorised z-range of 25 mm [176].

ImageJ (National Institute of Health, MD, USA) was used to characterise the SEM images. The surface areas of voids observed under the scanning electron microscope were calculated by fitting a polygon in ImageJ over sections.

The diameter of fibres were calculated by fitting an ellipsoid to the transverse section of fibres observed under different magnifications with the Quanta 200. The average height and width of the ellipsoids were further averaged to give an estimate of the fibre diameter. Higher magnifications allowed a higher precision of fibre diameter whilst lower magnifications allowed for a higher sampling.

6.4.2 Sample preparation

The samples were prepared using a three-step protocol: fixation, mounting and coating.

![Image of SEM samples with different preparation protocols]

*Figure 6-12: SEM samples with different preparation protocols*

Specimens were mounted on stubs appropriate for the particular scanning electron microscope function being used. To increase the quality of the images obtained from the SEM, a second batch of samples were coated using a sputter coater. The samples were coated with agar silver before being placed in the SEM chamber (Figure 6-13).
A sputter coater is a plasma chamber with low discharge capability which radiated a target made of heavy metal with argon atoms. Typically, the target consisted of 60% gold and 40% palladium. Gold was preferred because it has in theory, a high electron output for secondary electrons, whereas when palladium is added, it is because it provides a more contiguous surface of metal [177]. Also, the mounted samples were coated with silver.

![Figure 6-13: Carbon specimen sample embedded in resin and coated with agar silver](image)

Images of polished cross-sections samples were taken using the Quanta 200 in compositional imaging mode, which used backscattered electrons to highlight elemental composition with areas of higher average atomic number appearing brighter in images. This mode was helpful to distinguish the resin surrounding the fibres and/or any voids.
6.5 Torsion test

A Servo Hydraulic Instron 8802 (Tension and Torsion) 100 Load Cell (kNm) (Instron, MA, USA) from the Northwest Composites Centre was used for the torsion experiments.

![Picture of Instron 8802](image)

*Picture 6-1: Photography of the Instron 8802 used for torsion testing*

6.5.1 Torsion theory

Barré de Saint-Venant’s was a pioneer in developing a technique to measure torsion of non-circular specimens [178, 179].

In the 1990s, Saint-Venant’s theory was further developed by JM Whitney, who presented a solution to the torsional behaviour of non-circular cross sections which incorporated transverse shear deformation for the torsion of rectangular plates [180, 181]. Since, different test methods to evaluate shear modulus and shear strength of rectangular bards have been developed [182-184] and recommenced by the testing standard agencies, such as European Committee for Standardization and the American Standard of Testing Methods.

The BS EN ISO 14129:1998 Fibre reinforced plastic composites – Determination of the in-plane shear stress/shear strain response, including the in-plane shear modulus and strength by ±45° tension test method [185] was used in these experiments to determine in-plane shear stress/shear strain response, including the in-plane shear modulus and strength of 15 laminate samples.
6.5.2 Sample preparation

The tested laminates were all made from 2/2 twill prepregs and fabrics. The laminates were moulded from flat aluminium panels. Five layup variations were used to manufacture the panels:

- \([\pm 45/0](p/d/p)_s\) represents the symmetric layup of 2/2 prepreg and 2/2 dry carbon fabric at -45/+45 angles
- \([(-45/\alpha)/0/(\alpha)/+45](p/f/d/f/p)_{2s}\) represents the symmetrical layup of a 2/2 prepreg ply, MTM57 resin film and 2/2 dry carbon fabric at -45/0/+45 angles
- \([(-45/0/+45)(p/d/p)]_{2s}\) represent the symmetrical layup of UD prepreg and dry UD carbon fabric
- \([(-45/0/+45)(p/d/p)]_{2sri}\) represent the symmetric layup of 2/2 prepreg and 2/2 dry carbon fabric where both vacuum bagging and resin infusion are used as manufacturing processes
- \([\pm 45/0](p/p/p)\] represent a 3 ply 2/2 prepreg layup at -45/0/+45

The specimens were cut to the same lengths and widths, 200 mm by 50 mm. They were flat and free for many twists. The surfaces were free from starches and they conformed to these requirements by visual observation.

The test principle consisted of placing a rectangular laminate sample where cross-section of the fibres is oriented at ± 45° of the specimen axis onto a Hydraulic Instron. To determine the shear modulus, the strains parallel and perpendicular to the specimen axis are measured. The test is terminated at \(\gamma_{12} = 0.05\) if failure has not occurred before the rotation angle of the machine reached 45° (excluding premature failure at or within the grip). Figure 6-14 presents a schematic of a specimen sample under torsion.

\[\text{MTM57 resin film}\]
The in-plane shear stress $\tau_{12}$ is expressed as:

$$\tau_{12} = \frac{F}{2bh} \quad (6-14)$$

*Equation 6-14: In-plane shear stress*

Where $F$ is the instantaneous load applied on the specimen sample, $b$ the width of the sample and $h$, the thickness.

