Development of Composite Materials for Extreme Low Temperature (Hydrogen) Applications

Student Name: Patrick White

Registration No: B00753309

Module Code: EEE802

Course Title: MEng Mechanical Engineering

Supervisor: Dr Calvin Ralph

School of Engineering

Faculty of Computing and Engineering

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Summary

This project investigates the mechanical and thermal response of composites when exposed to cryogenic temperatures. This project shows their potential application in cryogenic material storage for greener fuel infrastructure. Specifically, this study compares the mechanical properties of 2D laminates and 3D woven, layer-to-layer carbon fibre composites.

Results show that 3D woven layer-to-layer composites outperform 2D laminates in terms of Young's modulus and UTS. Results also show that 3D woven layer-to-layer composites are better insulating material compared to 2D composite laminate composites. However, both materials become more brittle with increased exposure to liquid Nitrogen. Despite this limitation, implementing 3D woven composites in solid-state cryogenic Vessels could contribute to developing a greener fuel infrastructure.

Future research opportunities include exposing the same composite materials to liquid Hydrogen during tensile and bend testing. This would more accurately represent what the composite materials would experience when storing liquid Hydrogen. Furthermore, polymer liners could be investigated to reduce permeability, additives for the effects on mechanical and thermal performance when exposed to liquid Hydrogen and investigation of Hoop stress.

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Nomenclature

Symbol/Abbreviation	Meaning	Units
NIACE	Northern Ireland Advanced Composites and Engineering	-
CT	Computed Tomography	-
Vf	Fibre Volume Fraction	%
DIC	Digital Imagining Correlation	-
RTM	Resin Transfer Moulding	-
UTS	Ultimate Tensile Strength	MPa
2D	2 Dimensional	-
3D	3 Dimensional	-
CFRP	Carbon Fibre Reinforced Polymer	-
CF	Carbon Fibre	-
PEEK	Polyether ether ketone	-
PEAK	Polyarylether ketone	-
LCP	Liquid Crystal Polymers	-
PEI	Polyether Imide	-

Note on Access of Contents

Chapter 1. Background

Currently, society heavily relies on the use of fossil fuel to supply power to our homes, and our personal devices. However, due to this consumption, 1143 Giga Tonnes of carbon dioxide has been released into the atmosphere between 1970 and 2018, (K Ghosh, 2020). The use of fossil fuels is set to increase with a further 1122 Giga Tonnes expected to be released between 2018 and 2050, (K Ghosh, 2020). This will lead to a predicted increase of 1°C in global temperature between 2018 and 2050, (K Ghosh, 2020). Predictions have shown 0.1°C of the 1°C will be due to the aviation sector, (Klöwer et al., 2021). Aviation is one of many sectors notorious for the use of fossil fuels. Hydrogen may offer an alternative solution, however in its gaseous state, it is not viable for aviation applications. Solid-state hydrogen may offer a more energy-dense source over gaseous while also being more environmentally friendly than current fuels.

Liquid hydrogen offers more in terms of energy in comparison to gaseous hydrogen. Storage of liquid hydrogen is not a new idea, but the materials used for the storage of hydrogen is important for the development of incorporating liquid hydrogen as a fuel source and potentially replacing fossil fuels. Currently, metallic vessels are the main material used for the storage of liquid hydrogen. But this becomes a problem if large amounts of liquid hydrogen is required at any one time. Due to the metallic material, the vessel will have a large amount of weight associated and may not be a viable material for the storage of liquid hydrogen.

Composites have been known for offering high-strength and low-weight solutions, however, due to the temperature at which liquid hydrogen is stored, -250°C, the mechanical properties of the material may be compromised. Composite structures are complex in what they can offer concerning materials, structure, and manufacturing techniques. For example, 2D laminate and 3D woven composites offer different advantages and disadvantages due to differences in architecture and so these will have a different mechanical response to mechanical input. However, concerning low temperatures, cryogenic temperatures may produce a mechanical response that is different from composites not exposed to cryogenic temperatures.

Therefore, it is important to understand and characterise the mechanical properties of the composite when exposed to cryogenic materials such as liquid Hydrogen.

1.1 Aims and Objectives

The main research aim for this project is to develop knowledge and understanding of current technology and materials used for the manufacture of composite vessels for extreme low temperature applications. The aims are broken down into the following.

Aims:

- Evaluate the mechanical performance of composite materials when exposed to cryogenic temperatures including the mechanical response of 2D and 3D composites to cryogenic exposure.
- Investigate the thermal properties of 3D composite structures of more traditional 2D composites.
- Evaluate the micro-scale effects that cryogenic temperatures have on the structure of the 3D woven, layer-to-layer and 2D laminate composite architectures.

To achieve the aims set out, objectives were set, which include the following;

Objectives:

- Conduct a Literature review on the current issues surrounding this topic including current solutions surrounding the materials, technology and techniques used for composite cryogenic storage vessels.
- Manufacture 2D and 3D composites for material analysis ensuring similar material variables including Fibre volume fraction (Vf), fibre and matrix material.
- Exposure of both composite structures to liquid Nitrogen.
- Conduct mechanical testing involving tensile testing of 2D and 3D composites exposed to the liquid Nitrogen and compare them to baseline samples.
- Use Microscopy to analyse liquid nitrogen's effects on the matrix and fibre structure.
- Use micro-CT scanning to evaluate the extent of cracking of the 2D and 3D samples when exposed to liquid nitrogen and comparing with baseline samples.
- Conduct a thermal analysis study on 2D and 3D composite materials.
- Evaluate the data, concluding on what material is best suited for cryogenic storage with areas of suggested recommended research.

1.2 Project Plan

A Gantt chart (seen in Appendix A1) was created to help achieve deliverables and achieve milestones throughout the project. The Gantt chart is split up based on the deliverables seen as a green hexagon in the chart. As the needs of the project are always changing, the document allows for constant updating which is crucial for setting deadlines and managing time and resources. The document allows for live time tracking of tasks that require attention. If the project is starting to fall behind schedule, this will be defined by the red line (which represents the present day). If the project is behind the red line, the task or tasks that are not completed in time will stay purple instead of grey. Grey signifies the completion of a task.

Along with the Gantt chart, a test plan (seen in Appendix A2) was also created to be updated in tandem with the Gantt chart. This allowed for ease of organising materials and procedures, ensuring that the project was on task, and deadlines were met, while also serving as a guide during testing.

Chapter 2. Literature Review

2.1 Abstract

Hydrogen as a fuel has its advantages but currently, the main storage state of hydrogen is gaseous, liquid storage of hydrogen is less common. Liquid state storage offers more energy by volumetric density. However, metallic vessels are commonly used when liquid hydrogen storage exits. Metallic vessels do not offer any weight-saving opportunities compared to composite materials. Composite vessels offer more of a strength-to-weight ratio in comparison to metallic vessels. For storage of liquid hydrogen composite materials will have to withstand -253°C (20 K). Hydrogen is also a small molecule and so the permeability is a concern also. This project aims to research the development of composite materials for extreme low temperature applications. This includes liner materials and 3D woven preforms.

2.2 Introduction

Composite materials have opened many doors concerning weight-saving opportunities. A composite material can be designed around the needs of the application it is intended for. Thus, further adding to the argument of weight-saving opportunities.

Hydrogen-powered vehicles have been in focus as a potential alternative to fossil fuels. The literature states, that hydrogen may become the main source of energy in the future replacing fossil fuel alternatives, (Momirlan & Veziroglu, 2005). Therefore, it is important to further develop knowledge and understanding of composite design and materials to further benefit future infrastructure and reduce carbon emissions with hydrogen potentially replacing fossil fuels.

Currently, hydrogen is mainly stored as a gas under pressure in vessels. However, hydrogen as a gas lacks energy concerning volumetric density (Armaroli & Balzani, 2011). To increase the volumetric energy density, liquid hydrogen and slush hydrogen can be used in combination, (Armaroli & Balzani, 2011). The extreme low temperature required to keep hydrogen in a solid state raises a few issues surrounding composite design and composition to ensure that the structure is mechanically stable, safe, and reliable over an extended period.

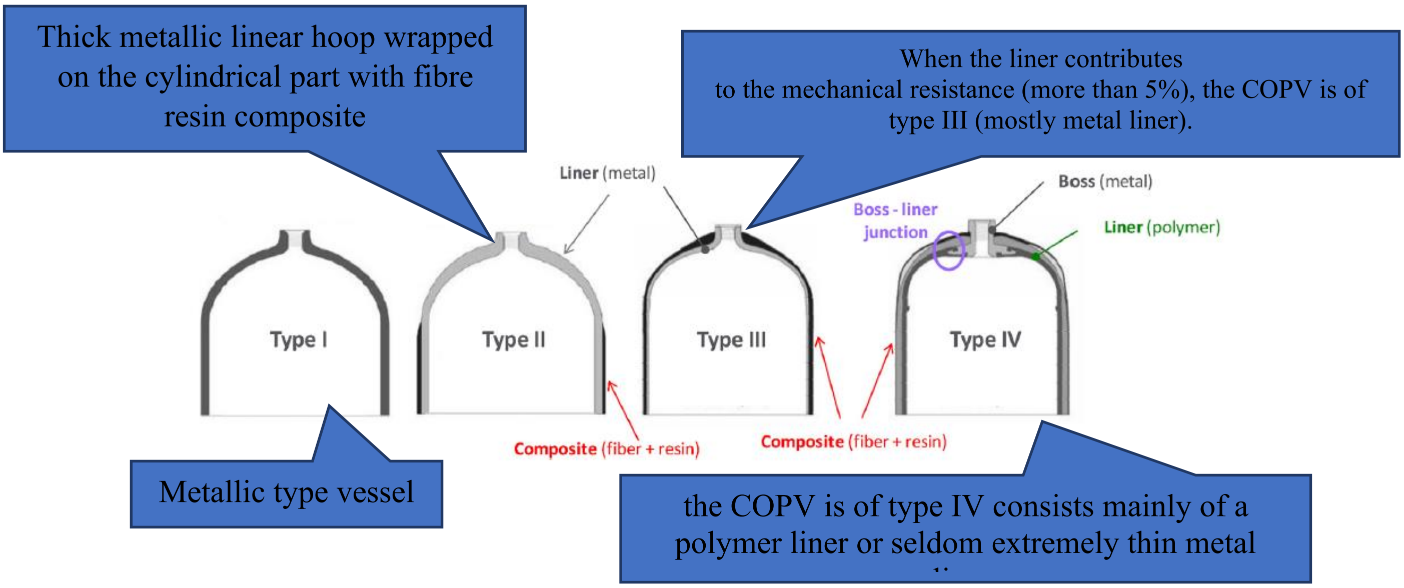
Solid hydrogen composite storage Vessels will have the ability to store a high volumetric capacity and so allowing more fuel to be stored in a smaller Vessel. Weight reduction can be decreased two-fold, as the Vessel would, potentially, be made from composite/polymer structures compared to metallic structures. Vessel volume will be reduced, further reducing the weight of the Vessel. These vessels can then be implemented into current hydrogen power vehicles to reduce weight and so increase range. They can be investigated for use in aerospace as the primary source of fuel. This would further reduce global fossil fuel emissions. Solid hydrogen composite storage Vessels could potentially be used in the military, aerospace, space, agriculture, and domestic sectors.

2.3 Review of Relevant literature

With a project of this nature, many variables can determine the success of the project. These variables that are mentioned in the literature are split into their relevant headings. It is important to first look at the current vessel design and structure.

2.3.1 Hydrogen storage and transport

Four main categories of hydrogen vessels have been mentioned repeatedly in the literature. These include type I, II, III and IV vessels. (Barthelemy et al., 2017) outlines the vessel types in detail concerning materials used and the structure of each category shown in Figure 1.



Thick metallic linear hoop wrapped on the cylindrical part with fibre resin composite

When the liner contributes to the mechanical resistance (more than 5%), the COPV is of type III (mostly metal liner).

Metallic type vessel

the COPV is of type IV consists mainly of a polymer liner or seldom extremely thin metal

Figure 1 Vessel types and their various material and structural configuration (Barthelemy et al., 2017)

Although this project is aimed at composite materials, it is important to evaluate all types of vessels and the materials and structure used for each vessel type. Currently, hydrogen can be stored as a gas, liquid or solid. For gaseous storage, metallic or steel vessels are the most common storage method, (Faye et al., 2022). Regarding Figure 1, it is fair to state that type I vessels are the most common. According to (Faye et al., 2022), these type I vessels have an operating pressure of 200 bar. The paper goes on to discuss composite cylinders (type II, III and IV) and how they can be used for the enhancement of volumetric storage (Faye et al., 2022). According to (Faye et al., 2022), composite vessels can withstand pressures as high as 800 bar.

For liquid hydrogen storage, (Abdalla et al., 2018 and Faye et al., 2022), state that the temperature required to liquefy hydrogen is -253°C (20 K). The vessel would require design for optimum insulation properties keeping in mind that the extreme cold may affect the material long term. Furthermore, It is important to note that storing liquid hydrogen, is energy intensive. The energy loss to store liquid hydrogen compared to gaseous hydrogen can be up to 40%, (Abdalla et al., 2018).

Transporting hydrogen comes with its problems. With hydrogen varying in different states within a range of temperatures and pressures, it can be an issue to transport. For example, hydrogen can be transported as a gas to which little energy input is required to maintain the gaseous state compared to liquid hydrogen (Abdalla et al., 2018). However in this state, as (Faye et al., 2022) paper points out, a kilogram of hydrogen gas can occupy 11m^3 at room temperature and pressure. Thus, if large amounts of gaseous hydrogen are required for any application, logistics and the efficiency of logistics are negatively impacted.

Furthermore, with liquid and solid hydrogen, the process of storing and transporting increases as the energy required to maintain these states increases. However, more hydrogen can be transported per unit of weight and volume. Also, with hydrogen being a highly flammable element, safety is a concern. Added pressures and extreme low temperatures required to maintain liquid and solid-state hydrogen add to these safety concerns.

2.3.2 Manufacturing techniques

Manufacturing techniques used to produce composite hydrogen fuel vessels are dependent on the materials and structure of the vessel. For thermosetting matrix material, filament winding is used, (Alves et al., 2022). For thermoplastics, tape layup is more suitable, (Atli-Veltin, 2018 and Alves et al., 2022). Both methods require the use of a mandrel for the composite to form around the profile of the vessel.

Thermoplastics are, however, complex to process compared to thermosets,(Alves et al., 2022). This is mainly due to the viscosity of the resins. Thermoplastic resins tend to be of high viscosity compared to thermosetting materials. Thermoplastic, once melted, (secondary bonds are broken) have long polymer chains which are hard to move by each other as thermosets will form a crosslinked structure formed through chemical bonding.

2.3.3 Composite materials for hydrogen storage

For composite hydrogen storage vessels, it is not only important to consider the materials, but the composite structure should also be considered as to what effects it has on the overall architecture of the vessel. And so subsequently, there are a few challenges associated with composites in contact with hydrogen.

Firstly, hydrogen is a small molecule, so small that permeability is an issue, (Barthelemy et al., 2017). Permeability is defined by (Sápi & Butler, 2020) simply as atoms passing through a material. Also, Composites and some polymeric materials can absorb water, with (Barthelemy et al., 2017) study stating that polyamides may absorb water up to several weight per cent. Both, permeability, and affinity for water absorption of composite materials can be reduced using liners, (Schutz, 1998).

(Sápi & Butler, 2020) detailed methods for reducing permeability including, the use of woven 3D composite preforms, toughened epoxy or thermoplastics resins and liners. However, (Sápi & Butler, 2020) paper only mentioned metal liners with no mention of polymeric liners. Whereas (Wang et al., 2022) study details the methods of modifying polymer liners for type IV storage vessels with no mention of 3D preforms. (Wang et al., 2022) mentions that high-density polyethylene (HDPE), polyamide (PA) and polyethylene glycol terephthalate (PET) are the most common liners used for type IV vessels. The paper goes on to detail methods of modification of matrix including, strength, thermal properties, gaining resistance and barrier properties. to achieve optimal weight reduction without compromising the mechanical performance of the liner and subsequently, the composite structure the use of polymer materials is required in place of metallic alternatives.

Although modifying the polymer liner and composite to reduce permeability and water absorption is important. It is also vital to consider other variables that may affect the structural integrity of the vessel. These variables include the coefficient of thermal expansion, depressurisation, leakage, material state when under load and cyclic temperature differences.

With a type IV vessel, there are several different materials used to produce the vessel. This presents the problem of different coefficients of thermal expansion (CTE) for different materials used for the structure of the vessel. (Schutz, 1998), discusses how materials interact with each other at varying temperatures. (Schutz, 1998) mentions that most materials under cooling will contract in length with carbon and aramid fibres expanding in the longitudinal direction during cooling.

Differences in CTE can lead to microcracking of the composite matrix. This is not ideal as the vessel's structural integrity will be compromised. Exposing the vessel to further mechanical damage under load. CTE is a worrying variable that is mentioned in the relevant literature, (Kim et al., 2007, Barthelemy et al., 2017, Sápi & Butler, 2020).

(Schutz, 1998) also mentions that glass fibres do not expand in the longitudinal direction due to their stiffness. The paper goes on to mention that this can be used for design to help prevent internal stresses build within the matrix and so reduce micro-cracking. This implies that although materials have different CTE, it is important to design around the needs and wants of the material properties under extreme cold and hot conditions.

Depressurisation is also a worry for vessels under pressure. With sudden pressure release of a carbon fibre composite pressure vessel results in the deformation of the liner, (Barthelemy et al., 2017). This could be a problem in the life cycle of the vessel whether accidental or purposefully quick emptying of the vessel. This may be a particular issue for maintaining the vessel as an accidental release of a high-pressure composite vessel during maintenance could result in permanent damage to the vessel and is also a health and safety concern.

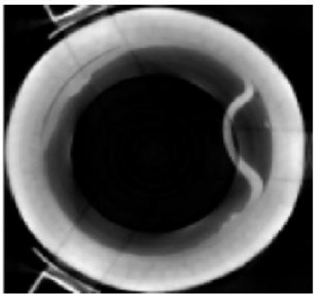


Figure 2 Deformation of polymer liner (Barthelemy et al, 2017)

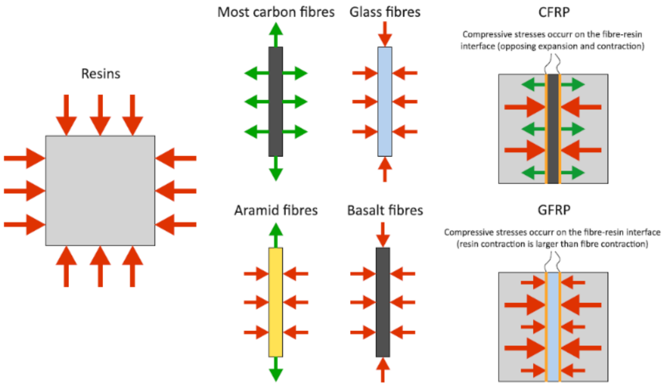


Figure 3 Summary of resin, fibre, and composite state during cooling (Kim et Al, 2007)

2.3.4 Extreme low temperature

The challenges associated with composites for extreme low temperature applications have been addressed. Several modifications can be carried out to the composite concerning the architecture of the composite itself and the structure of the vessel. These modifications include blending, integration of films, liners, development of resin systems, composites and 3D woven preforms.