The in-plane shear strength $\tau_{12M}$, expressed in megapascals is expressed as a function of the instantaneous load at failure by the product of twice the specimen cross-sectional area.

**Figure 6-14: Drawing of a laminate test sample for torsion testing. Sample showing axes**
\[ \tau_{12m} = \frac{F_m}{2bh} \]  

(6-15)

*Equation 6-15: In-plane shear strength*

Where the test is terminated before failure, the value of \( F_m \) is that of the load measured at \( \gamma_{12} = 0.05 \).

The in-plane shear modulus is expressed as:

\[ G_{12} = \frac{\tau_{12}'' - \tau_{12}'}{\gamma_{12}'' - \gamma_{12}'} \]  

(6-16)

*Equation 6-16: In-plane shear modulus*

Where \( \tau_{12}' \) is the shear stress at a strain \( \gamma_{12}' = 0.001 \), \( \tau_{12}'' \) is the shear stress at a strain \( \gamma_{12}'' = 0.00 \).
CHAPTER VII

7 MOULD FABRICATION

Moulds are usually constructed from hardened tool steel but it is possible to use other materials such as CSM providing the moulds are well maintained. Two complex moulds were manufactured and used for vacuum bagging. The first, an aluminium mould was manufactured by CNC (see 11.1 Aluminium mould, page 188).

The second was a CSM mould shaped as a fan blade Picture 7-1.

Figure 7-1: Aluminium mould

Picture 7-1: Blade from Siemens, part number BD81562
Because of the curves and sharp corners in the design, the mould could only be manufactured if it was split into four parts. To allow ejection of components with undercuts, parts of the mould had to open at 90° to the main mould opening directions. The blade pattern was first manufactured using silicone; however, the surface finish of the silicone blade was not adequate for making a split mould.

The metallic blade was used as the pattern instead. The blade was therefore “divided” into parts, two nose ends and two tail ends.

![Blade divided in 4 sections for moulding](figure7-2)

The punch was made of two parts, one obverse nose end and tail end. Similarly, die was also made of two parts, a revers nose and tail ends. Each part of the mould was made individually. Flanges were necessary to support the mould structure but also separate the four sections during the mould manufacturing process. White fluted signboards were used as barrier material, and attached to the blade using plasticine.

For any moulding process, the mould would require flanges to be extended beyond the point where the mould part ends. These extensions are important for a number of reasons: first, with repeated usage, a mould tends to become chipped and damaged. By adding extensions, the damages are transferred to the extra area created by the barriers. Also, the barriers provide the additional stiffness required to ensure the mould is stiff and straight.
Once the barriers had been created, the entire blade was cleaned with acetone and left to dry for 15 minutes. Then a single coat of a release agent (Easycomposites Ltd, Cheshire, UK) was applied on each section and left to dry. The process was repeated five times as recommended by the manufacturer. An epoxy tooling gel coat was applied on one of the 4 sections of the blade and left to dry for several hours.

![Image](image.png)

Figure 7-3: Tooling gel coat applied on the obverse tail end of the mould

In total, 3 coats of epoxy gel were applied on the obverse tail end of the mould. The gel coat was a barrier between the surface of the blade and that of the mould. A thin barrier would allow prints through from the CSM and leave irregular marks on the mould surface. Also a thin barrier would easily crack and allow for poor quality final parts.
After the four layers of tooling gel coat had dried, lugs were created at regular intervals using small pyramid shaped filleting wax. These allow the mould to properly lock when required.

![Image showing logs on the mould](image.png)

*Figure 7-4: Logs’ print through on reverser nose end of the mould.*

A 100gsm of CSM is laid on the mould surface. This thin mat would insure a surface free distortion, ready for the main bulk CSM layers to be applied. The thin layer was brushed with a single coat of coupling coat. The tooling resin was an epoxy which had different characteristics from the tooling gel coat (vinylester resin, Easycomposites Ltd, Cheshire, UK).

The coupling coat was a barrier between the two resins which acted as an interface to insure total bonding between the two resins. Then, 2 plies of 300 gsm CSM and 4 plies of 400gsm of CSM were cut to shape and laid up onto the mould surface. They were then coated with an epoxy tooling resin catalysed with Methyl Ethyl Ketone Peroxide (MEKP) at 2%. The layup was left to cure overnight.

The same process was further repeated three more time to complete all the sections of the mould. The blade was left in the mould during the whole process. Before the mould was split, the flanges were drilled at regular intervals to ensure accurate alignment for the assembly bolts.
Figure 7-5: Holes on mould flanges

The mould was left to rest for 24 extra hours before it was split open, Figure 7-6.

Figure 7-6: CSM mould

The finished mould was polished to a professional finish using first 400 grit silicon carbide sanding paper, then to 600, 800 and finished with 1200 grits using wet sanding. Once sanded, the mould was left with a satin finish. A polishing compound Polarshine T10 from easycomposites Ltd was applied by hand on the surface with a cloth to a full gloss finish.
Figure 7-7: Part made from UD prepreg and UD fabric. Aluminium mould

Figure 7-8: Part made 2/2 prepreg and 2/2 fabric. Blade mould
Table 7-1: Common materials used for mould making, summarises the materials used the most to make mould besides metal. They each have their strength and weaknesses [186, 187].

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
<th>End Use</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Polyester GRP</td>
<td>Low</td>
<td>Ambient temperatures to mould polyester or vinylesters parts</td>
<td>Polyester resin mould have poor dimensional accuracy and are prone to distortion, they are not sub optional for producing epoxy parts</td>
</tr>
<tr>
<td>Epoxy Putty</td>
<td>High</td>
<td>Used for vacuum bagging and infusion of intricate parts</td>
<td>Easy and fat to use, is compatible with temperatures up to 80°C after a post cure cycle</td>
</tr>
<tr>
<td>Epoxy/Epoxy Glass</td>
<td>Medium/High</td>
<td>Used for vacuum bagging and infusion of larger structures</td>
<td>Offers a method for reducing cost and increasing strength over the epoxy putty for larger structures.</td>
</tr>
</tbody>
</table>

*Table 7-1: Common materials used for mould making*
CHAPTER VIII

8 RESULTS AND DISCUSSION

8.1 Differential scanning calorimetry and Dynamic mechanical analysis

As described above, the heat flow signal is composed of several parts, but traditional DSC can only measure the sum of those parts and illustrate that sum in a single signal. With Modulated Differential Scanning Calorimetry (MDSC), multiple signals are generated in a single experiment so that each of the components of the total heat flow signals can be shown and analysed independently.

All the samples weighed 5mg for consistency. The first samples from the 2/2 prepreg were used to obtained both dynamic and isothermal measurements for the curing process. Figure 8-1 shows a DSC curve obtained from the 2/2 prepreg. For dynamic measurements, the 2/2 prepreg was scanned from -50 to 300°C.

![DSC curve](image)

*Figure 8-1: Dynamic cure curve of the 2/2 prepreg at the heating rate of 5°C/min*
Figure 8-1 outlines 2/2 prepreg heat flow as a function of temperature. The graph is used to obtain information on $T_g$, the enthalpy of crystallisation, the characteristics transition temperatures, the percentage of cure and the heat capacity. Enthalpy is a thermodynamic parameter used to determine the thermal events of a material under constant pressure. The enthalpy change of a system is the sum of the heat flowing into it and the work done by it.

The glass transition temperature was measured at 97.40°C. (Figure 8-2) and determined by using the point of inflection method. The point of inflection, $T_{i,g}$, was obtained by determining the temperature of the maximum in the derivative DSC signal [188]. It was observed that the glass transition was registered at a lower temperature than the one suggested by the manufacturer (120°C). This was due to the slower heating rate of 5°C/min. Lower heating rate favours a large number of chemical groups to react in the epoxy. Above the glass transition, 2/2 prepreg polymer chains posed a notable mobility. For the glass transition, there was no dip or peak, either. This was because there was no latent heat given off, or absorbed, by the polymer during the glass transition. In the glass transition it was only possible to observe a change in the heat capacity of the polymer [189].

It is verified that the onset of an exothermic event is registered at a lower temperature of 124.22°C for a slower heating rate because the lower heating rate favours a larger number of chemical groups to react. The enthalpy and the order of reaction are related to the area above the DSC curve, which is directly proportional to the epoxy groups consumed during the cure [190].
The percentage of cure is found to be at 77.01% when it reached the cure temperature of 135.09°C (Figure 8-3). This cure temperature was reached after 35.22 minutes (Figure 8-4).

Figure 8-2: Tg of 2/2 prepreg at 5°C/min ramp.

Figure 8-3: Percentage of cure at 5 °C/min ramp as a function of T
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

The enthalpy $\Delta H$ was calculated by integrating the area between the peak of the heat flow curve and its baseline, it was found to be 22.99 J/g [191] (11.3 Heat capacity unit formulation, page 189).