2.3.4.1 Blending

For polymeric materials exposed to extreme low temperatures, blending has been used for optimising the material for extreme low temperature exposure. (McKeen, 2008) discusses polycarbonate resin, Polyethylene terephthalate (PET) and that it has enhanced fatigue resistance and impact resistance at low temperatures. There have been other sources discussing how blending affects material properties at low temperatures including (Subramanian, 2017). Polycarbonate can also be blended with polyethylene which at low temperatures has a high level of energy absorption. (Subramanian, 2017) also mentions other polymers able to blend with Polycarbonate including, PS, PP, PMMA, PS, ABS and some polyesters. The blending of existing polymers for the development of a polymeric liner for liquid hydrogen storage is possible and is an avenue of exploration. Along with blending, Plasticizers can be used to help aid the development of polymeric liners for extreme low temperature conditions. A study has shown that for processing purposes, plasticizers can be used on PVC which can also help to enhance low-temperature properties, (Subramanian, 2017). Along with blending and plasticizers, fillers and nanofillers can also be used for further development. There has also been some research into clay-based films used for barrier properties in composite vessels.

2.3.4.2 Films

Films can be used as gas barriers and insulators (Ebina et al., 2017). (Ebina et al., 2017) mentions how a clay (silica-based) film can be sandwiched between the outer composite shell and the liner as demonstrated in Figure 4

Other literature sources have also researched clay with organic binders. (Yonemoto et al., 2009) study, the application of CFRP [carbon fibre reinforce polymer] with hydrogen gas barrier characteristics to fuel Vessels of space transportation systems goes further into integrating clay-based film into the vessel. The study describes two processes of integrating, *"Claist"* film (Clay + *AIST* [Advanced Industrial Science and Technology]).

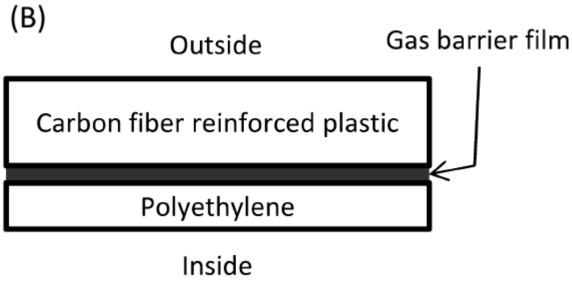


Figure 4 Structure of a composite/polymer liner vessel with integrated film (Ebina et al, 2017)

This film is integrated into the vessel design via a sandwich, where the film is sandwiched between prepreg materials. The other process involves fabricating the composite prepreg with the film integrated into the composite prepreg. The two processes are shown in Figure 5.

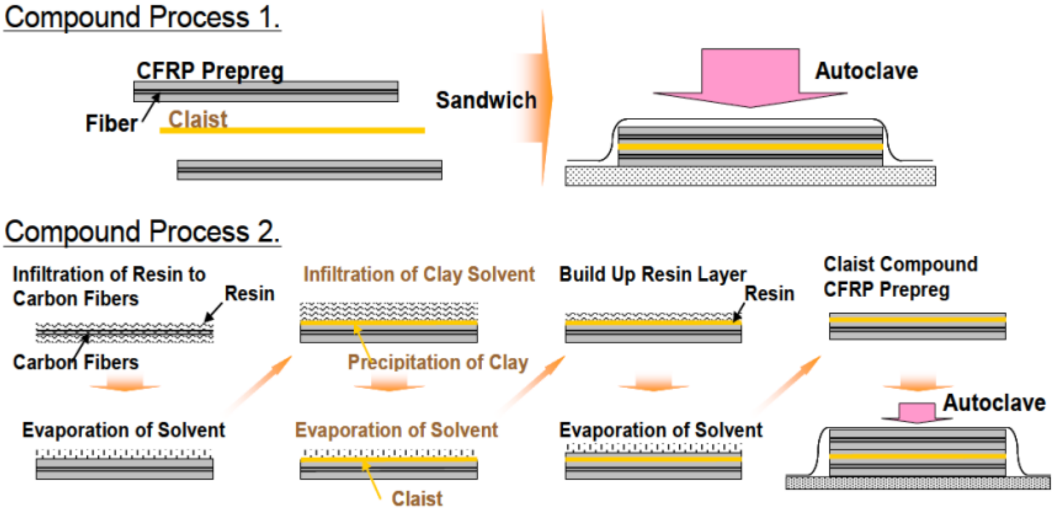


Figure 5 Methods of integrating clay-based films in composite storage vessels, (Yonemoto et al, 2009)

2.3.4.3 liners

The integration of liner materials will serve as a barrier to permeation while also insulting the composite material from the extreme cold. (X. Wang et al., 2022) the study mentioned that typical polymer liners used for type IV hydrogen vessels include, HDPE, PA, PET and series materials of polyether. The study suggests that modification of these polymer materials is required to enhance properties such as ageing, strength, thermal stability, and barrier properties.

Methods that can be used for the modification of polymers include fillers, processing optimisation and utilisation of micro-structures. The most effective method is the use of targeted modifiers, which include fibres, fillers (including flake fillers), nanomaterials and anti-ageing additives, (X. Wang et al., 2022).

About fibres, Chen et al., 2021 study discusses the performance of Carbon fibre, PEEK (polyether ether ketone) (CF/PEEK) polymer composite in cryogenic conditions. The study states that CF/PEEK composite manufactured using the autoclave process will result in low permeability of composite. However, the study stated that after cryogenic cycling of quasi-isotropic and cross-ply laminated, the test resulted in micro cracking and delamination. (X. Wang et al 2022 and X. Chen et al., 2011) both agree that nanomaterials can have a positive effect on polymer performance in extreme low temperatures and to use liners for cold conditions, modification of the polymer is required using fillers.

2.3.4.4 Resin Systems

There has been some development of resin systems for cryogenic fuel Vessels. (Dingemans et al., 2007) study into Novel liquid crystal thermoset resins for cryogenic fuel Vessel applications describe engineering plastic with good mechanical properties. The study evaluates the performance of Thermotropic liquid crystal polymers (LCP) concluding that LCP is a material that should be considered for the use of cryogenic storage vessels.

There is literature on the effects of toughening epoxy resin via the addition of thermoplastic materials. Blending thermoset and thermoplastic materials has been shown to improve material toughness at cryogenic temperatures, (Liu et al., 2021). Lui`s paper mentions some thermoplastics that can be used for improving toughness, tensile strength, and impact strength including, polyaryletherketone (PAEK) polyurethane (PU) and polyethersulfone (PES).

Other studies have demonstrated the same trend with different thermoplastic materials. Polyether Imide (PEI) blending with thermoset epoxy has demonstrated increased impact resistance and impact strength at cryogenic temperatures (He et al., 2013). However, there seems to be little research carried out on purely thermoplastics resins exposed to cryogenic temperatures. A study into the performance OF Polypropylene (PP) tapes concluded, at low temperatures, polymers become brittle but polypropylene tape showed increased ductility at -196°C, (Atli-Veltin, 2018). With studies on both epoxy resins, thermoplastics and blending of the two. The best resin system seems to be a blending of the two systems.

2.3.4.5 Composites

Composites have the opportunity to reduce overall weight by 25% in comparison to metallic Vessels, of which composites have higher strength (Qiu et al., 2021). The problem surrounding composites for cryogenic storage is that the fibre and matrix strength and bonding will be affected as mentioned previously. There has been little research on the development of composite materials for low-temperature applications but there is relevant literature surrounding the matrix, (Qiu et al., 2021). However, NASA has developed a composite material for the potential storage and transportation of liquid hydrogen. The material is known as Cycom 5320-1/IM7 according to (Qiu et al., 2021).

Literature on this material shows that the composite's architecture helps prevent microcracking. The material involves the use of automatic fibre placement for its manufacture. The technique of manufacture has been shown to eliminate hydrogen permeability, (Gomez & Smith, 2019). The study went on to say that the technique reduced the weight and cost by 30% and 25% respectively compared to that of metallic vessels.

Overall, it has been found that cryogenic temperatures have a positive effect on the mechanical properties of composites, generally improving strength; however, ductility, impact and fracture resistance are negatively impacted, (Sápi & Butler, 2020).

2.4.6 3D woven preforms

3D woven composite materials involves the interlacing of composite materials,(X. Chen et al., 2011), to form a 3D composite preform structure as demonstrated in Figure 6. The process is different from the laminate layup of composite materials, also known as 2D composites. 3D composites offer through-thickness yarns (X. Chen et al., 2011), which have many advantages over traditional 2D laminate structures.

The through-thickness yarns produced by the weaving process have been shown to improve impact resistance, and resistance to delamination and produce near-net shape structures, (Bannister, 2004). (Dahale et al., 2019) study agree with the findings of (Bannister, 2004) in that the difference between 2D and 3D structures is that 3D structures have through-thickness properties. 3D structures have also shown resistance to interlaminar radial and shear stresses, (Dahale et al., 2019).

Figure 6 Comparison of 2D laminate and woven 3D preform (X. Chen et al., 2011)

There are not many studies on how the mechanical properties of 3D woven and 2D laminate structures are affected by extreme low temperatures. However, there is some literature on how high temperatures affect 3D woven composites. Composite failure patterns are highly dependent on temperature; high temperature leads to a more plastic composite with an increase in the bonding breakages between the fibre-matrix interface, Dang et al., 2020). This will not lead to a complete failure if the composite has a 3D perform, due to the through-thickness yarns reducing delaminating, (Dahale et al., 2019). However, permeability may be of concern if the perform is damaged. With 2D laminate composite structures, there is no through-thickness support and so it can be said that 2D laminate structure would lead to a more devasting failure compared to 3D preforms due to lack of trough thickness support.

2.4 Analysis methods for extreme low temperature composites

Specific test standards and procedures are dependent on variables such as materials used, and conditions to which the composite may be exposed. There is a range of various testing methods that can be utilised for the testing of composite in extreme low temperature applications. However, relevant literature has pointed out several standards that can be used for the analysis of materials that have been subjected to extreme low temperatures. It is important that both destructive and non-destructive testing is carried out due to the structure of composites. Cracking in composites may not be visible and may require imaging to detect damage not visible to the naked eye which is important to note through the testing stage of this project.

From the literature, ASTM D3039 is the most common standard used for tensile testing of polymer matrix composites (Gates et al., 2003, Kim et al., 2007). The standard will most likely be used for the evaluation of composite samples for this project. (D. Wang et al., 2019) the study pointed out various standards that can be used for the evaluation of composite materials;

of these standards mentioned, ISO 19881 is of interest for this project. The standard summarises the materials manufacture and test requirements for each material for composite hydrogen gaseous storage. Although this standard is used for gaseous storage vessels it can be used for references for future testing.

Other standards that are of interest include ISO 527-4 which is like ASTM D3039 for tensile testing of composite samples. ISO 14126, ASTM D3410 and ASTM D6641 are standards that look at the compression performance of composites in the in-plane direction. ASTM D7905 is a standard used for determining composite materials' fracture toughness. ISO 13003 and ASTM D3479 are used to evaluate fatigue behaviour under tensile cyclic loading. Although all standards mentioned are not directly used for testing composites at extreme low temperatures, they can still be utilised for testing composite samples at low temperatures. Standards associated with liquid hydrogen and nitrogen exposure of materials include ASTM D2512-17, which is aimed at evaluating material response to liquid oxygen. This standard also allows for evaluating materials' exposure to liquid nitrogen also. Table 1 summarises the standards mentioned and how they can be utilised.

Along with the testing standards outlined above, other testing methods that can be used for the evaluation of composite/liner samples include microscopy analysis of sample cross-sections to evaluate defects, Differential scanning calorimetry (DSC) for determining glass transition temperatures. Thermal mechanical analysis (TMA) to study the effects of differences in the thermal expansion of various materials. Gravimetric method for testing the permeability of the composite/liner samples.

Table 1 Summary of relevant test standards

Standard	**Scope**
ASTM D3039 & ISO 527	Details test methods for tensile testing of composite materials with polymer matrix. The test focuses on in-plane tensile properties.
ISO 19881	Material design, manufacture and testing of refillable hydrogen vessels including composite vessels
ISO 14126 & ASTM D3410 & ASTM D6641	Compressive testing of composites parallel to lamination layers
ISO 13003 & ASTM D3479	Fatigue testing of composites

2.5 Current Regulations and Patents for composite hydrogen storage vessels.

From the literature, there are a few regulations surrounding hydrogen storage vessels. (D. Wang et al., 2019) study into the development of regulations, codes and standards on composite vessels outlines some important standards shown in Figure 7.

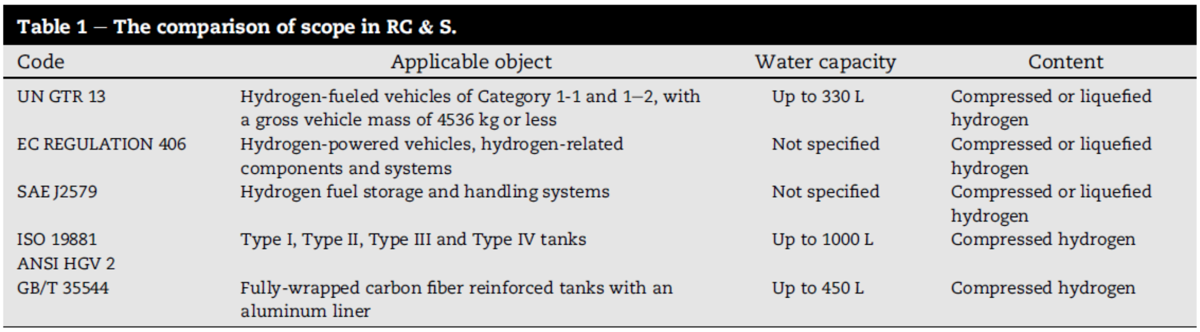


Table 1 – The comparison of scope in RC & S.

Code	Applicable object	Water capacity	Content
UN GTR 13	Hydrogen-fueled vehicles of Category 1-1 and 1–2, with a gross vehicle mass of 4536 kg or less	Up to 330 L	Compressed or liquefied hydrogen
EC REGULATION 406	Hydrogen-powered vehicles, hydrogen-related components and systems	Not specified	Compressed or liquefied hydrogen
SAE J2579	Hydrogen fuel storage and handling systems	Not specified	Compressed or liquefied hydrogen
ISO 19881 ANSI HGV 2	Type I, Type II, Type III and Type IV tanks	Up to 1000 L	Compressed hydrogen
GB/T 35544	Fully-wrapped carbon fiber reinforced tanks with an aluminum liner	Up to 450 L	Compressed hydrogen

Figure 7 Summary of regulations, codes and standards surround composite tanks (D. Wang et al, 2019)

There are also some patents for the hydrogen storage Vessel concept. (Ornath, 2010), patent of a metal matrix composite hydrogen storage Vessel details how a hydrogen vessel with a hydride core is made. The patent also details how the Vessel can be coupled to be used as a fuel Vessel. However, the patent has no mention of liquid hydrogen storage or polymeric liners. Although it is important to understand the ingenuity that is behind the invention of the hydrogen storage Vessel.

Patents for the storage of liquid hydrogen include (Hernaiz Lopez et al., 2023). This details the structure of a composite vessel with a metallic liner for gaseous and liquid hydrogen storage. Like (Ornath, 2010) the patent has no mention of polymer liners, however the patent details methods of structural reinforcement of composite vessels to prevent buckling. There is a patent for polymer liners in composite vessels, (Yasuharu, 2009), details the use of polyamide resin liner for gaseous storage of hydrogen but again no mention of liquid hydrogen storage.

Patents for the use of 3D woven structures include (Steele & Stenger, 1994) patent for pressurised gas storage. The patent details a woven composite storage Vessel for cars to replace fuel Vessels. However, the shape of the Vessel (cuboid) is of concern as high pressures may affect the structural performance of the Vessel.

It is evident from research into relevant patents for 3D woven cylinder storage vessels, more research and development are required for this technology to be a viable alternative to current storage vessels and Vessels.

2.6 Conclusion

It is clear from the literature that more focus is required for the development of composite materials for the storage of liquid hydrogen and consequently for the development of composite materials for extreme low-temperature applications. The development of lightweight composite vessels is of particular interest. There are several avenues for the potential development of composites for this application. These include the modification of polymer liners, the development of 3D woven structures and the effects of the coefficient of thermal expansion in comparison to 2D laminate composites. Successful implementation of composite vessels for low-temperature applications could improve the energy and transport infrastructure with the reduction in carbon emissions with hydrogen as a potential substitute for fossil fuels. The technology can be used for the aviation sector as the main fuel substitute as well as the agricultural, automotive and transport sectors.

Chapter 3. Methodology

3.1 Research Design

For this project, a quantitative approach was taken as the mechanical properties of composite materials are of interest. It was thought that the 3D woven material may be a better architecture to use in place of 2D laminate architecture since 3D woven composites have better interlaminar strength (Bannister, 2004) and so would offer better mechanical strength we exposed to cryogenic temperatures.

The research strategy used for this project involved exposing two different composite architectures to liquid nitrogen in place of liquid hydrogen. Liquid Nitrogen was used in place of liquid Hydrogen as Ulster University does not have the facilities for handling liquid Hydrogen. Liquid Hydrogen is also more expensive whereas liquid Nitrogen is less so and offers a cryogenic temperature of -196°C, a difference of -54°C. The two composite structures include 2D laminate and 3D woven layer-to-layer carbon fibre composites.

Composite specimens from each material group (2D & 3D), are then to be exposed to liquid nitrogen and then compared to baseline specimens. Tensile and thermal testing was conducted. Microscopy images are then to be taken and the data can be analysed to determine what effects cryogenic temperatures have on the sample groups and what sample group will be the best material for a hydrogen storage vessel. CT images were also taken of tensile failure specimens to analyse the failure mechanisms involved.

3.2 Materials Methodology

3.2.2 Material processing and preparation

Summary of composite materials

For this project, Hex force HS06K 5H Satin carbon fibre was used for 2D laminate (0/90 orientation plys) composite. Toray T700 carbon fibre was used for weaving the 3D layer-to-layer structure. Both are considered to have the same carbon fibre material with the same material properties. Both composites have the same resin material. The thermosetting material consists of Mouldlife Prime 37 resin and Gurit Ampreg 3X slow hardener.

3D Woven fabric manufacture

To produce the 3D woven fabric, A Jacquard Controlled weaving loom was used, located in NIACE (Figure 8). The machine provides the ability to weave fibre materials, thus achieving a 3D woven fabric structure.

Three main types of weave patterns can be used for 3D fabric. These include a layer to layer, through thickness and XYZ structure (Figure 9). For this project, a Layer-to-layer structure was used as this was already on hand.

Figure 8 Jacquard Controlled Weaving Loom located in NIACE (UKRI, 2023)

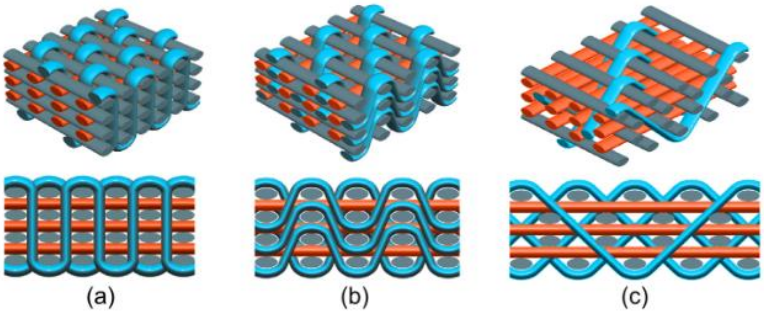


Figure 9 XYZ (a), Layer to layer (b) and through thickness (c) woven structures (Thomas. G, 2018)

To create a layer-to-layer structure the material in the loom was grouped. The number of fibres per group can vary through the reed (Figure 11) and so a group can have two fibre strands or six fibres for example, but for the material used for this project, three fibres are placed within a group.

The layer-to-layer fabric structure contains four warps per layer, Figure 10. This represents one group of fibres and thus is represented as group 1.