Two further heating rates were carried out using the DSC dynamic heating method, 10 and 15°C/min. If the % of cure is too low, the resin and the part itself may fail as the resin will exhibit a low $T_g$. At 5°C/min, the $T_g$ was 22°C lower than the manufacturer’s suggestion. The heat capacity $C_p$ for each heating rate was found to be 38.61 J/g and 64.13 J/g. The heat capacities increased with the heating rates as energy is required to increase the samples ‘temperatures by one degree [192]

Figure 8-5 shows the heat flow results for 10 and 15°C/min heating ramps. The percentage of cure at 10 and 15°C are 61.39 and 45.85% respectively. It took 12.96 minutes for the temperature to reach 146.71°C when the ramp was at a rate of 15°C/min. At different cure temperatures, the isothermal cure heat is different. The glass transition temperature $T_g$ was found to be decreasing with increasing heating rates. The manufacturer for 2/2 prepreg did not recommend a dynamic cure cycle.

\[\text{Figure 8-4: Percentage of cure at 5 °C/min as a function of time (t)}\]
From Figure 8-4 it was deduced that a slower ramp rate would allow 2/2 prepreg to cure more uniformly overall. As mentioned earlier, this would be due to the fact that lower heating rate favours a larger number of chemical groups to react. Further, it was showed that for higher heating ramps as in (Figure 8-6), percentages of cure were much lower. Figure 8-5 illustrates the dynamic DSC curves of 2/2 prepreg at different heating rates.

From the literature the appropriate heating rate is the one which provides the largest heat of reaction [193], 64.13 J/g. Ideally, the heat of reaction should be independent of the heating rate. However, several reasons can influence this: if the heating rate is too fast, there may not be enough time for the reaction to proceed to completion. If the heating rate is too slow, its signal may be too low for the DSC to detect all of the heat being evolved [194].

![Dynamic DSC curves of 2/2 Vary-prepreg at 5°C/min, 10°C/min and 15°C/min heating rate](image)

*Figure 8-5: Dynamic DSC curves of 2/2 Vary-prepreg at 5°C/min, 10°C/min and 15°C/min heating rate*
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

Figure 8-6: Percentage of cure at 10 and 15 °C/min as a function of T

The resin rich and resin starved stacks were combinations of prepregs, film and dry fabrics. The ideal heating ramp was one that would suit all the materials in the layups, so that the final part would be suggested to the least stresses during curing. The glass transitions at 5, 10 and 15°C/min ramping rate are represented in (Figure 8-7). At 10 degree heating ramp was chosen as the ideal dynamic ramp for the cure.

Figure 8-7: Glass transitions at 5, 10, 15°C/min. Tg is decreasing with increasing temperature.
The unidirectional prepreg DSC curves were also recorded.

![DSC of MTM57 prepreg at 5, 10, 15°C](image)

**Figure 8-8: DSC of MTM57 prepreg at 5, 10, 15°C**

The reading for all 3 ramping rates did not provide readings for Tgs. At 5 °C/min and 15°C/min ramping rates, the system curing temperature noticeably increased.

![DSC of MTM57 with cure temperatures](image)

**Figure 8-9: DSC of MTM57 with cure temperatures**
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

The ramping temperature at 5 and 15°C were the only one which provided reading for cure temperatures. At 5°C/min, the sample cured at 134.22°C, the cure temperature increased with ramping temperature to 153.26°C.

The DMA analysis for a 2 ply - 2/2 prepreg provided values for the storage and loss modulus values. The frequency was fixed at 1Hz with a 5°C/min heating rate.

Figure 8-10: DMA analysis of 2 ply - 2/2 prepreg at 1Hz

Figure 8-10 shows the storage and loss modulus of the 2/2 prepreg under tension, there is well defined glass transition for the laminate, which is around 90°C. The DSC experiments on 2/2 prepregs gave a glass transition fluctuating around similar boundaries. Since the material has crosslinked, it has no melting point and in this respect reassembles an amorphous material. The storage modulus graph is declining to near zero. However, after the glass transition, the values of the storage modulus mean that the 2/2 is still exhibiting load bearing characteristics
Figure 8-11 tanδ plateaus after the system has crosslinked.

Figure 8-11: DMA of 2 ply -2/2 prepreg as a function of loss modulus and Tan δ

The intersection of the displacement and modulus shows that the system has fully reacted.

Figure 8-12: DMA analysis of 2 ply 2/2 prepreg as a function displacement
For a resin starved layup, Figure 8-13 shows the DMA analysis of 2/2 prepreg/dry fabric as a function of storage and loss modulus and tanδ. On this reading, the Tg reflects literature [195].

The glass transition temperature using the DMA was determined between 92 and 93°C. In earlier experiments, the DMA analysis of 2 ply -2/2 prepreg at 1Hz the Tg was determined to have a Tg around 90°C.

Figure 8-13: DMA of a resin starved 2/2 prepreg and dry fabric layup.
The spider diagram below represents the effect of the 3 heating rates (5, 10, and 10°C) on the glass transition, enthalpy, time, and percentage of cured system of the 2/2 prepreg.

Spider diagram
In the literature, there are clear differences between Tg, enthalpy, and heating rate; to choose the best cure heat, with no rheology data available, a different approach was taken to choose the most appropriate heating ramp.
8.2 Scanning Electron Microscopy and Optical Microscopy

In Figure 8-14, an estimation of fibre orientation ratios were carried out on 2/2 Twill and UD prepregs and dry fabrics. Fibre orientation can be observed in optical micrographs (A) and confirmed using SEM (B). Optical micrographs display a much higher surface area, allowing an estimate of the different fibre orientation ratios (C). Arrows point out different orientations with red for fibres in the warp direction, green for fibres in the weft direction and orange for transverse fibres.
Figure 8-14: 2/2 prepreg and dry fabric layup. (-45/0/+45)

Sample obtained using aluminium mould
The mounted unidirectional prepregs in Figure 8-15 illustrate the fibre to resin distribution. The top left image was that of a 3 ply UD prepreg layup (p/f/d/f/p)(-45:/0:/+45). The part is resin rich. Fibre directions are clearly identifiable. The resin and fibres seem to form a homogenous surface at a lower magnification. However, at 3000 x, the resin appeared to be a combination of small solid like stones (red arrows) scattered around the fibres (image in the green contour).

Figure 8-15: 3 plies UD prepreg
(p/f/d/f/p)(-45:/0:/+45)
Figure 8-16: 2/2 prepreg, 6 plies layup

\((-45/0/+45)(p/d/p)^2\)

Figure 8-16 shows the presence of voids in 2/2 prepreg and dry layups. The samples were taken from the corner edges of the part made from the obverse nose end tip of the blade (Figure 8-17). Although a randomised sample collection was collected, it was not possible to see any angles, sharp corners or curvatures in the sample specimens.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

Figure 8-17: Obverse nose end of blade part

Figure 8-18 shows the presence of voids between the 3 UD (-45/0/+45)(p/d/p) plies. The sample was resin starved and delaminated: the plies did not bind properly. The fibres in the dry fabric between the prepreg plies were parallel to the nominal fibre direction layup. Each ply in the layup could be identified individually under the scanning electron microscopy. However, it was not possible to determine the resin to fibre ratio.

Figure 8-18: SEM of UD prepreg (p/d/p)(-45/0/0/+45) sample
Although the samples were cut from a combination of either flat plates, aluminium mould or the nose end of the blade, no real contour could be noticed once test specimens were cut from the parts and conditioned for characterisation. The defects which were recorded were characterised as voids. The voids did not seem to be caused by any one conclusive effect, either during layup, curing or sample preparations. All the samples, made from specimens prepared for the SEM and the optical microscope by a mounting or coating preparation protocol, presented overall a good bonding of plies. Surfaces, under the microscopes did not provide enough information to suggest that ply/ply or ply/tool interfaces were not free of wrinkles.

Figure 8-19 shows an SEM of a sample of 2/2 prepreg (p/f/d/f/p)(-45/:α//0/:α/+45)² using a back scattered electron scanning method. The image was magnified to 500 x.
The scanning electron microscopy on the 2/2 prepreg/film/dry fabric layup revealed voids on a number of samples. In this example, the voids are pointed out by arrows. The largest (red arrow) has a surface area of over 34000 µm². The total volume of those voids is not possible to estimate from SEM sections.

In contrast, Figure 8-20 shows the scanning electron microscopy of a 3 ply 2/2 prepreg layup. Although the ply sequencing can be easily determined and a B-stage resin is already part of the system, the surface of the samples showed “pseudo-voids”
These voids were inconsistent throughout the analysis. They did not depend on the process used during the manufacturing of the part. These voids surface areas had huge variations starting from 23 $\mu$m$^2$ and increasing to surface areas over 36168 $\mu$m$^2$. The largest void area is represented by the yellow arrow.