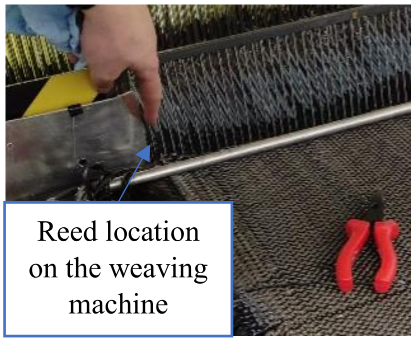


Figure 11 Reed location on the Jacquard Controlled weaving loom.

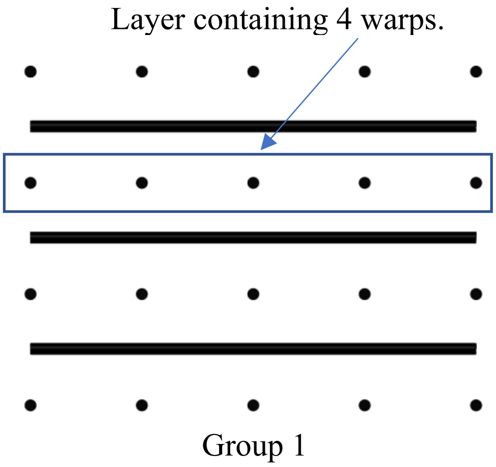


Figure 10 3D layer to layer structure, Group 1

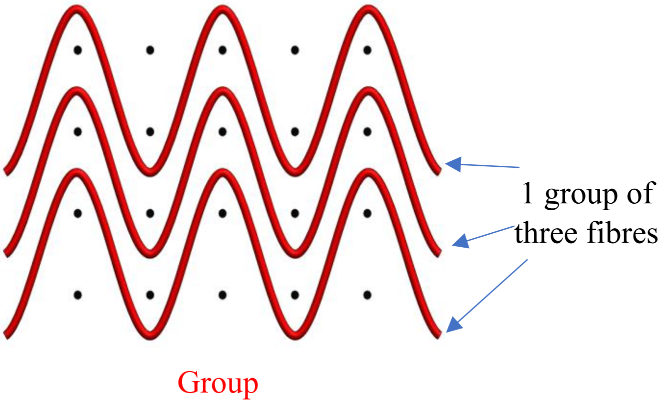


Figure 12 3D layer to layer structure, Group 2

Within group two (Figure 12), the fibres are not symmetrical and are unbalanced. To solve this, further groups were added. Another group, group three (Figure 13) where the fibres are placed straight through the existing group. These are known as stuffers which is represented by group three.

Group four (Figure 14) contains the inverse of group two. Further balancing the structure by adding the inverse of group two will add symmetry to the structure.

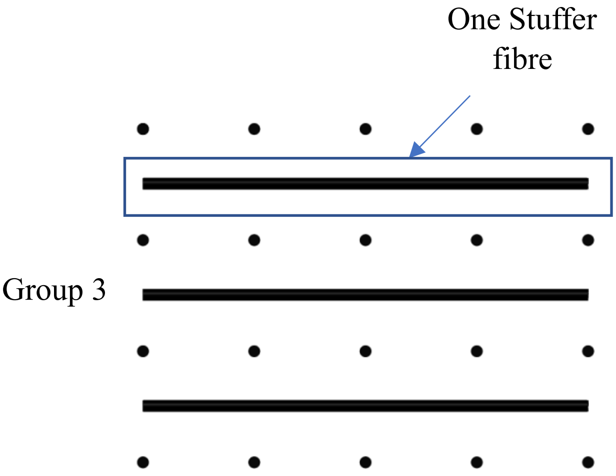


Figure 13 3D layer to layer structure, Group 3

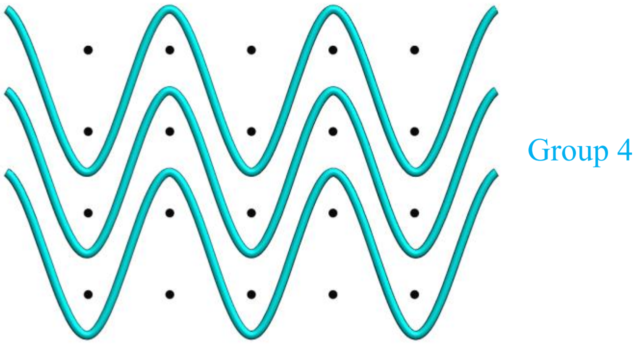


Figure 14 3D layer to layer structure, Group 4

A unit cell (Figure 15) contains these four groups and is repeated throughout the composite structure to create the woven layer-to-layer structure.

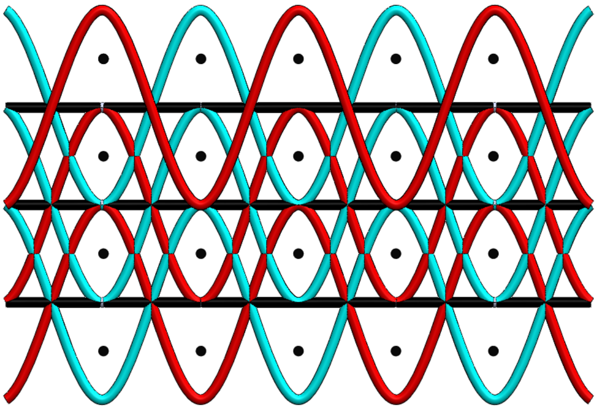


Figure 15 3D layer to layer structure, unit cell

The structure of the 2D composite used for this project contains a less sophisticated structure in comparison to 3D woven, layer-to-layer composites. 2D composite involves the stacking of fabric, one on top of another with no interlaminar connections. The structure will have a 0/90 fibre orientation. The resin system is used to hold the layers in place.

Figure 16 2D structure, six carbon fibre sheets

3D & 2D Plaque processing

The fibres were then processed to make the final composites using Resin transfer moulding (RTM) process located in NIACE (Figure 17). This manufacturing technique offers a higher potential fibre volume fraction compared to other techniques such as hand lay-up and resin infusion due to A more consistent consolidation pressure offered by the RTM.

Figure 17 RTM machine located in NIACE.

Setting up the RTM machine is important which includes setting the finial composite depth. Referred to in the RTM machine manual as cavity thickness. Adjustment to the cavity thickness was carried out at room temperature.

The procedure for setting mould cavity depth is as follows:

1. The depth gauge should be zeroed by placing it on a flat surface on the corners of the cavity shown in Figure 18.
2. All the upper and lower locking nuts should be slacked and located underneath the mould cavity shown in Figure 19.
3. The hand wheel shown in Figure 19. should be lowered to increase the depth of the mould cavity.
4. At this point a depth of 2mm was required as there is a 1mm clearance between the glass top and mould cavity,
5. Each corner can be lowered to 2mm sequentially.

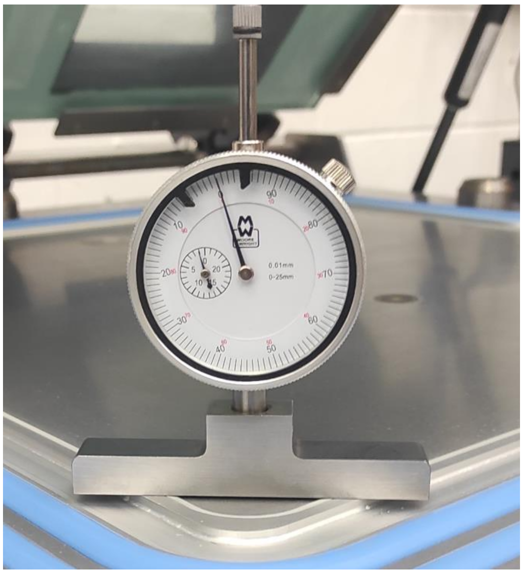


Figure 18 Zeroing depth gauge using cavity corners.

6. The six locking nuts at the bottom of the mould cavity can then be tightened until the depth gauge reads 3-4 microns at the corresponding corners.
7. The top locking nuts should then be tightened, bringing the depth gauge back to 3-4 microns.

At this point, the RTM machine has a mould cavity depth of 3mm, and it is ready to start the moulding procedure.

Figure 19 Locking nuts under mould cavity.

1. The resin piping is prepared and installed from the resin vacuum pot shown in Figure 20. It is important to note that the pipe end should be parallel to the moulding track with no sharp edges to prevent barriers to resin flow. A 1mm gap between the mould cavity and pipe should be maintained.
2. A second resin pipe is cut and installed into the resin catch pot to catch resin when a vacuum is drawn. This prevents damaging the vacuum from drawing in resin into the pump. Again, the pipe end must be parallel to the mould cavity to ensure proper resin flow. A 1mm gap between the mould cavity and pipe end should be kept, illustrated in Figure 21.

Figure 20 Resin pipe installation from resin vacuum pot to mould.

3. After installing resin piping, the mould face and resin track should be heated to 30°C.
4. A release agent (Freekote 770-NC) is then applied to the mould face and the glass top to ensure ease of release when fully cured.
5. The fabric can then be placed onto the mould face ensuring that the fabric does not interfere with the seal illustrated in Figure 23.
6. The glass top of the RTM machine can now be lowered.

7. 10 bolts are then tightened to secure the glass top. A cross-hatch tightening pattern must be followed to prevent compromising the seal.
8. Clamps are then placed on both resin pipes located at the vacuum resin pot (Figure 24, (b)) and the resin catch pot (Figure 24, (a)) so to create a vacuum within the RTM tool.
9. A vacuum can then be drawn to -1 bar.
10. Once the vacuum has been drawn, 30mins is left to observe a pressure drop which indicates a leak in the system.

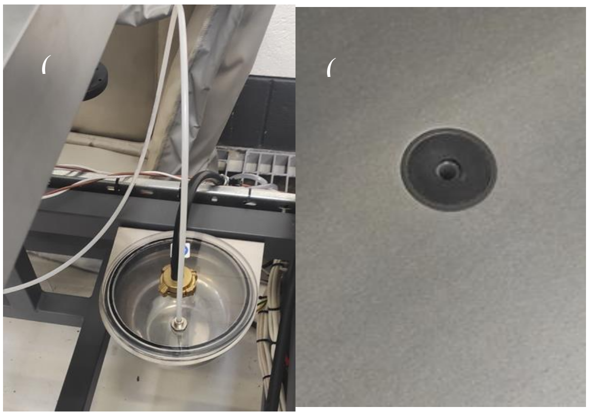


Figure 21 Installing resin pipe from resin catch pot (a) to mould (b)

NB: It was observed that there was a slight loss in pressure, Figure 22. However, I was informed that this was just a known source leak from the resin catch pot and vacuum pump and should not affect the 3D plaque.

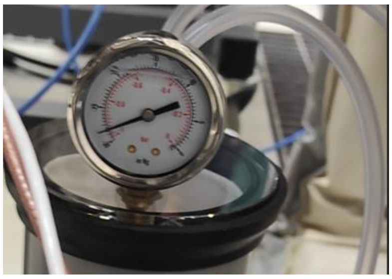


Figure 22 Pressure loss

Figure 23 Placing fabric on the mould face ensuring seal is free from interference.

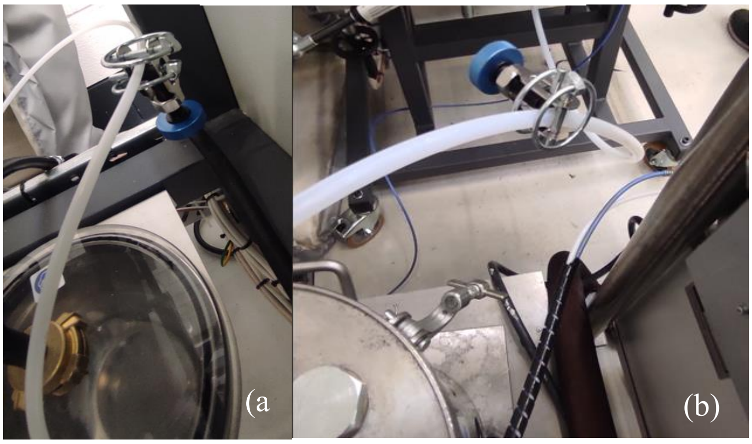


Figure 24 Installation of resin pipe clamps to the catch pot (a) and vacuum resin pot (b)

11. Once it has been confirmed there are no pressure leaks, the resin can be prepared.
12. Prime 37 resin and ampreg 3X hardener was used for processing the 3D plaque. For mixing, a 100:29 ratio is used (Resin: hardener).
13. 1000 grams of resin was measured with 290 grams of hardener.

14. Both the resin and hardener were then mixed, illustrated in Figure 25. It is important to record the time of mixing to ensure there is enough time allowed for work before the resin enters a gel state.

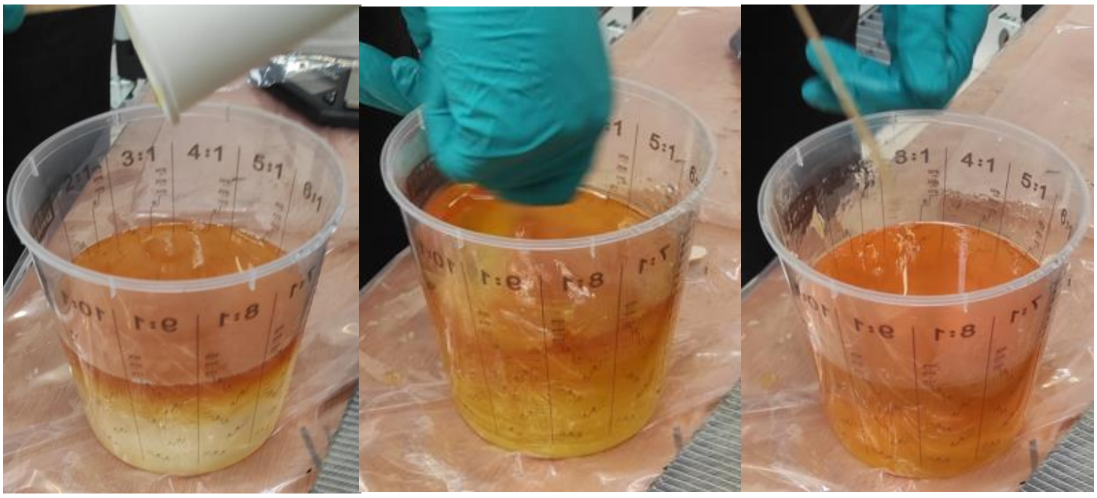


Figure 25 Mixing of the resin and hardener with a ratio of 100:29.

15. Mixing of the resin and hardener introduces air bubbles (Figure 26) and so degassing of the resin is required.
16. The resin is placed into the vacuum pot where it is allowed to degas for 30mins under -1 bar of pressure.
17. Once degassing of the resin was complete, the clamps can be released from both resin lines.
18. The resin will flow into the mould cavity.
19. The RTM machine is then switched to vent, where trapped pressure (negative pressure) is released and resin is allowed to flow easier.
20. The first proportion of the resin flowing into the mould will be foam which is caught into the catch pot.
21. Once the foam is in the catch pot, the resin pipe is then clamped off again to stop further resin to flow into the catch pot.
22. The RTM machine is then switched back to pressure to apply further forcing resin through the mould.
23. The mould cavity and resin track temperature is then increased to 50°C from 30°C to start the curing cycle.
24. The plaque is allowed to cure for 16 hours at 50°C.

Figure 26 Illustration of air bubbles formed when mixing.

Initially, the 3D woven composite plaque was made. As this material is considered as one whole layer instead of multiple layers. Measurements of the woven 3D fibre were taken and is summarised in Table 2.

Table 2 3D fabric dimensions

	Length (cm)	**Width (cm)**	**Thickness (cm)**	**Weight (grams)**
Value	48	29.5	0.19944	244

With these values, the areal weight can be calculated:

$$Areal\ weight\ (A_F) = \frac{fabric\ weight}{length * width} \tag{1}$$

$$Areal\ weight\ (A_F) = \frac{244}{48 * 29.5}$$

$$Areal\ weight\ (A_F) = 0.172317\ g/cm^2$$

To calculate the fibre volume fraction of the composite, further variables are required. These include Fibre density, Fabric thickness. Using the manufactures specification sheet (Figure 27), the fibre density of the carbon fibre fabric is 1.8 g/cm^3.

A summary of the known variables is summarised below:

Fabric thickness (t) = 0.19944cm

Areal weight (A_F)= 0.172317 g/cm^2

Number of layers (plies) (N) = 1

Fibre density (ρ_f) = 1.8 g/cm^3

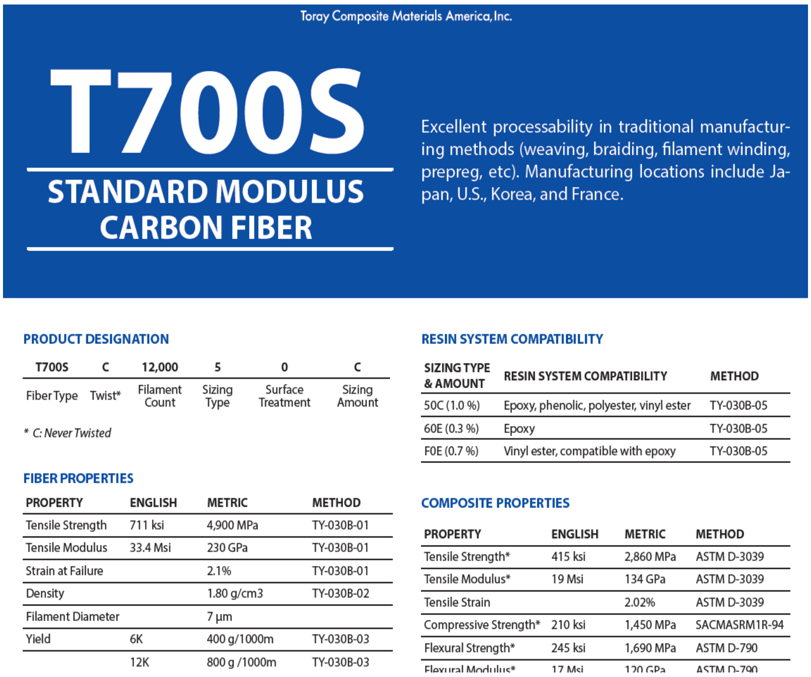
The fibre volume fraction (V_f) can be calculated using these variables:

$$V_F = \frac{N * A_F}{\rho_F * t} \tag{2}$$

$$V_F = \frac{1 * 0.172317}{1.8 * 0.19944}$$

$$V_F = 0.48$$

$$V_F = 48\%$$



Toray Composite Materials America, Inc.

T700S

STANDARD MODULUS CARBON FIBER

Excellent processability in traditional manufacturing methods (weaving, braiding, filament winding, prepreg, etc). Manufacturing locations include Japan, U.S., Korea, and France.

PRODUCT DESIGNATION

T700S	C	12,000	5	0	C
Fiber Type	Twist*	Filament Count	Sizing Type	Surface Treatment	Sizing Amount

** C: Never Twisted*

FIBER PROPERTIES

PROPERTY	ENGLISH	METRIC	METHOD
Tensile Strength	711 ksi	4,900 MPa	TY-030B-01
Tensile Modulus	33.4 Msi	230 GPa	TY-030B-01
Strain at Failure		2.1%	TY-030B-01
Density		1.80 g/cm3	TY-030B-02
Filament Diameter		7 µm	
Yield	6K	400 g/1000m	TY-030B-03
	12K	800 g /1000m	TY-030B-03

RESIN SYSTEM COMPATIBILITY

SIZING TYPE & AMOUNT	RESIN SYSTEM COMPATIBILITY	METHOD
50C (1.0 %)	Epoxy, phenolic, polyester, vinyl ester	TY-030B-05
60E (0.3 %)	Epoxy	TY-030B-05
F0E (0.7 %)	Vinyl ester, compatible with epoxy	TY-030B-05

COMPOSITE PROPERTIES

PROPERTY	ENGLISH	METRIC	METHOD
Tensile Strength*	415 ksi	2,860 MPa	ASTM D-3039
Tensile Modulus*	19 Msi	134 GPa	ASTM D-3039
Tensile Strain		2.02%	ASTM D-3039
Compressive Strength*	210 ksi	1,450 MPa	SACMASRM1R-94
Flexural Strength*	245 ksi	1,690 MPa	ASTM D-790
Flexural Modulus*	17 Msi	120 GPa	ASTM D-790

Figure 27 Carbon Fibre Specification sheet

Knowing the theoretical 3D woven composite plaque fibre volume fraction as 48%. It is important to achieve a theoretical fibre volume fraction of 48% for the 2D composite plaque. This allows for fair comparison through experimentation. To ensure that a theoretical fibre volume fraction of the 2D composite is the same as the 3D composite sample, the number of piles required for the 2D composite sample will need to be calculated.

The fibre volume fraction is already defined at this point as a theoretical value of 48%. The density of the carbon fibre will be the same for fair comparison through experimentation, 1.8 g/cm^3. The desired thickness of the 2D composite is 2.5mm (as per ASTM D3039). The areal weight of the 2D laminate sheets is specified on the manufacturer's specification sheet as 375 g/m^2.

Using the variables summarised below, the number of required 2D laminate plies to achieve a theoretical fibre volume fraction of 48% can then be calculated:

Thickness (t)= 2.5mm

Fibre density (ρ_f) = 1800 kg/cm^3

Areal weight (A_F)= 0.375 kg/cm^2

$$V_F = \frac{N * A_F}{\rho_F * t}$$

$$N = \frac{V_F * \rho_F * t}{A_F} \tag{3}$$

$$N = 5.837\ plies$$

To produce a composite that is balanced and symmetrical, 5.837 plies will not achieve this. So, 6 plies were used for the making of the 2D composite sample. The same process was used to produce the 2D composite. The RTM procedure used for the making of the 3D woven sample will also be used for the making of the 2D composite.

Processing of the 3D composite material taken place on the 15th of March 2023 at NIACE. The following sequence was followed.

- RTM machine set up 9:20-10:00 am.
- Mixed Epoxy at 10:15 am.
- Started vacuum at 10:18 am.
- 30minute degassing.
- Started resin diffusion at 10:45 am and allowed to cure for 16 hours.

Processing of the 2D composite material taken place on the 29th of March 2023 at NIACE. The following sequence was followed.

- RTM machine set up 1:42-2:25 pm.
- Mixed Epoxy at 2:40 pm.
- Started vacuum at 2:40 pm.
- 30minute degassing.
- Started resin diffusion at 3:10 pm and allowed to cure for 16 hours.

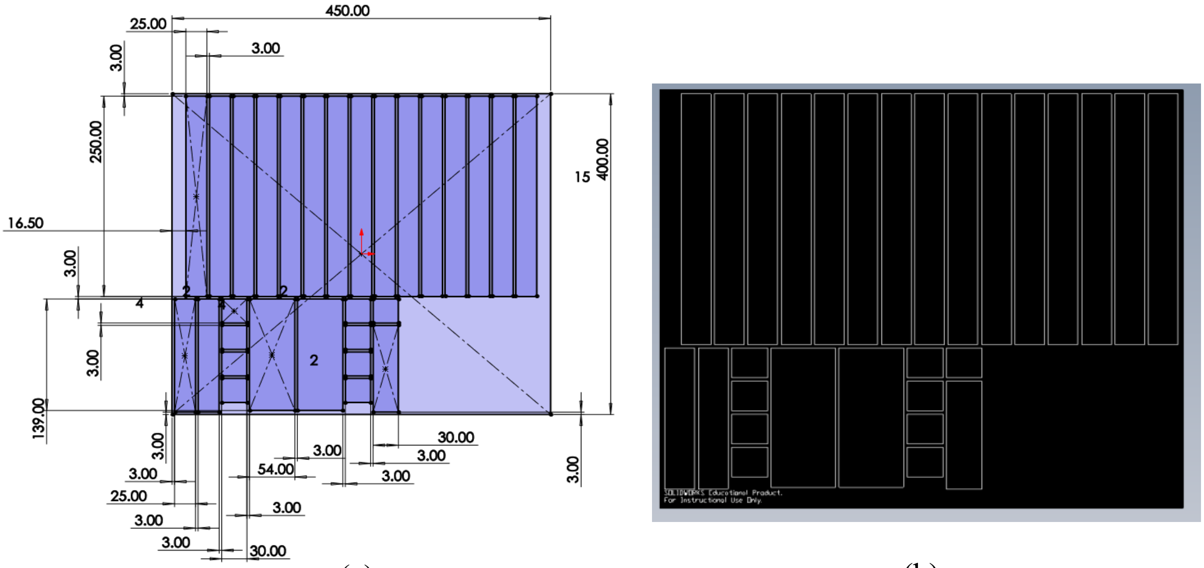
Sample sizing and Plaque cutting

With composite plaque sizes finalised per each composite structure (2D and 3D). Each plaque was prepared for extracting specimens that could be used for testing. To determine the number and size of samples required for this project it was important to summarise what tests were required.

Tensile testing is of main importance for testing Nitrogen exposure. For tensile testing, standard ASTM D3039/D30309M-17 outlined sample dimensions. Concerning standard ASTM D3039/D30309M-17, both composite samples, 2D and 3D are considered to be a balanced and symmetrical composite. Therefore, the required width is 25mm, a length of 250mm and a thickness of 2.5mm. The final sample size for the composite samples was 25mm in width, 250mm in length and 2mm in thickness. There was no tolerance stated in the ASTM D3039 standard for the thickness. A thickness of 2mm was more achievable for the manufacturing process chosen for this project compared to the guideline of 2.5mm. Five specimens were required for baseline, short exposure and cyclic (long) exposure. That's a total of 15 specimens per composite material as a minimum (Figure 28 and Figure 29).

For other microscopy and fibre volume fraction, 30X30mm square samples were used based on the remaining area of the 3D material (3D plaque had less space for large specimens). It was thought that 30X30mm specimens were sufficient for microscopy analysis and fibre volume fraction experimentation. At least three samples were required per composite for microscopy analysis.

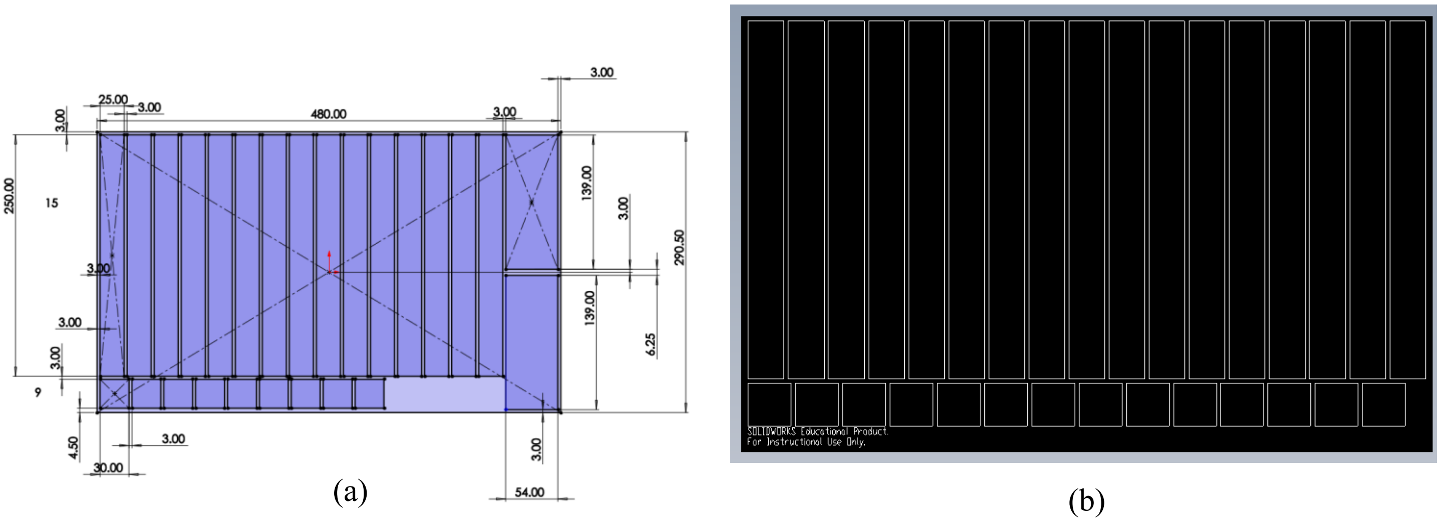
To determine the specimens required for thermal analysis experimentation. The specimens needed to be big enough in surface area so to ensure that liquid Nitrogen could be easily placed on the surface of the materials. From the remaining 3D plaque material, 139mmx59mm would be sufficient to support liquid Nitrogen. Two specimens per composite material would be sufficient.



(a) (b)

Figure 28 2D Solidworks drawing (a) and DXF file (b)

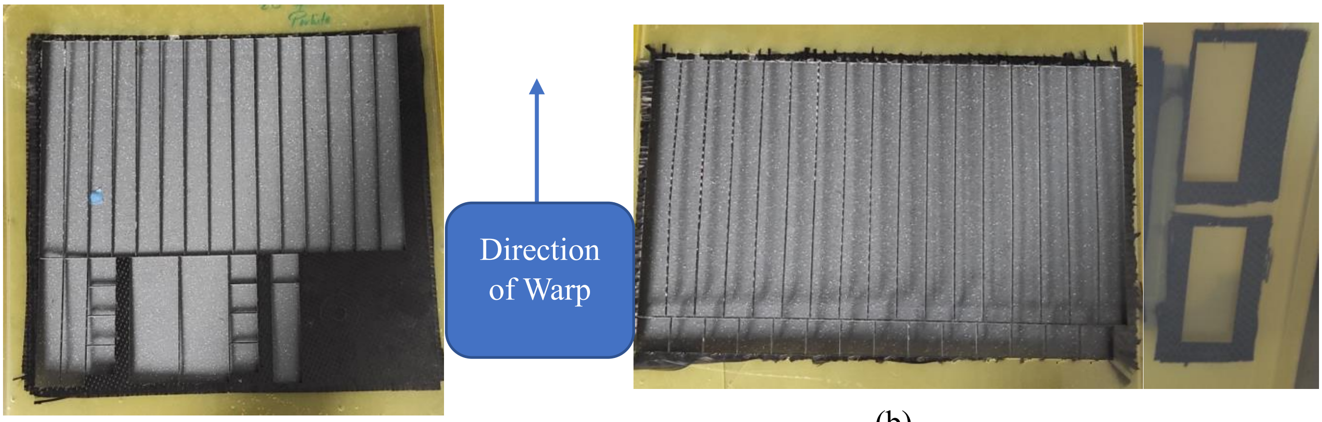
Solidworks was used to create the DXF file needed for cutting the correct size specimens according to the standard ASTM D3039. The overall plaque size for the 2D composite was 450mm x 400mm, a thickness for this is not required for the DXF file. The 3D composite plaque was 480mm x 290.5mm. The differences in plaque dimensions were due to the limited supply of layer-to-layer 3D fabric. Once the overall dimension of the specimens and the number required were finalised, any spare space on the plaque was used to create spare material specimens. These files were then sent to get cut using the water jet cutting machine at Ulster University. A study was conducted to evaluate the damage abrasive water jet has on 2D laminate carbon fibre composites. The study found that waterjet cutting offers no thermal input to the composite and so there is a lack of thermal damage to the composite structure compared to mechanical cutting techniques, (Demiral et al., 2022).



(a) (b)

Figure 29 3D Solidworks drawing (a) and DXF file (b)

Tensile test samples were cut in the warp direction for both 2D and 3D materials as shown in Figure 30.



(a) (b)

Figure 30 Cut plaques using water jet cutter, 2D (a) and 3D (b)

Once the plaques were cut and before tensile testing, 180-grit sandpaper was superglued onto the specimens for gripping tabs. This helps to prevent slippage between the tensile machine vice jaws and the surface of the composite specimen. This technique also offered the advantage of saving time compared to epoxy tabs or DIC.

Sample Conditioning

After waterjet cutting, the samples were left in a controlled environment for 24hrs + before any testing was conducted. The mechanical room with a temperature of 21°C and 50%RH. This is to ensure that environmental factors do not influence the mechanical response of each of the sample groups. Specimens exposed to liquid Nitrogen were left in the same room for conditioning after liquid Nitrogen exposure and before tensile testing.

3.3 Testing and analysis Methodology

3.3.1 Specimen Exposure

Exposing the composite materials to liquid Nitrogen is important in this project as liquid Nitrogen is close to the temperature of liquid Hydrogen. Liquid Nitrogen has a temperature of -196°C whereas liquid Hydrogen reaches -250°C. Liquid Nitrogen was used in place of liquid Hydrogen as Ulster University does not have the facilities for handling liquid Hydrogen. The exposure plan used for the exposure of sample sets is outlined in Figure 33. These specimens were then used for tensile testing.

To expose the specimens to liquid nitrogen, some materials that were required include:

- Cryogenic container (Figure 31).
- Type K thermocouple with temperature readout meter (Figure 32).
- Fume Cupboard.
- High temperature tape.
- Safety Visor.
- Safety Gloves.
- Stopwatch.
- Liquid Nitrogen.

Figure 31 Cryogenic container, safety visor and gloves.

This procedure summarises one exposure cycle. This procedure was carried out five times in total for the cyclic (long) exposure sample.

1. With a cryogenic container full of liquid nitrogen and in a fume cupboard, the specimens were lowered into the liquid nitrogen slowly (to reduce nitrogen splashing due to large temperature differences) one specimen at any one time. (Safety visor and gloves are to be worn to prevent injury).

Figure 32 High temperature tape and type K thermocouple and digital read out meter.

2. After 15 minutes, the samples were flipped over and placed back into the liquid Nitrogen to ensure even exposure to the specimens. The specimens can all be lifted and flipped over at once (as the specimens were already below room temperature).
3. The samples are then exposed for the reminder 15 minutes where they are then removed and allowed to return to room temperature.
4. A Thermocouple is placed on the surface of a specimen to monitor the temperature of the specimen. The time taken for the specimens to come back up to room temperature was approximately 30 minutes.

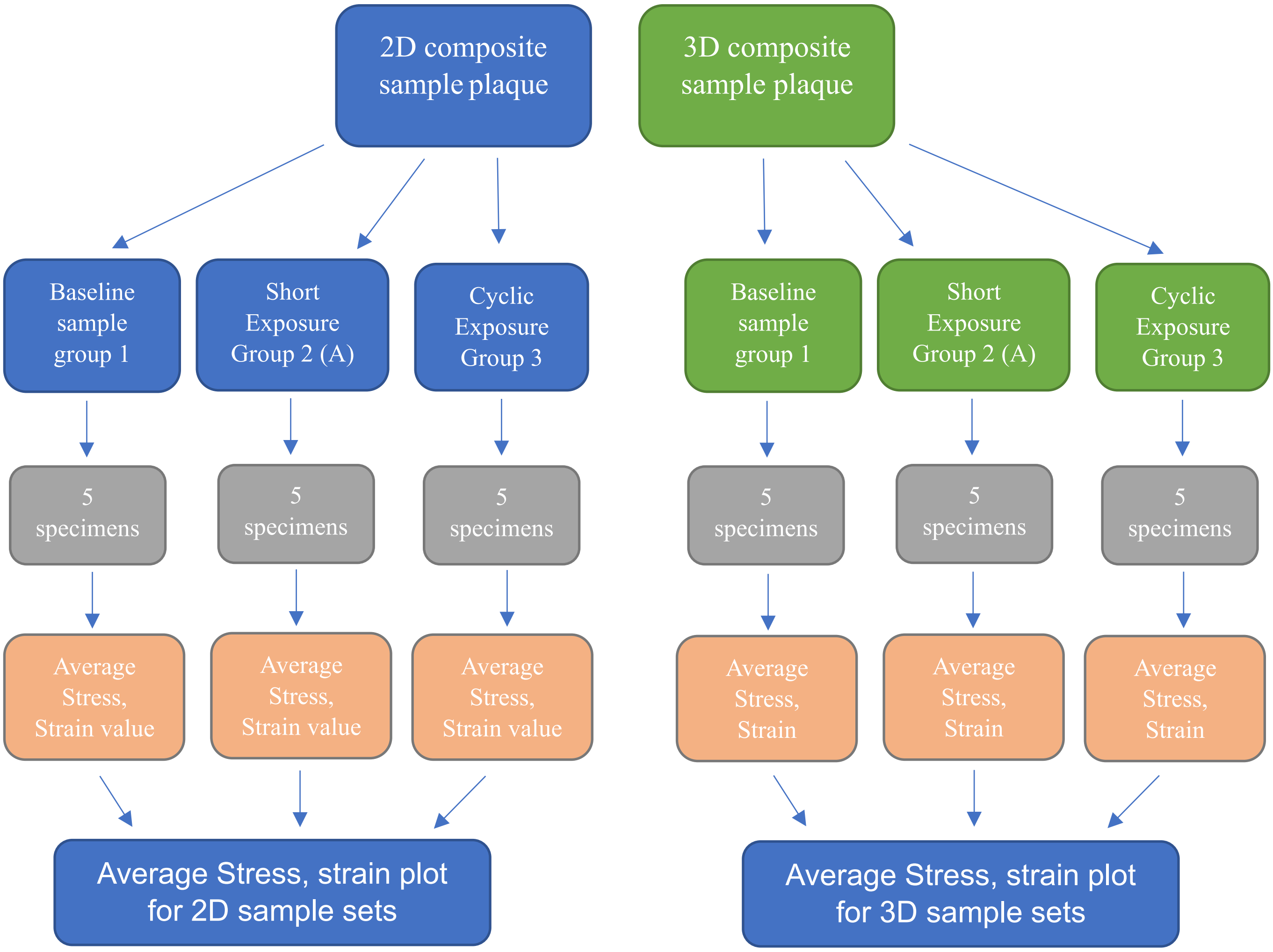


Figure 33 Summary of liquid Nitrogen exposure for tensile test specimens

Group one- Baseline testing. This group contained samples that were just conditioned and then tested with no exposure to liquid Nitrogen.

Group two- short-term exposure to Liquid nitrogen. This involved a single 30-minute exposure cycle. Flipping the specimens over 180° and placing them back in the liquid nitrogen after 15 minutes for even Nitrogen exposure.

Group three- Cyclic (long) exposure to Liquid nitrogen. This involved 5 X 30-minute exposure cycles. Flipping the specimens over 180° and placing them back in the liquid nitrogen after 15 minutes for even Nitrogen exposure.

For Microscopy analysis, 30X30mm tabs were exposed to liquid nitrogen. The exposure procedure is similar to that of the tensile test exposure procedure. One tab per sample group was used for analysis and comparison. A baseline tab which was not exposed to liquid Nitrogen, a short exposure and a cyclic (long) exposure stab was used for comparison.

The short exposure procedure was the same as that of the tensile specimens, One 30-minute exposure cycle. However, because the tabs were smaller than the tensile specimens, the tabs did not require flipping for even exposure. The cyclic exposure was different from the tensile equivalent. The tabs were kept in liquid Nitrogen for 8 hours. This was the time in which the liquid Nitrogen had evaporated from the cryogenic container. Using the procedure, any differences in how the composite reacted to the liquid Nitrogen may be more obvious between baseline and short exposure specimens.