![Figure 8-21: SEM of 3 ply 2/2 prepreg sample at -45/0/45](image)

Some of the samples were processed to extract a fibre to resin ratio. A sample obtained from the blade mould with a 2/2 prepreg and MTM57 resin film layup is represented in Figure 8-22. Here, some electron micrographs displayed fibres (red arrow) embedded in resin (orange arrow). These were processed with ImageJ as described on the left to estimate the number of black (fibres) and white (resin) pixels.
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

1. 8 bit Greyscale Scanning Electron Micrograph displaying fibres and resin

2. Crop and sharpen image

3. Threshold and convert to binary image

4. Extract pixel values

Figure 8-22: Micrographs of 2/2 prepreg and dry fabric
Samples obtained from obverse nose end of blade part
Micrographs of 2/2 prepreg and dry fabric layup were cropped in ImageJ and transformed in 8 bit Greyscale images. The extracted pixel values on the 8 bit Greyscale scanning Electron Micrographs are thresholded into two colours: black and white. At face value, these results would imply that the dark regions extracted were voids and the white regions the fibres. The resin would be in between these two thresholds. This is not strictly true as the images obtained were only topographic, and the resin and voids could not be differentiated.

The diameter of fibres present in 2/2prepreg, dry fabric and MTM57 resin film was calculated by fitting an ellipsoid to the transverse section of fibres observed under three different magnifications (7000x, 2000x and 500x) with a scanning electron microscope.

The average height and widths of the ellipsoids were further averaged to give an estimate of the fibre diameter. Higher magnifications allowed a higher precision of fibre diameter whilst lower magnifications allowed for a higher sampling. As such, 500x magnification allowed the sampling of over 50 transverse sections whilst 2000x yielded 31 samples and 7000x yielded 8 sections. The average diameters (with standard error of mean (SEM)) observed were 7.55±0.21, 7.37±0.25 and 7.12±0.33 µm, respectively. Measurements at 2000x magnification (below) offer the best sample size to precision trade-off. Raw data are presented in the appendix.
In conclusion, the largest voids surface areas were found on 2/2 ((p/f/d/f/p)(0/:α/-45/0/+45/:α/0))^2 At 34000 µm².

Random samples taken from the micrographs of 3 plies 2/2 prepreg layups were also cropped and transformed in 8 bit Greyscale images using ImageJ. The same method of extracting the pixel values on the 8 but Greyscale scanning Electron Micrographs were used. The thresholds between the white and black colours were not clearly identifiable. This result was not expected because it was possible to isolate and measure some of the dark regions registered on the UD samples (assumed to be void regions), hence the name “pseudo-void”.
Both the aluminium mould and the chopped strand mould generated good surface finished parts. However, with repeated use, the chopped strand mat mould required further surface treatment so as to maintain a mirror surface finish. Epoxy gel coat was used on the mould surface Figure 8-24.

Figure 8-24: surface finish of the blade reverse nose end
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

The percentage of voids are imaged from the top surface of the samples. (see 11.4.3 % of voids page 193 for sample section):

Figure 8-25: % of void in a 1cm x 1cm sample

It should be noted that the % of the voids was based on cross-sectional areas of 1cm x 1cm as determined from the SEM images.
8.3 Torsion testing

De-lamination is one of the major failure modes. Inter-laminar shear stresses are the source of failure, unique in composite structures. With the different layup sequences which were tested under torsion, no specimens exhibited the presence of any out of plane stresses at ply/plply interfaces.

In the tableau, different layup were used to manufacture the parts. Resin infusion and vacuum bagging were used as manufacturing processes.

Each part was made of a combination of prepreg, dry and/or resin (in liquid or film form).

The part laminate orientation codes were slightly amended to accommodate notation for the type of inserts: prepreg, fabric or film. All the parts used vacuum bagging and only one case used both vacuum bagging and resin infusion.

The following notations were used to label and track each characterisation:

- \([\pm 45/0](p/d/p)]\) represents the symmetric layup of 2/2 prepreg and 2/2 dry carbon fabric at -45/45 angles
- \([-45/(\alpha)/0/(\alpha)/+45](p/f/d/f/p))]_2s\) represents the symmetrical layup of a 2/2 prepreg ply, MTM57 resin film  and 2/2 dry carbon fabric at -45/0/45 angles
- \([-45/0/45](p/d/p))]_2s\) represents the symmetrical layup of UD prepreg and dry UD carbon fabric
- \([-45/0/45](p/d/p))]_2si\) represent the symmetric layup of 2/2 prepreg and 2/2 dry carbon fabric where both vacuum bagging and resin infusion are used as manufacturing processes
- \([\pm 45/0](p/p/p)]\) represent a 3 ply 2/2 prepreg layup at -45/0/45

\(^9\)MTM57 resin film
Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

<table>
<thead>
<tr>
<th>Layup sequence</th>
<th>$[(\pm 45/0)(p/d/p)]_4$</th>
<th>$[(-45/(\alpha/0)/(\alpha/45)]$</th>
<th>$[(45/0/45) (p/d/f/p)]_{2s}$</th>
<th>$[(45/0/45) (p/d/p)]_{2air}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of sample</td>
<td>Sample sequencing number</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Position (mm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Load (kN)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rotation (°)</td>
<td>0</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Torque (N.m)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>$\tau_{12}$</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$\tau_{12M}$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\epsilon_x$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\epsilon_y$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma_{12}$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 8.1: In-plane shear testing of 2/2 prepreg
In Table 8-1, the numbers 1, 2, 3…group samples with the same layup. Column A represent a 3 ply 2/2 prepreg layup. This layup was used as the baseline for the characterisation of the subsequent layups.