3.3.3 Mechanical Testing

Tensile Testing

Tensile testing machine Zwick Z100 (Figure 34) was used for the tensile testing of the specimens. This machine was used for tensile testing as it has the highest load cell on-site (100KN). in comparison to other machines, The Zwick also has hydraulic clamps which offer consistent clamping force per specimen. Thus preventing bias between specimens due to unequal clamping force. The testing of the specimens was conducted in accordance with standard ASTM D3039/D30309M-17 (ASTM, 2017). Materials used include:

- Zwick Z100 tensile machine with an extensometer
- Engineers square
- Vernier Callipers

Figure 34 Zwick Z100 tensile testing machine

The tensile testing procedure is as follows:

1. Specimens' width and thickness were measured and input into the software.
2. Specimen is placed in the chuck of the machine. Keeping in mind that the specimen should be as straight as possible. An engineer's square can be used as a reference.
3. The test regime is then started, where a preload is applied to the specimen. This is to take the slack out of the apparatus. The test will then pause.
4. The extensometer is then placed onto the specimen.
5. The test is then resumed, where the machine will apply load until 2% strain is observed.
6. The test will then pause for a second time, where the extensometer is then removed to prevent damage to the extensometer during specimen failure. Note, the removal of the extensometer should be carried out as quickly as possible so to ensure accurate strain readings.
7. The test is then resumed until failure.
8. Data collected on the Zwick can then be exported to an Excel spreadsheet.

The rate at which the test specimen was loaded was based on head speed displacement of 2mm/min as per ASTM D3039M-17.

3.3.4 Physical Testing

Thermal Analysis

There is no current standard to measure the cryogenic thermal performance of carbon fibre composite materials. The purpose of this test is to evaluate the thermal conduction performance of each material, 2D laminate and 3D woven composites.

Required materials:

- Two 80X40X25mm mild steel sections
- Araldite two-part 2K adhesive
- Stopwatch
- Type K thermocouple with temperature read out meter
- Device capable of capturing video
- Fume Cupboard
- High temperature tape
- One 78X38X25 polystyrene foam block
- Two 40X40mm wooden blocks
- Liquid Nitrogen
- Safety Visor
- Safety Gloves

This test set-up involved using box steel 80X40X25mm to contain liquid Nitrogen on the surface of the composite samples. The box section was adhered to the composite plaques of size 139X54X2mm using Araldite (Figure 35). This approach would simulate the contact that the liquid Hydrogen would have if the liquid Hydrogen was stored in a composite vessel. Araldite was used for adhering the box section to the composite specimens as technical staff at Ulster University suggested it was a very versatile glue and would cope with the low temperature without leakage.

The test procedure is as follows:

- Place the thermocouple on the bottom side of the composite specimen, securing it with a generous amount of high-temperature tape (Figure 36).
- Turn on the thermocouple temperature gauge to video record the temperature.
- Place the specimen in the fume cupboard on top of the two 40X40mm wooden blocks, ensuring that the thermocouple is not in contact with the wood or fume cupboard (Figure 37).

- A video recording of the stopwatch and thermocouple readout meter is started.
- Pour a small amount of liquid Nitrogen into the box steel, allowing the composite and steel to lower in temperature for 10 seconds.
- The stopwatch is started at the same time as the first pour is started.
- After 10 seconds, more liquid Nitrogen is poured into the box section. The level of liquid Nitrogen should be close to the top.
- 78X38X25 polystyrene foam block is then placed on top of the steel box section to limit Nitrogen loss due to evaporation.
- The test is allowed to run for three minutes, ensuring the camera used for videoing the stopwatch and thermocouple readout is being recorded in focus.
- After three minutes, the recording and stopwatch can the stopped.


Figure 35 80X40X20mm box section with composite specimens


Figure 36 Thermocouple, composite attachment

This method was used as there was no capability of recording surface temperature with time at Ulster University. The test was conducted three times per composite specimen. Allowing 30 minutes after the test for the composite specimens to come back up to room temperature.


Figure 37 Thermal test apparatus

3.3.5 Imaging

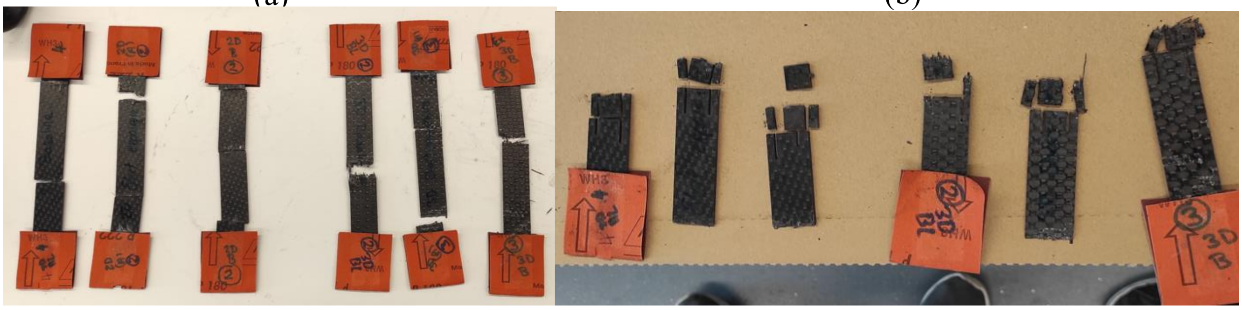
CT scanning

Micro-CT scanning of tensile test failures was conducted as crack propagation during failure could lead to more information with regards to how specimens failed. The structure of the composite and matrix was of interest to evaluate the effects of how liquid Nitrogen exposure affected the failure mechanics of each material.

A Bruker SkyScan, an X-Ray microtomography CT machine was used for scanning the specimens. SkyScan 1275 software was used for the preparation and initialisation of the scan and CTvox and CTAn software was then used for processing the CT images.

A random selection of specimens from each sample set was chosen from the tensile test specimens (Figure 38 (a)). With the scanning of specimens taking up to 40 minutes, it wouldn't be viable to scan anymore than one specimen per sample set. This gave a total of six specimens required for CT scanning.

Once the samples were selected at random, small 10x10mm samples were then cut from the selected specimens to be scanned using the micro-CT machine (Figure 38 (b)). A Dremel was used for cutting the 15x15mm tabs from each specimen as this was the only method available for cutting the small tabs. This was carried out by the technical staff within Ulster University.



(a) (b)

Figure 38 Random selection of tensile test specimens (a) and CT specimen tabs (b)

Specimen tabs were then placed into the micro-CT machine as per Figure 39. Wax was used for securing the tab for scanning.

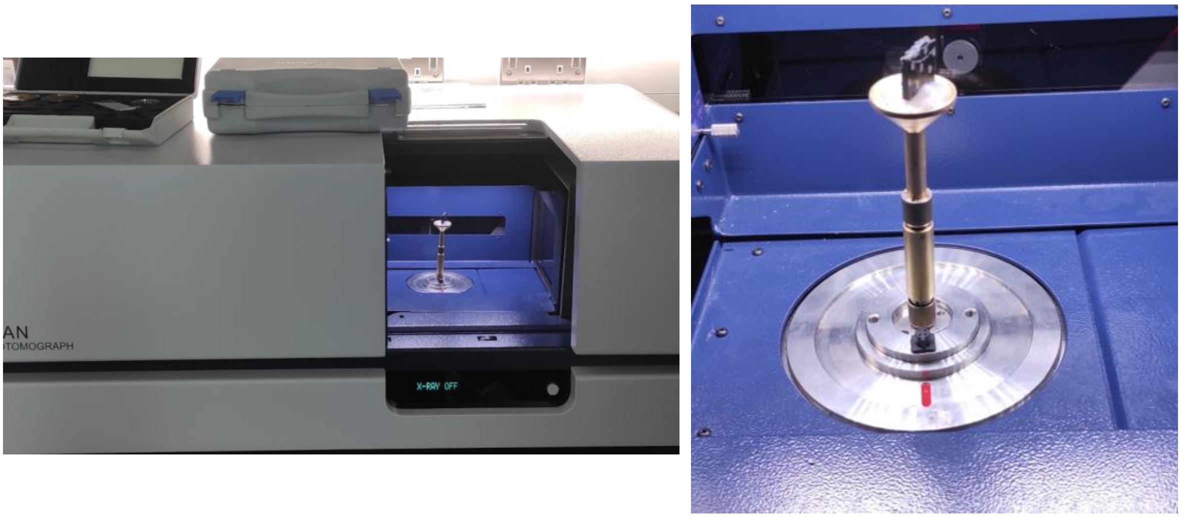


Figure 39 CT specimen tab set-up

Microscopy

Microscopy imaging was used to evaluate the effects of exposing the composite materials to liquid Nitrogen. 30x30x2mm composite samples were exposed to liquid Nitrogen with the same exposure procedures as that of the tensile testing specimens. The specimens were then potted with epoxy resin, and following curing, they were sanded and polished. This was done by the technical staff within Ulster University.

The Olympus SZ microscope (Figure 40) was used along with AmScope software to analyse the specimens and record the images. A total of three images were taken per sample to cover the entire surface area of each specimen.

Figure 40 Olympus SZ microscope and AmScope software

3.3.6 Statistical Analysis

ANOVA

For the analysis of tensile testing specimens, it is important to establish a statistically significant difference between sample sets to definitively prove a hypothesis. Two general hypotheses are associated with the tensile testing of the exposure specimens. The Null hypothesis is that there is no significance in UTS and Young modulus between baseline, short and Cyclic (long) exposure sample sets. The Alternative: there is a significant in UTS and Young modulus between baseline, short and Cyclic (long) exposure sample sets.

ANOVA testing is perfect for testing differences in variances between multiple groups. The test is also quick and requires little computational processing power. For this reason, ANOVA was used to provide the correct hypothesis per material group.

Microsoft Excel was used for the analysis of the data. Six sample sets were tested for tensile testing. Each sample set had 5 specimens as mentioned previously. The test will be used on UTS and young's modulus for each material, 3D and 2D composite.

A 95% confidence limit was used for the data and therefore a P value of 0.05. This confidence limit was used for if the test was carried out many times, 5% of the time the null hypothesis will be accepted wrongly which is known as a false positive. This test will not present any risk if a false positive is concluded for the result of this study.

The procedure for the ANOVA test is as follows:

- With sample sets properly structured in an Excel spreadsheet, select the 'Data' tab and then open, 'Data Analysis, illustrated in Figure 41.
- 'ANOVA: Single Factor' was selected from the analysis tools.
- The data on which the ANOVA test is being carried out is then selected as illustrated in Figure 42.
- The output range was selected. This is where the ANOVA data will be presented in the spreadsheet (Figure 42).

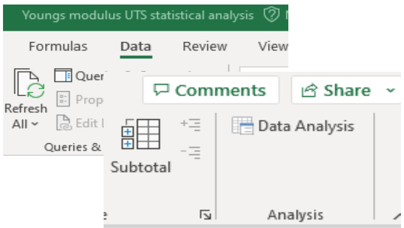
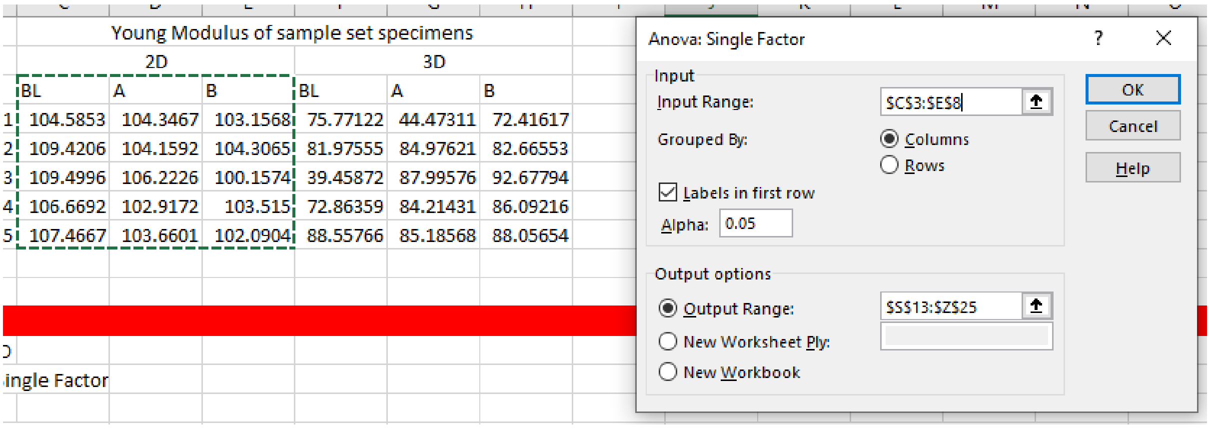


Figure 41 Excel ANOVA Data analysis location



	Young Modulus of sample set specimens					
	2D			3D		
	BL	A	B	BL	A	B
1	104.5853	104.3467	103.1568	75.77122	44.47311	72.41617
2	109.4206	104.1592	104.3065	81.97555	84.97621	82.66553
3	109.4996	106.2226	100.1574	39.45872	87.99576	92.67794
4	106.6692	102.9172	103.515	72.86359	84.21431	86.09216
5	107.4667	103.6601	102.0904	88.55766	85.18568	88.05654

Anova: Single Factor

Input

Input Range: $C$3:$E$8

Grouped By: ● Columns ○ Rows

☑ Labels in first row

Alpha: 0.05

Output options

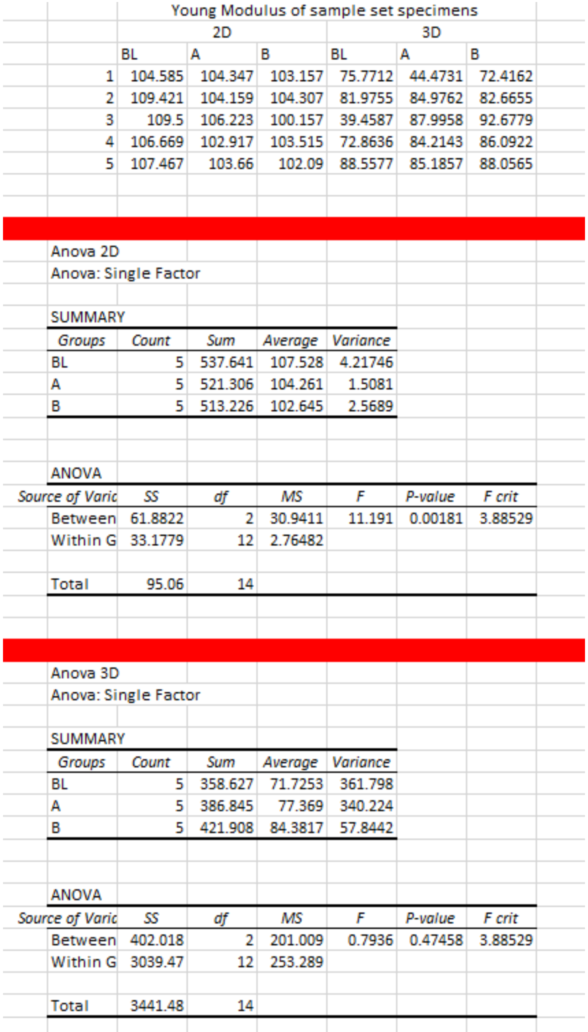
● Output Range: $S$13:$Z$25

○ New Worksheet Ply:

○ New Workbook

Figure 42 ANOVA Data range example

- Excel then automatically places statistics within the output range as illustrated in Figure 43.
- This procedure should be repeated per sample set with two AVNOVA tests mechanical properties (i.e. Two ANOVA tests for UTS and two for young's modulus).



Young Modulus of sample set specimens

	2D			3D		
	BL	A	B	BL	A	B
1	104.585	104.347	103.157	75.7712	44.4731	72.4162
2	109.421	104.159	104.307	81.9755	84.9762	82.6655
3	109.5	106.223	100.157	39.4587	87.9958	92.6779
4	106.669	102.917	103.515	72.8636	84.2143	86.0922
5	107.467	103.66	102.09	88.5577	85.1857	88.0565

Anova 2D

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
BL	5	537.641	107.528	4.21746
A	5	521.306	104.261	1.5081
B	5	513.226	102.645	2.5689

ANOVA

Source of Varia	SS	df	MS	F	P-value	F crit
Between	61.8822	2	30.9411	11.191	0.00181	3.88529
Within G	33.1779	12	2.76482			
Total	95.06	14				

Anova 3D

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
BL	5	358.627	71.7253	361.798
A	5	386.845	77.369	340.224
B	5	421.908	84.3817	57.8442

ANOVA

Source of Varia	SS	df	MS	F	P-value	F crit
Between	402.018	2	201.009	0.7936	0.47458	3.88529
Within G	3039.47	12	253.289			
Total	3441.48	14				

Figure 43 2D young's modulus example ANOVA test

Chapter 4. Results and Discussion

The question that is to be answered is what composite architecture would be more suitable for the storage of cryogenic materials; 2D laminate or 3D layer-to-layer composite architecture. Composite structures offer weight-saving opportunities and can be implemented into the design of liquid Hydrogen storage vessels for weight savings in comparison to metallic vessels. However, composites vary in structure and so mechanical response will vary. Comparing 2D laminate and 3D layer-to-layer composites' response to liquid Nitrogen exposure will determine the effect cryogenic temperatures have on the mechanical response of these structures.

4.1 Tensile testing and statistical analysis

4.1.1 Tensile testing and statistical analysis

After tensile testing of the 30 specimens, the UTS and young's modulus were calculated. Average stress and strain graphs were also plotted to show any obvious trend differences between the sample sets (Figure 44 & Figure 47). To analyse the UTS and young's modulus of each sample set, statistical analysis was used. This tool will determine if there is a significant statistical difference between sample sets per composite material. In turn, this will further reinforce any observations for the data retrieved from tensile testing of composite specimen exposure to liquid Nitrogen.

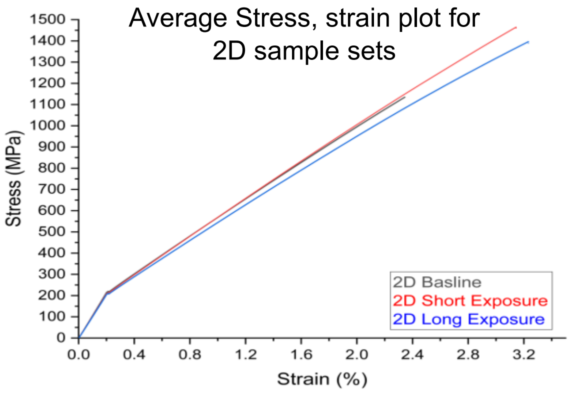


Figure 44 Average 2D stress, strain plot for Baseline, Short and cyclic (long) exposure

Looking at the average stress, strain graphs for 2D material (Figure 44), it is evident that liquid Nitrogen has some effect on the composite. This becomes more evident when looking at UTS and Young's modulus mean bar graphs, there is a small increase in the UTS between baseline and short exposure specimens (Figure 45). There is then a small decrease in the mean UTS between short exposure and cyclic (long) exposure specimens, however, the cyclic exposure mean UTS for the 2D specimens is still higher than the baseline means UTS. However, the mean error bars overlap and so it can be argued that there may not be a significant difference between baseline and exposed specimens.

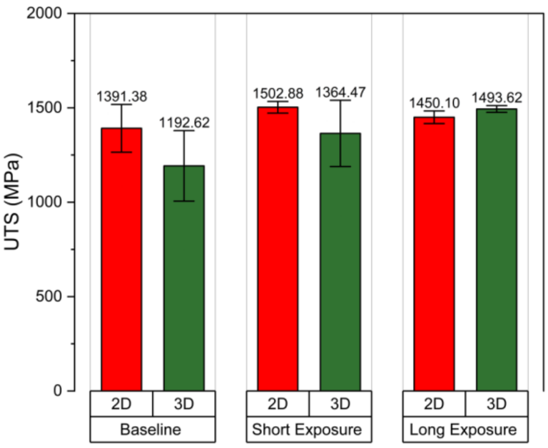


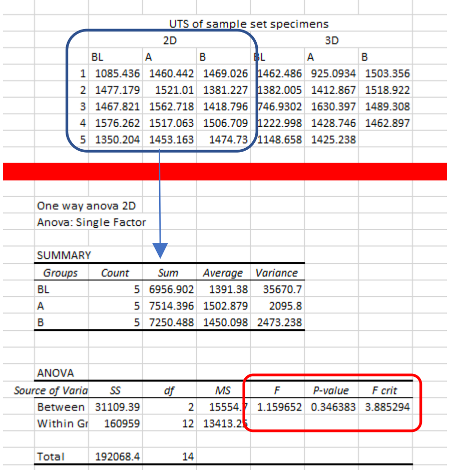
Figure 45 UTS Mean UTS for 2D & 3D baseline, short and Cyclic (long) exposure with Mean error bars.

Interrupting the ANOVA test for the 2D sample set can explain more about the data. What is important from the ANOVA test is the F, P and F critical values outlined in Figure 46.

If the F value is greater than the F critical value, there is a significant difference between the specimens. If the P value is smaller than 0.05, the Alternative hypothesis is accepted. If the F value is smaller than the F critical value, there is no significant difference between the specimens. If the P value is larger than 0.05, the Null hypothesis is accepted.

NB, The Null hypothesis is that there is no significance in UTS and Young modulus between baseline, short and Cyclic (long) exposure sample sets. The Alternative hypothesis is that there is a significance in UTS and Young modulus between baseline, short and Cyclic (long) exposure sample sets.

For the 2D specimens, there is no significant difference between the UTS of each specimen when comparing base samples with cyclic exposure and short exposure specimens. Although the UTS bar chart illustrates an Increase in UTS and then a 3.64% decrease in UTS with increased exposure to liquid Nitrogen. Statistically, there is no significant difference between the baseline specimen's short exposure and cyclic (long) exposure specimens. Therefore, it can be said that Nitrogen exposure has no significant effect on the UTS of 2D specimens.



UTS of sample set specimens

	2D			3D		
	BL	A	B	BL	A	B
1	1085.436	1460.442	1469.026	1462.486	925.0934	1503.356
2	1477.179	1521.01	1381.227	1382.005	1412.867	1518.922
3	1467.821	1562.718	1418.796	746.9302	1630.397	1489.308
4	1576.262	1517.063	1506.709	1222.998	1428.746	1462.897
5	1350.204	1453.163	1474.73	1148.658	1425.238	

One way anova 2D
Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
BL	5	6956.902	1391.38	35670.7
A	5	7514.396	1502.879	2095.8
B	5	7250.488	1450.098	2473.238

ANOVA

Source of Varia	SS	df	MS	F	P-value	F crit
Between	31109.39	2	15554.7	1.159652	0.346383	3.885294
Within Gr	160959	12	13413.2			
Total	192068.4	14				

Figure 46 2D UTS ANOVA interpretation

For the mean UTS of the 3D specimens, the mean UTS increases with increasing exposure to liquid Nitrogen. Comparing baseline with short exposure there was an increase of 12.59% and 8.65% between short exposure and cyclic exposure. This trend is seen in the stress-strain graph and the mean UTS bar chart.

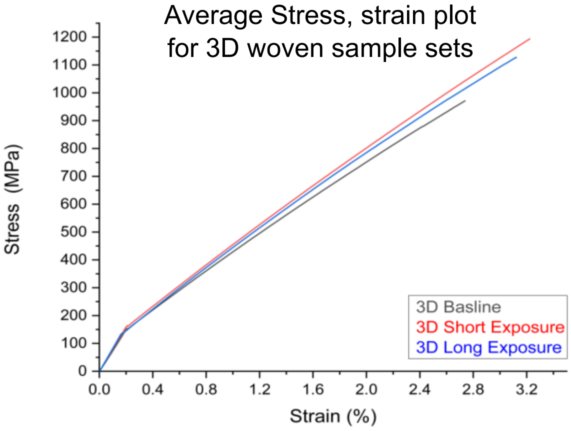


Figure 47 Average 3D stress, strain plot for Baseline, Short and cyclic (long) exposure

Statistical analysis of the 3D specimens proves there is a significant difference between baseline, short exposure and cyclic (long) exposure. Therefore, liquid Nitrogen has a significant effect on the UTS of 3D specimens.

There is a decrease in the mean young modulus of the 2D composite specimen illustrated in Figure 44 & Figure 48. There is a 3.04% decrease in the mean Young's modulus between 2D baseline and short exposure specimens. There is a further decrease of 1.55% between short exposure and cyclic exposure.

ANOVA test has concluded that there is a significant difference between the specimens and therefore exposure to liquid Nitrogen has a negative effect on the young's modulus of 2D composite material.

For the 3D composite material, the stress, strain graph (Figure 47) and bar chart (Figure 48) seem to suggest that with increasing exposure to liquid Nitrogen, there is an increase in Young's modulus of the specimens. However statistical analysis seems to suggest the opposite. There is no significant statistical difference between the individual specimen young modulus for baseline, short exposure, and cyclic exposure. Therefore, Liquid nitrogen does not increase Young's modulus of the 3D composite material.

The statical analysis is summarised below in Table 3 and Table 4.

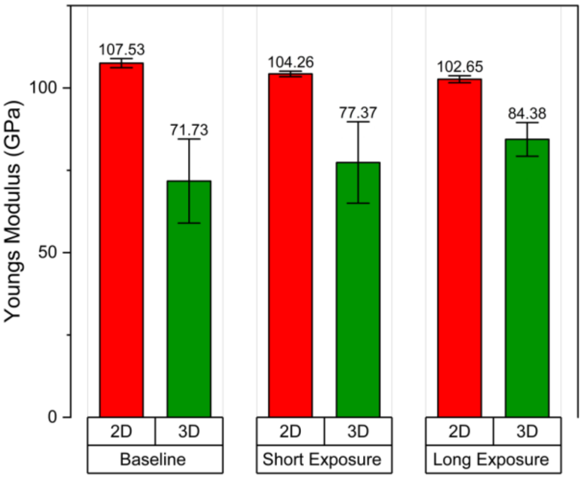


Figure 48 Mean Youngs modulus for 2D & 3D baseline, short and Cyclic (long) exposure with Mean error bars.

Table 3 UTS Statistical anlysis summary

UTS Summary

	F Value	F critical	P value	Difference type	Explanation
2D					
BL vs A vs B	1.159651938	3.885293835	0.34638258	No Significant difference	Proves that statistically, liquid Nitrogen did not have a negative impact on the UTS of 2D composite material.
3D					
BL vs A vs B	5.101837552	4.458970108	0.037301272	Significant difference	Proves that statistically, liquid Nitrogen exposure increases the UTS of the 3D composite material.

Table 4 Young's Modulus Statistical anlysis summary

Youngs modulus Summary

	F Value	F critical	P value	Difference type	Explanation
2D					
BL vs A vs B	11.19098677	3.885293835	0.001807601	Significant difference	This proves that statistically, Liquid nitrogen exposure decreases Young's modulus of 2D composite material.
3D					
BL vs A vs B	0.793596028	3.885293835	0.474579736	No Significant difference	Proves that statistically, liquid Nitrogen exposure does not affect the Youngs modulus of the 3D material.

From the statistical analysis of the tensile test data. It was proven that the UTS of the 3D woven, layer-to-layer carbon fibre structure saw an increase in UTS with increased exposure to liquid Nitrogen. However, the 3D woven composite structure has seen no statistically significant change in the young's modulus of the material when comparing the baseline specimens to specimens exposed to liquid Nitrogen.

This same pattern is observed in other studies with glass, epoxy woven fibre composites showing an increase in modulus of strength (UTS) when exposed to cryogenic temperatures, (Y. Li et al., 2022). A 7-16% decrease in the tensile properties of carbon fibre composite was seen with a reduction in temperature (Meng et al., 2020). The same trend was seen for this project however the reduction in tensile properties wasn't as severe with a reduction seen between 1.5-3.64%.

Other literature sources that have tested 3D multi-axial warp knit (MWK) composites have seen an improvement in tensile properties when exposed to liquid Nitrogen, (D. Sen Li et al., 2014). It was suggested that exposure to cryogenic temperature leads to impairment of how initial structural defects react to tensile loading and so essentially weakening the effect these structural defects have on the mechanical response of the material (Y. Li et al., 2022). It has also been suggested that the adhesion between the fibre and the matrix was enhanced with increased exposure to liquid Nitrogen, although the brittleness of the composite saw an increase when exposed to Nitrogen (D. Sen Li et al., 2014). The interfacial adhesion increases the tensile properties of the 3D woven composite structure which is seen within the project in terms of UTS.

Comparing 2D composite material, there was no statistical change in the UTS of the 2D composite material with increasing exposure to liquid Nitrogen. There was, however, a decrease in the mean young modulus with increasing exposure to liquid Nitrogen. It was seen in relevant studies that cryogenic temperatures affect the toughness of the matrix, changing the failure pattern of laminate carbon fibre-reinforced polymer structures (Meng et al., 2020). This is also a feature observed in this project, where the failure pattern changes with increased exposure to liquid Nitrogen. This is because once thermosets are exposed to cryogenic temperatures, the crosslinking structure will become more brittle, (D. Chen et al., 2021b). Due to the lack of through-thickness support offered by the 2D laminate, delamination will occur when under stress, (Cui & Ruiz, 1994). Hence the reduction in UTS with increased exposure to liquid Nitrogen.

Concerning the matrix material. The resin used is classified as a thermosetting polymer due to having an exothermic reaction during cure. Thermosetting polymers are known for having a complex cross-linked 3D microstructure, (Kausar, 2017). A study was conducted where hyperbranched polymers were exposed to cryogenic temperatures where it was found that a smaller free volume exists at a temperature of -77K [-196°C] compared to room temperature (Zhao et al., 2021). The small volume being the microstructure of the matrix material will decrease in size when exposed to cryogenic temperatures, (Zhao et al., 2021). This reduction in free volume can cause stress within the matrix material, thus leading to premature cracking of the matrix for both 2D laminate and 3D woven, layer-to-layer materials.

Looking more in-depth at the structure for each material (2D & 3D). 3D woven structure is known to be less prone to delamination due to the through-thickness fibres, (Bannister, 2004). Due to the through-thickness support, any cracks caused by differences in the thermal coefficient of thermal expansion (thermal stress, (Timmerman et al., 2001)) and free volume (Zhao et al., 2021) would be less likely to cause delamination of the composite in comparison to 2D laminate structured composites. 2D laminate composites do not offer the same through thickness support and so have a higher likelihood of delaminating due to differences in coefficient of thermal expansion and free volume reduction.

4.1.2 Tensile testing Observations

It was observed through tensile testing of the composite materials, that the fracture location of the specimen changes with increasing exposure to liquid Nitrogen. As seen from Figure 49 the failure pattern changed with increasing exposure to liquid Nitrogen for both 2D and 3D structures. This pattern was observed throughout the testing of the 2D and 3D specimens.

2D Baseline

2D Short Exposure

2D Long (Cyclic) Exposure

3D Baseline

3D Short Exposure

3D Long (Cyclic) Exposure

Figure 49 Comparison of failure patterns of 2D and 3D composites with increasing exposure to liquid Nitrogen

4.3 Microscopy

From the analysis of the microscopy images, it can be seen throughout each material that there is no significant change in the microstructure of each specimen once exposed to liquid nitrogen.

Looking closer at the images taken by the microscope and comparing 2D exposure specimens, Figure 50. It can be seen that there are no signs of cracking of both the matrix and the fibre. Also, there are no signs of delamination of the fibre layers of the 2D specimens. This may be due to the fact that the conditions were just not harsh enough to induce any visible structural change to the composite or a higher magnification may be required to show damage at a nano level.

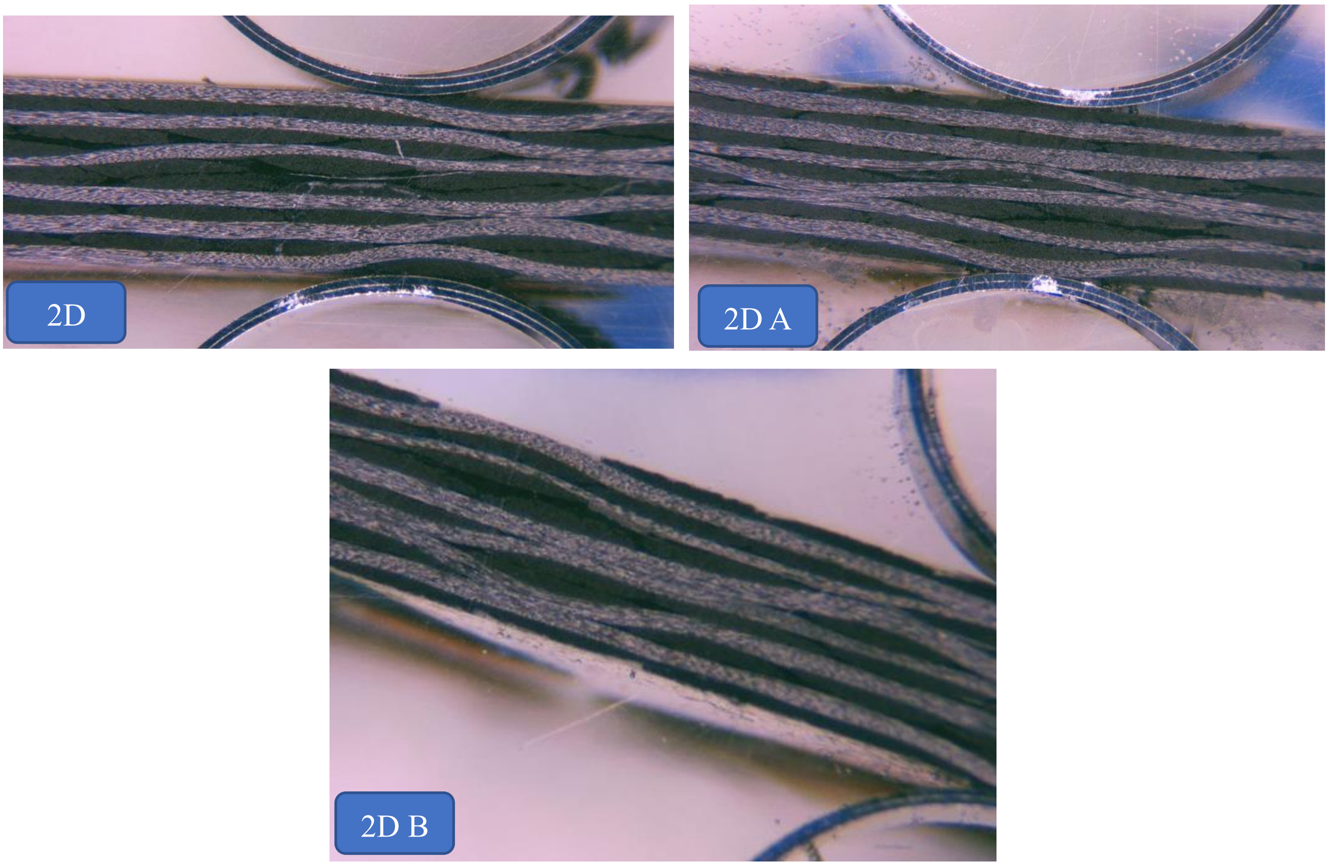


Figure 50 2D microscopy images comparing baseline (BL), short exposure (A) and Cyclic exposure (B)

Comparing the 3D specimens (Figure 51), there seems to be no change to the microstructure of the material with bassline specimens and exposed specimens.

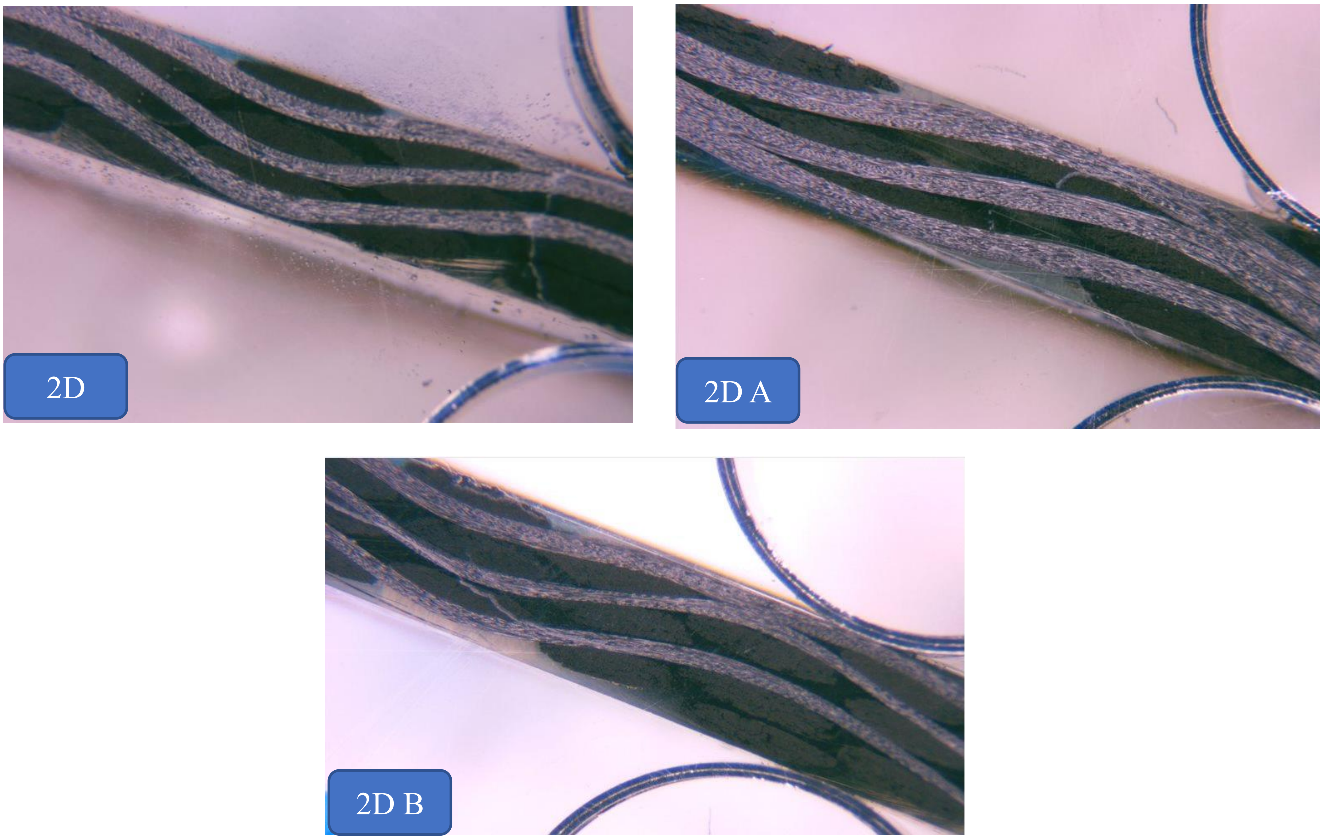


Figure 51 3D microscopy images comparing baseline (BL), short exposure (A) and Cyclic exposure (B)

Again, looking at the matrix and fibre, there seems to be no cracking throughout each sample analysed. Given that there are no obvious signs of change to the composite microstructure, the conditions may not have been harsh enough to induce any visible structural change to the composite or a higher magnification is required to show damage at a nano level.

4.2 Thermal Analysis

Plotting of the average temperature vs time values (illustrated in Figure 52), it can be seen that the 2D material conducted the cold at a faster rate within the first 60 seconds with a rate of -2.51°C/s compared to -2.19°C/s for the 3D material. However, the 3D material conducted a higher temperature than the 2D with the 3D material having a minimum temperature of -132.567°C whereas the 2D composite had a minimum temperature of -144.067°C.