The recorded results from the torsion machine are compiled in Table 8-1. The loads applied on the samples were extremely small, in the order of $10^{-5}$. The resulting rotations, shear stresses and strains did not affect the structure of the specimens. No specimen failure was recorded. The components of all out of plane stresses are zero. Hence, cohesive and adhesive failure do not take.
CHAPTER IX

9 CONCLUSION AND RECOMMENDATIONS

9.1 Conclusion

The present research set out to investigate whether introducing resin rich or resin starved fabric stacks during the forming stage of a prepreg part would result in the production of high end OOA carbon fibre composites.

The following conclusions have been drawn:

1. From the thermal characterisation and microscopy investigation, some conclusions can be made. The in-plane shear testing confirmed that the characterised samples did not fail during torsion. No significant shear stresses, shear strengths and modulus could be determined by the torsion testing using BS EN ISO 14129-1998 method.

2. The 2/2 twill prepreg (with slip layers) produced the smallest % of voids compared to the 3 ply prepreg layup. By introducing stacks of resin rich or resin starved layer between the plies, it has been argued that control of friction can be achieved hence improving the quality of the final parts. The largest voids found in parts made using wet lubricants were measured to between around 34000 and 35000 μm$^2$ compared to voids found in 3 ply prepreg parts at 36168 μm$^2$.

3. Two moulds were made during the research. One was manufactured using aluminum and the other using chopped strand mats. The different material for the mould manufactured were decided based on the hypothesis that CTE would have an impact during curing cycles. The aluminum mould produced parts with a more consistent finish. Vacuum Bagging and Resin Infusion were used as manufacturing processes for the various parts. A 2/2 twill prepreg and UD prepreg were used to make the parts. A MTM57 resin film was also used as lubricant in the layups.

4. For the 2/2 twill prepreg, transition temperature was found to be between 90 and 100°C. The glass transition temperature was found to be closer to 100°C when differential calorimetry was used for thermal characterisation. Using dynamic Mechanical Analysis, the Tg was found to be around 90°C.
9.2 Recommendations

The images obtained using SEM can be further improved using fluorescent dyes such as Rhodamine B or cyromazine. Semi-thin section (1-2 μm thick) preparation of samples to be investigated under optical microscope can be a potential powerful tool for characterisation, although ultrathin (>200 nm thick) sections are typically used for transmission electron microscopy, resolving details at magnifications of up to 100,000x.

The characterisation of the effects of introducing resin rich or resin starved stacks in prepreg layups could benefit from introducing heat prior to consolidation.

All the layups done in relation to the experiments were either carried on flat surfaces or by using a vacuum bag on a die mould during consolidation (complex shapes). By replacing the vacuum bag with a frame such as that of a rigid T-frame (Figure 9-1), the layers can potentially move more freely with respect to one another.

![Example frame to improve drapability](image)

Figure 9-1: Example frame to improve drapability

Many promising studies have already been done investigating of the effect of clamps on composite manufacturing during their manufacturing processes. This frame, in combination with a compression press can be pushed onto the fabric, through the frame. The loads required for the press can be accessed at a later stage.
As in a the picture frame experiment [200], the T frame can impose shear behaviour to the plies. Strips of steel can be used to pin the sample on one or more sides, eliminating potential problems with slippage. However, any misalignment with the fibre and the flat face of the setup may potentially have a great effect on the measured stiffness. To witness deformation before and after the experiment, video recording of the experiment can be processed with Digital Image Correlation (DIC). The DIC technique enables a calculation of displacement and strain fields on an object surface by comparing sequential images during loading of an object. DIC has proven to be very effective at mapping deformations [201-203].

For applications outside of the aerospace or military industries, a detailed characterisation of this magnitude on the impact of introducing resin rich or resin starved stacks in the manufacturing of complex carbon fibre prepreg parts can be costly. Prepreg manufacturing has already hugely improved the quality of final parts made using liquid processing. The processing time for out-of-autoclave manufacturing has become very attractive to industries which could not afford to invest with this technology. Today, prepregs find uses in sporting goods, automotive, civil engineering, wind energy and transportation markets.