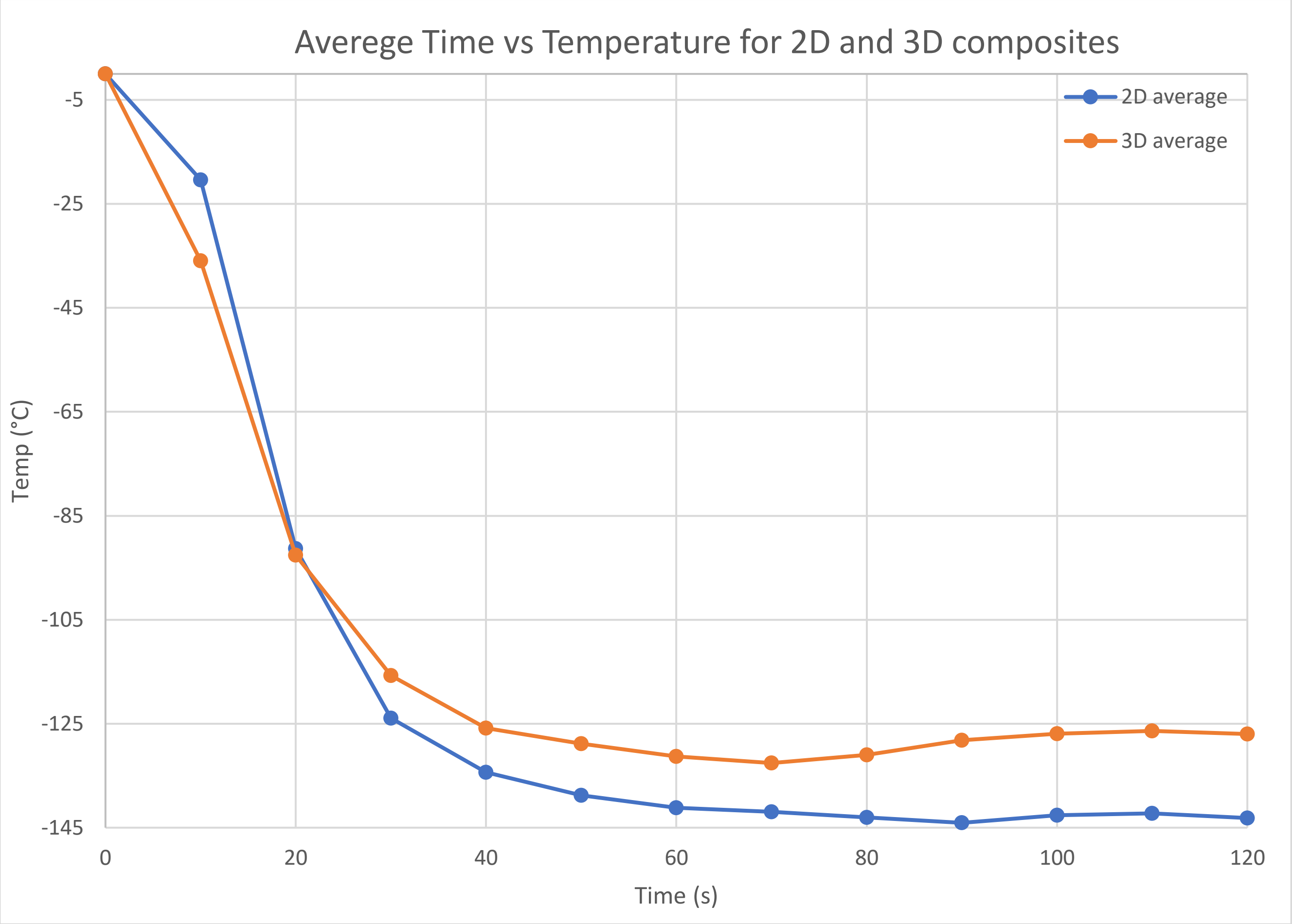


Figure 52 Average Time vs Temperature for 2D and 3D composites

The construction of both composite architectures is the determining factor of the thermal conductivity of the composite material. Composites are considered an anisotropic material, (Mazov et al., 2015). Mechanical properties of the material will change with different directions of applied load, the same can be said with the thermal conductivity properties.

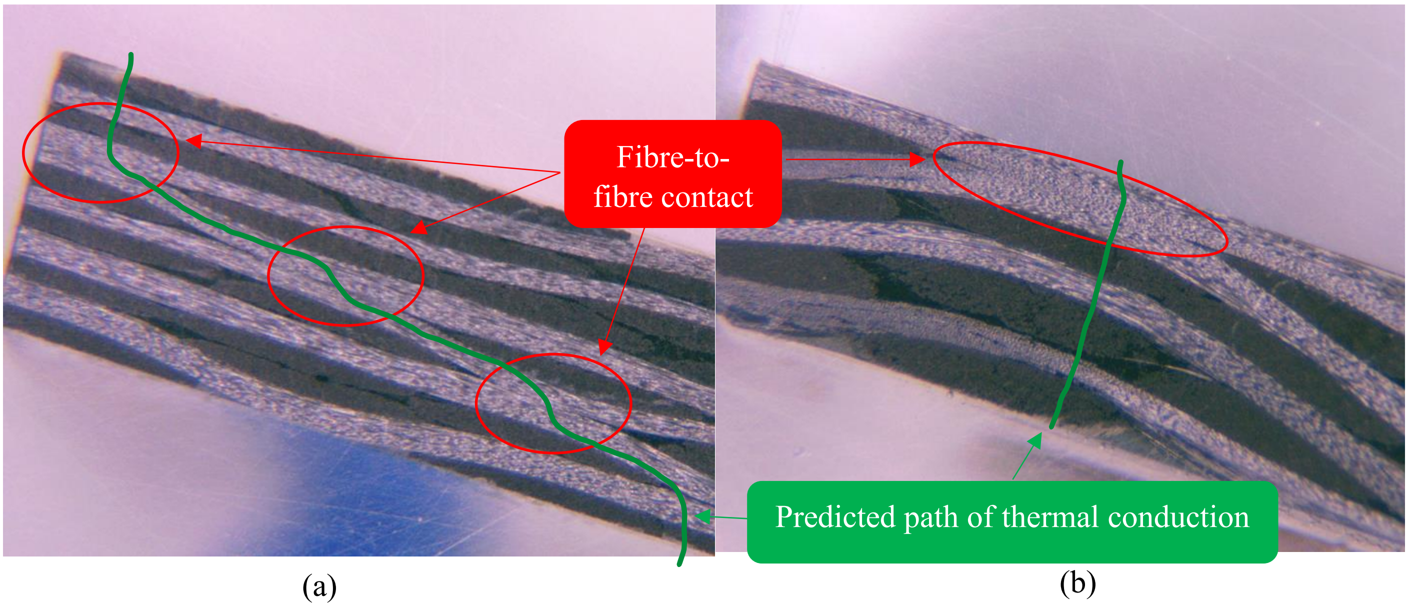
Studies have suggested that fibre alignment influences the thermal properties of a composite as fibres are the main path for thermal conduction, (Burger et al., 2016; Takizawa & Chung, 2016).

A closer look at the fibre alignment of each composite material shows more about the mechanics of thermal conduction (Figure 53). The microscopy image shows that from layer to layer, 2D material (Figure 53 (a)) has more fibre-to-fibre contact spots compared to that of 3D material (Figure 53 (b)). The heat transfer mechanism at play here is conduction as composite is a solid material, (Burger et al., 2016). It has already been stated that Carbon fibre has a higher thermal conductivity than that of matrix material (Burger et al., 2016; Takizawa & Chung, 2016). Looking at the thermal conduction formula (4), the higher the thermal conductivity variable (k) the higher the rate of thermal transfer by conduction (Q).

$$Q = -kA\frac{\Delta T}{\Delta x} \tag{4}$$

Heat flows in the path of the highest thermal conductivity (Çengel et al., 2017), in this case, it is the carbon fibre. Due to the 2D material having more fibre-to-fibre contact, there will be less thermal resistance from the matrix material and a higher thermal conductivity from the fibre for heat flow. As a result, the rate of transfer (Q) will be more for the 2D material than the 3D material. This was demonstrated with the results shown previously as the 2D material has a rate of -2.51°C/s compared to -2.19°C/s for the 3D material showing that 2D material has a higher rate of thermal conduction.

Concerning the minimum temperature conducted by each material, this may be due to the fibre volume fraction of each of the materials. If composite structures have a higher Vf, more carbon will be present in the composite, further decreasing the temperature. This can also be seen in Figure 53 with the dark black indicating resin-rich areas. Resin-rich areas will have a lower thermal conductivity compared to a fibre-rich area and so, conduct less of the cryogenic temperature from the liquid Nitrogen. It can be seen that the 2D specimen has fewer resin-rich areas and a lower temperature conduction than that of the 3D specimen.



(a) (b)

Figure 53 Microscopy images of 2D (a) and 3D (b) specimens

4.4 CT scanning

CT scanning of tensile test specimens has shown that with increased liquid nitrogen exposure, the composite material becomes more brittle. When comparing 2D laminate composite specimens exposed to liquid Nitrogen and baseline specimens, the fracture pattern changes. Comparing the baseline specimen, Figure 55 with the cyclic exposure specimen Figure 56, there is a clear change in how the specimens fractured under tensile load. This further consolidates the fact that with increased exposure to liquid Nitrogen, the composite becomes more brittle. A clean break seen in Figure 56 shows that the material is more brittle.

As mentioned previously. This is due to the change in the polymer matrix microstructure. The small volume being the microstructure of the matrix material will decrease when exposed to cryogenic temperatures, (Zhao et al., 2021). This phenomenon was observed during tensile testing illustrated in Figure 49.

Along with the change in fracture pattern, a void can be seen in sample 2, a 2D short exposure specimen illustrated in Figure 54. This may have been a point of failure for this specimen and voids are not uncommon during the manufacture of composites and they are classified as an imperfection in composites structures, (Hagstrand et al., 2005).

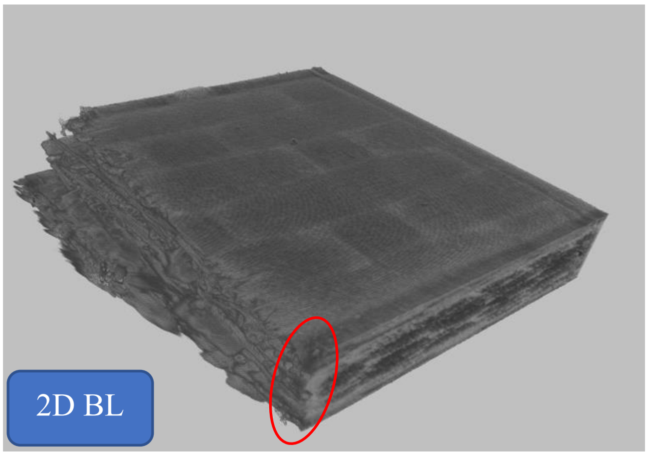


Figure 55 Sample 1, 2D Baseline tensile test failure CT image

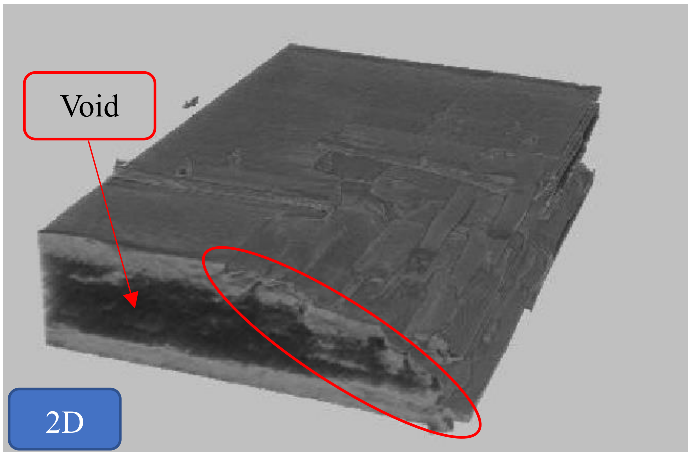


Figure 54 Sample 2, 2D Short Exposure tensile test failure CT image

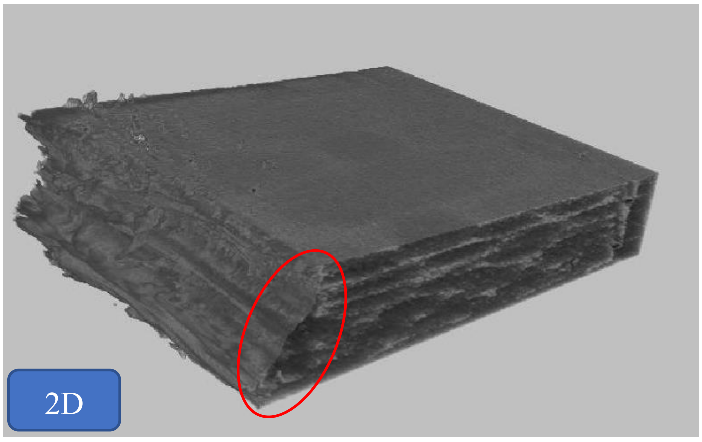


Figure 56 Sample 3, 2D Cyclic (long) exposure tensile test failure CT image

Comparing 2D specimens with 3D specimens show that the same fracture phenomenon is seen in the 3D specimens. That is, the point of fracture is more clearly defined with increased exposure to liquid Nitrogen. The difference in fracture pattern can be seen in Figure 57 and Figure 58. This trend is like that seen with the 2D specimens. However, there are some other microstructural differences seen with the 3D specimens that are not seen with the 2D specimens.

Specimen 6, 3D cyclic (long) exposure, (Figure 59) has some matrix cracking and fibre pull-out. This is not seen with the baseline or short exposure specimens (Figure 57 & Figure 58), nor with the 2D specimens previously.

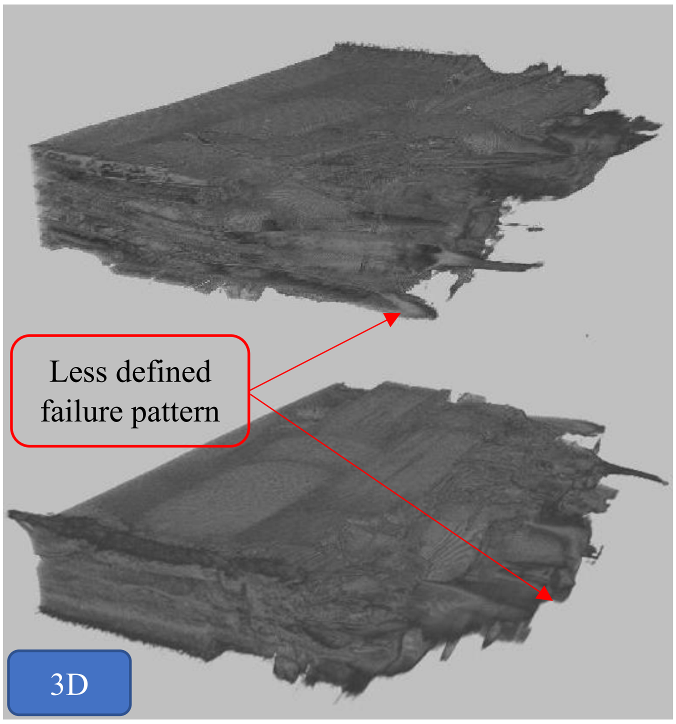


Figure 57 Sample 4, 3D Baseline tensile test failure CT images.

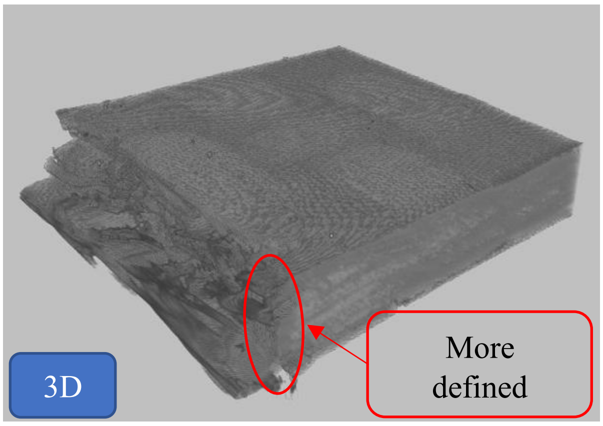


Figure 58 Sample 5, 3D Short Exposure tensile test failure CT image

The matrix cracking (Figure 59) is due to the more brittle nature of the composite as it was exposed to liquid Nitrogen. When the specimen failed, the crack propagated through the composite specimen. This led to a matrix, fibre interface failure which is further reinforced by the fact that fibre pull-out was observed from the 3D cyclic exposure specimen. It was mentioned earlier that small volume being the microstructure of the matrix material will decrease when exposed to cryogenic temperatures, (Zhao et al., 2021). The reduction in small volume causes residual stress to build up in the matrix of the composite. This seems to be the case as with residual stress build-up in the matrix-fibre interface, fibre pull-out was observed when the 3D composite specimens were exposed to cyclic exposure to liquid Nitrogen. A study investigating failure mechanisms of 3D woven composites has found that deboning of the matrix, fibre interface between binder yarns and matrix is the main mechanism for damage, (Yu et al., 2015).

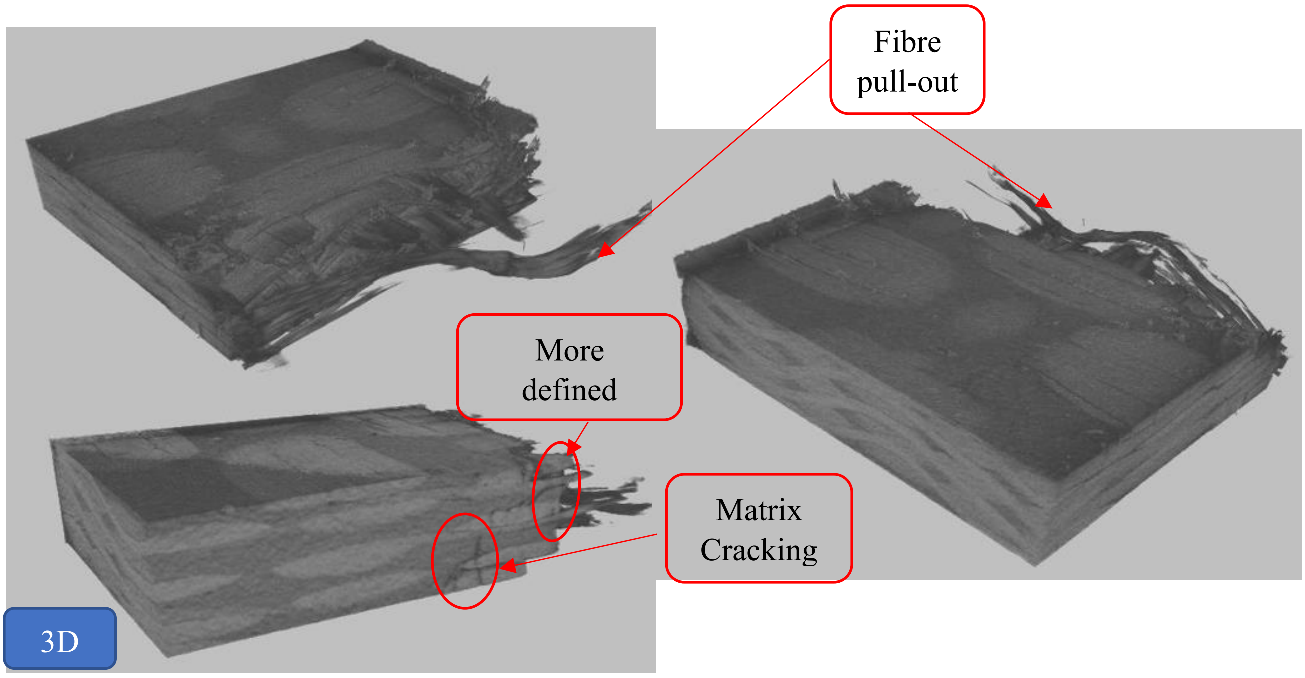


Figure 59 Sample 6, 3D Cyclic (long) exposure tensile test failure CT images

Chapter 5. Conclusion

To conclude, this study has compared the mechanical and thermal response of 2D laminate and 3D woven layer-to-layer when exposed to cryogenic temperatures, with the aim of determining which composite architecture would be more suited for the storage of cryogenic materials such as liquid Hydrogen and liquid Nitrogen. The findings from this study are as follows:

- 3D woven layer-to-layer composite materials increase in UTS with no change to Young's modulus of the material when exposed to cryogenic temperatures.
- 2D laminate composites have no change in UTS with increasing exposure to cryogenic temperatures. However, there is a decrease in Young's modulus.
- Both 3D woven layer-to-layer and 2D laminate composites become more brittle when exposed to cryogenic temperatures.
- Thermal conductivity of the 3D woven layer-to-layer composite is less than that of the 2D laminate composite.