The forces which drive carbon fibre supply and demand are numerous and complicated. Few indicators have the capacity to substantially shift the carbon fibre market. However, large acquisitions by multinational companies such as Cytec Industries or TenCate Corporation are evidence that major producers are confident that the use of composites in higher volume is set to grow. Companies in the automotive or construction industries have been forecasted to increase the usage of carbon fibres and/or advanced composites in their manufacturing processes by 3.4 billion dollars by the end of the current year, Figure 9-2 [204].
On the other hand, global carbon fibre production is expected to reach 102.460 metric tonnes by 2020 [205]. The prepreg industry, once a niche industry is expected to reach an estimated value of £3.91 billion by 2019 [206]. For the manufacture of advanced composite parts, in terms of value, aerospace and defence are still the leaders in using materials such as prepregs for various applications, followed by wind power applications [207]. Figure 9-3 shows a cost breakdown for carbon fibre polymer structure composites used in the aerospace industry [208, 209].

Beside the aerospace industry, companies spend a large part of their manufacturing costs on tooling and quality control. Research and development are key to successfully attract “high street industries” into the composite world. Reducing defects encountered during manufacturing processes, improving quality of finish on parts, reducing curing cycles, making raw materials more accessible and investing in recycling are some of the concerns which need addressing.
The automotive industry is one of the fastest-growing industries in the marketplace and appears to be in the early stages of a long-term and substantial increase in the application of carbon fibre to structural and semi structural production vehicle components.
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London : Chapman and Hall.


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Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers


11 APPENDIX

11.1 Aluminium mould
11.2 Vary-Preg physical and chemical properties

- Vapour Pressure @ 25°C Negligible
- Appearance Flexible Solid
- Colour Black
- Volatile Content <1% By weight
- Odour slight
  - Inflammable point >150°
  - Decomposition temperature >250°
  - Self-ignition point >290°
  - Specific gravity 1.7g/cm³
- Solubility insoluble in water

11.3 Heat capacity unit formulation

The heat flow was expressed in W/g (J/sec/g). The ratio of the product of the temperature and the heat flow by the heating rate gave the enthalpy in J/g

\[
\left(\frac{J}{sec \cdot g}\right) \left(\frac{\circ C}{\circ C/sec}\right) = J/g
\]
11.4 SEM calculations

11.4.1 Hole sizes in wet lubricated samples

<table>
<thead>
<tr>
<th>Surface (square microns)</th>
<th>Hole 1</th>
<th>Hole 2</th>
<th>Hole 3</th>
<th>Hole 4</th>
<th>Hole 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDF5Se5_018</td>
<td>21690</td>
<td>8405</td>
<td>5056</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>PDF5mix1_013</td>
<td>3024.599</td>
<td>8144.601</td>
<td>6270.05</td>
<td>34684.58</td>
<td>14285.37</td>
</tr>
</tbody>
</table>

11.4.2 Fibre diameter

The unit of measurement is μm

The samples are numbered as follow:

Sample α dryX_00Y

α represents the sample layup sequence

X the sample number

Y is the image sequencing number automatically generated by the SEM.

<table>
<thead>
<tr>
<th>Sample 1 dry3_001</th>
<th>Area</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
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<tbody>
<tr>
<td>Average</td>
<td>43.76390323</td>
<td>115.2248</td>
<td>83.70968</td>
<td>188.7419</td>
<td>62.20829</td>
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Height

<table>
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<tr>
<th></th>
<th>7.245323</th>
<th>Average diameter</th>
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<td></td>
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<td></td>
<td>0.266051</td>
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Manufacture and characterisation of carbon fibre prepreg stacks containing resin rich and resin starved slip layers

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<tbody>
<tr>
<td>1</td>
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<td>31</td>
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<tr>
<td>2</td>
<td>61.337</td>
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<td>3</td>
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<td>186</td>
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<tr>
<td>4</td>
<td>42.338</td>
<td>110.21</td>
<td>39</td>
<td>216</td>
<td>24.858</td>
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<td>5</td>
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<td>42</td>
<td>201</td>
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<td>6</td>
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<td>216</td>
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<td>8</td>
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<td>39</td>
<td>212.125</td>
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<tr>
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<td>4.928054</td>
<td>15.79726</td>
<td>11.26491</td>
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<tr>
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<tr>
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<td></td>
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<td>0.20806</td>
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11.4.3 % of voids

<table>
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<tr>
<th>Layup sequence</th>
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<th>p/d/p</th>
<th>p/f/d/f/p</th>
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</thead>
<tbody>
<tr>
<td>Maximum void surface area (rounded at 3 decimal, μm²)</td>
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<td>34000</td>
<td>35000</td>
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<tr>
<td>Percentage (%)</td>
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The notations p, d, and f stand for prepreg, dry fabric and resin film respectively.