These results show that with the current test procedures, 3D woven, layer-to-layer is favoured over the 2D laminate architecture for the storage of liquid Hydrogen. Both materials prove they become more brittle; however, the mechanical properties of 3D architecture did not decrease during exposure to liquid Nitrogen. The 2D laminate architecture shows a decrease in Young's modulus of which the material will deform more easily under load compared to baseline specimens. Thermal conduction of the 3D architecture was also less than that of the 2D laminate architecture and so the 3D architecture has a higher thermal resistance and therefore has a better architecture for potential insulating properties compared to 2D laminate composites.

There were however challenges associated with this project including exposing the composite materials to liquid Hydrogen. The facilities were not available for handling liquid Hydrogen and the results may not be a true reflection of how each material reacts when exposed to liquid Hydrogen compared to liquid Nitrogen. The exposure procedure itself was a challenge.

Each tensile specimen needed to be flipped within the cryogenic container to try and achieve even exposure of the specimens to liquid Nitrogen. However, the specimens may not have been exposed evenly and so this may not be accurately presented in the results.

Considering these limitations, further research opportunities include exposing the same composite materials to liquid Hydrogen and evaluating the mechanical and thermal response using the same procedures outlined in this project. This may show that a further reduction in temperature (-54°C) may have further effects on the young modulus, UTS and structural integrity of each composite architecture.

Furthermore, through thickness and XYZ woven structures should be tested and compared with 3D layer-to-layer and 2D laminate composites. Tensile and bend testing can be performed during cryogenic exposure of the specimens. This would more accurately represent what the composite architectures would experience if liquid Hydrogen was stored in composite vessels of the same materials (2D laminate carbon fibre and 3D woven layer-to-layer carbon fibre). Intensive cyclic exposure to cryogenic temperatures along with high temperatures could also be tested so to simulate how the composite would perform in a hot climate containing a cryogenic liquid.

Hoop stress could also be evaluated during exposure to liquid Hydrogen. The structure of the composite may persuade mechanical stresses under cryogenic exposure and mechanical loading. Investigations into reducing the brittleness of composite when exposed to cryogenic temperatures should also be investigated.

Furthermore, polymer liner materials could be tested in tandem with composite structures to understand how heat conduction changes from the composite architecture and the polymer liner while also investigating permeability. Additives to the matrix material are another possible avenue of investigation. Additives such as fibres and particles could be tested to determine the mechanical and thermodynamic effects it has over composite with no additives.

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Chen, D., Li, J., Yuan, Y., Gao, C., Cui, Y., Li, S., Liu, X., Wang, H., Peng, C., & Wu, Z. (2021b). *polymers A Review of the Polymer for Cryogenic Application: Methods, Mechanisms and Perspectives*. https://doi.org/10.3390/polym1303

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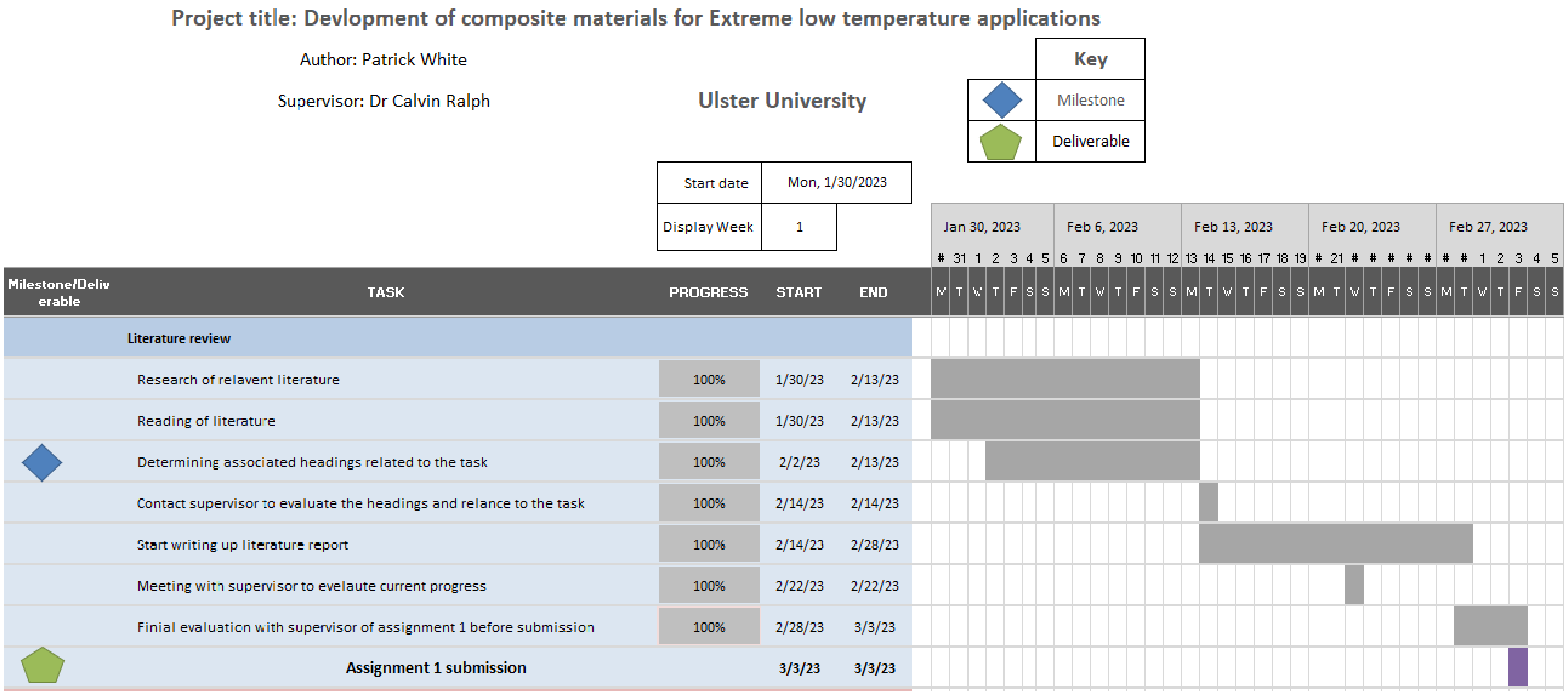
Appendix A1: Project Gantt Chart



Project title: Devlopment of composite materials for Extreme low temperature applications

Author: Patrick White

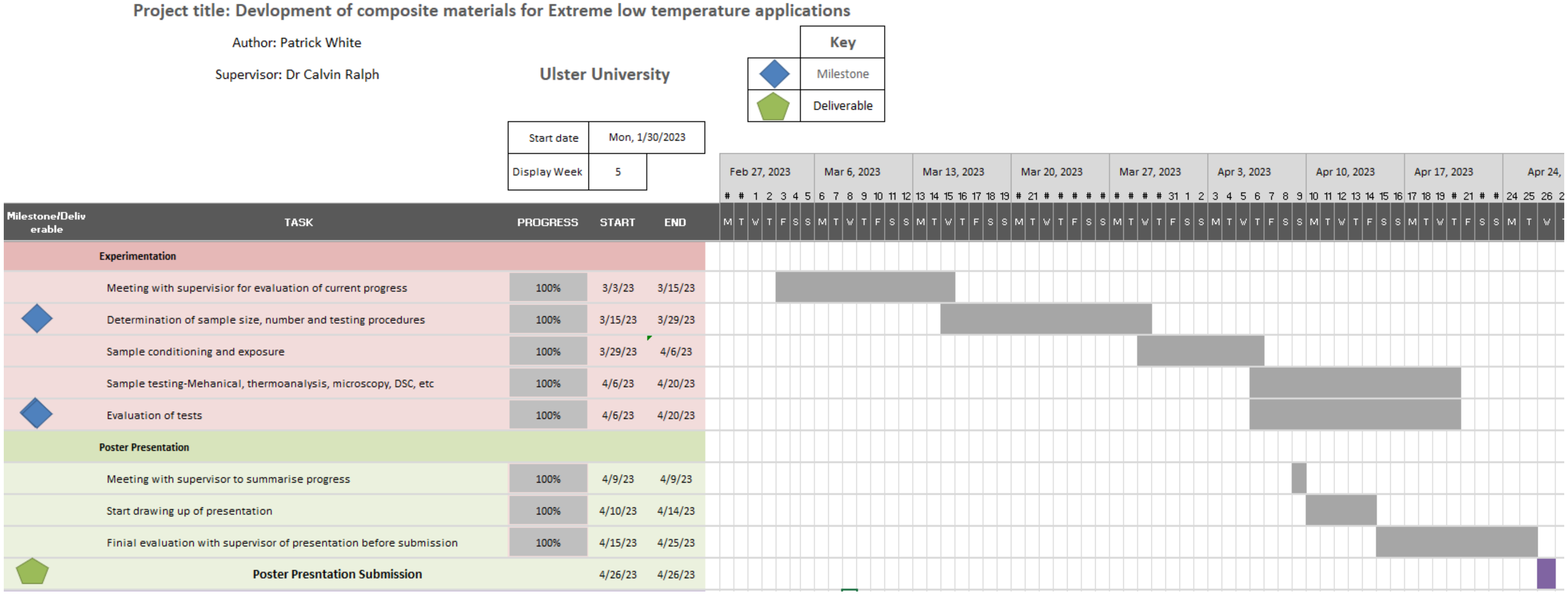
Supervisor: Dr Calvin Ralph

Ulster University

	Key
◆	Milestone
⬟	Deliverable

Start date	Mon, 1/30/2023
Display Week	1

Milestone/Deliverable	TASK	PROGRESS	START	END
	Literature review			
	Research of relavent literature	100%	1/30/23	2/13/23
	Reading of literature	100%	1/30/23	2/13/23
◆	Determining associated headings related to the task	100%	2/2/23	2/13/23
	Contact supervisor to evaluate the headings and relance to the task	100%	2/14/23	2/14/23
	Start writing up literature report	100%	2/14/23	2/28/23
	Meeting with supervisor to evelaute current progress	100%	2/22/23	2/22/23
	Finial evaluation with supervisor of assignment 1 before submission	100%	2/28/23	3/3/23
⬟	**Assignment 1 submission**		**3/3/23**	**3/3/23**



Project title: Devlopment of composite materials for Extreme low temperature applications

Author: Patrick White

Supervisor: Dr Calvin Ralph

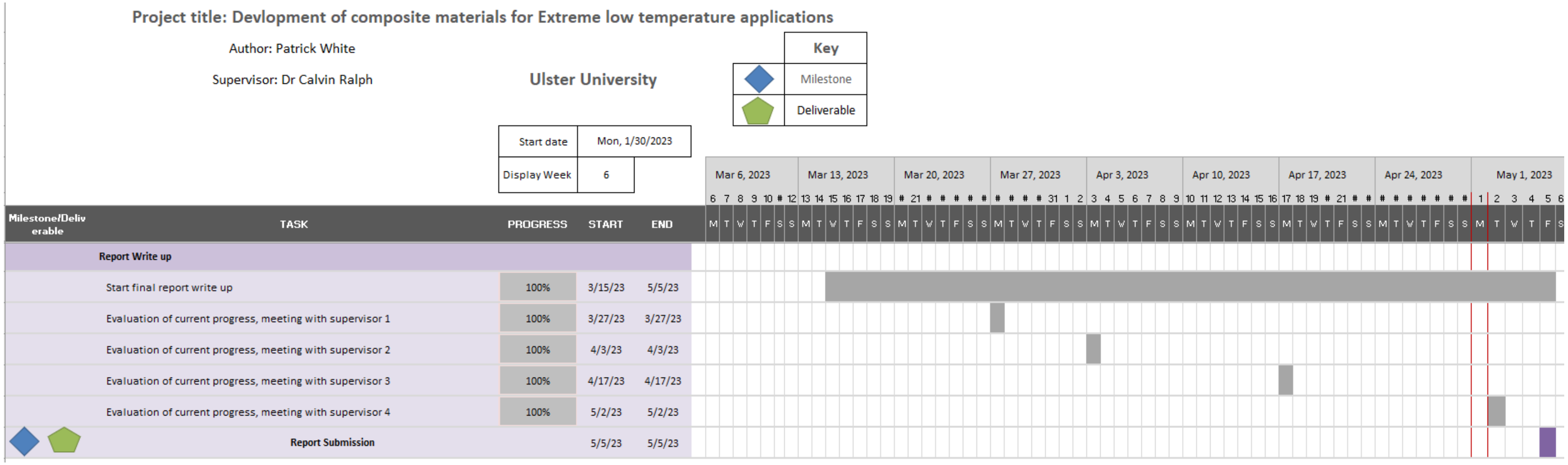
Ulster University

	Key
◆	Milestone
⬟	Deliverable

Start date	Mon, 1/30/2023
Display Week	5

Feb 27, 2023 · Mar 6, 2023 · Mar 13, 2023 · Mar 20, 2023 · Mar 27, 2023 · Apr 3, 2023 · Apr 10, 2023 · Apr 17, 2023 · Apr 24,

Milestone/Deliverable	TASK	PROGRESS	START	END
	Experimentation			
	Meeting with supervisior for evaluation of current progress	100%	3/3/23	3/15/23
◆	Determination of sample size, number and testing procedures	100%	3/15/23	3/29/23
	Sample conditioning and exposure	100%	3/29/23	4/6/23
	Sample testing-Mehanical, thermoanalysis, microscopy, DSC, etc	100%	4/6/23	4/20/23
◆	Evaluation of tests	100%	4/6/23	4/20/23
	Poster Presentation			
	Meeting with supervisor to summarise progress	100%	4/9/23	4/9/23
	Start drawing up of presentation	100%	4/10/23	4/14/23
	Finial evaluation with supervisor of presentation before submission	100%	4/15/23	4/25/23
⬟	**Poster Presntation Submission**		4/26/23	4/26/23



Project title: Devlopment of composite materials for Extreme low temperature applications

Author: Patrick White

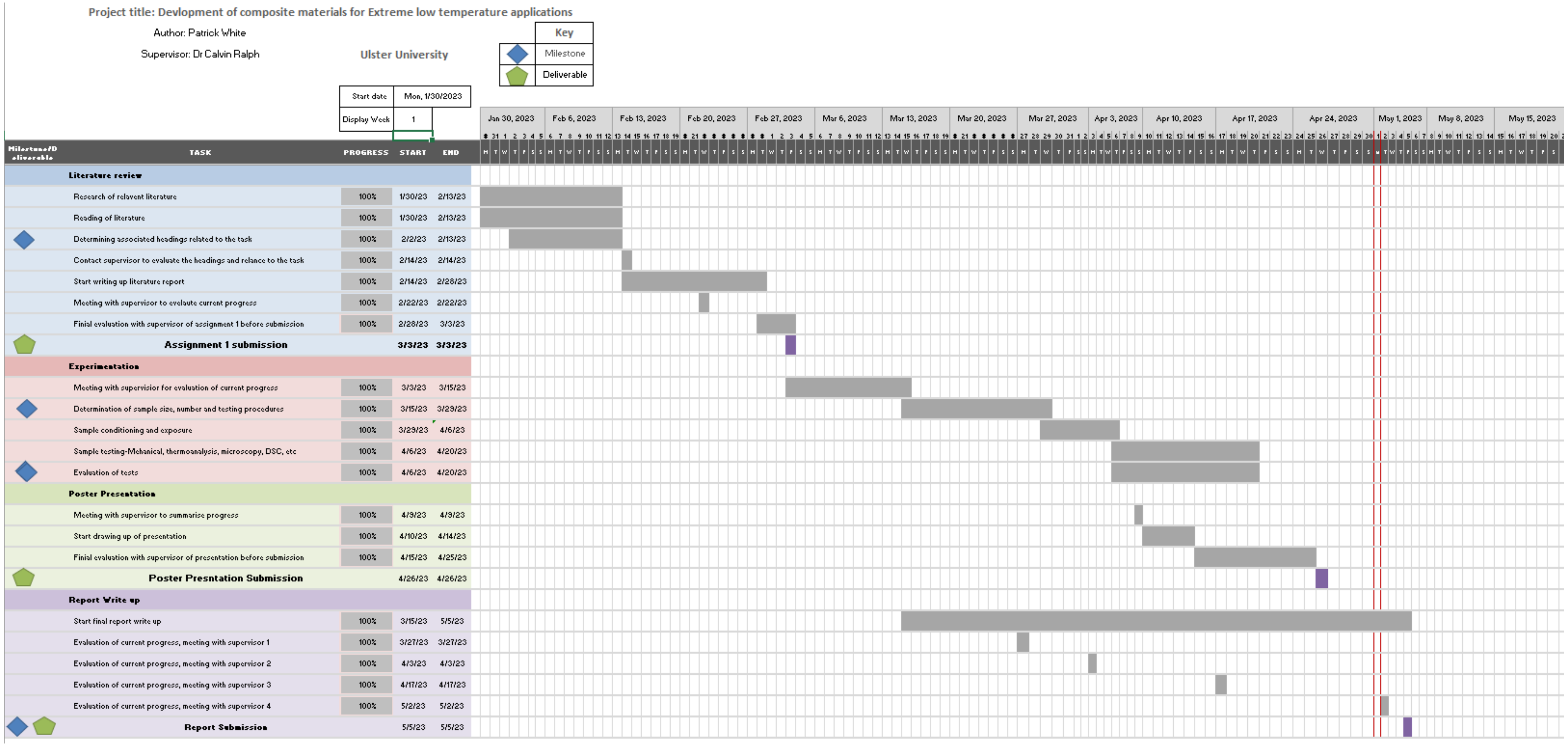
Supervisor: Dr Calvin Ralph

Ulster University

	Key
◆	Milestone
⬟	Deliverable

Start date	Mon, 1/30/2023
Display Week	6

Milestone/Deliverable	TASK	PROGRESS	START	END
	Report Write up			
	Start final report write up	100%	3/15/23	5/5/23
	Evaluation of current progress, meeting with supervisor 1	100%	3/27/23	3/27/23
	Evaluation of current progress, meeting with supervisor 2	100%	4/3/23	4/3/23
	Evaluation of current progress, meeting with supervisor 3	100%	4/17/23	4/17/23
	Evaluation of current progress, meeting with supervisor 4	100%	5/2/23	5/2/23
◆ ⬟	**Report Submission**		5/5/23	5/5/23



Project title: Devlopment of composite materials for Extreme low temperature applications

Author: Patrick White

Supervisor: Dr Calvin Ralph

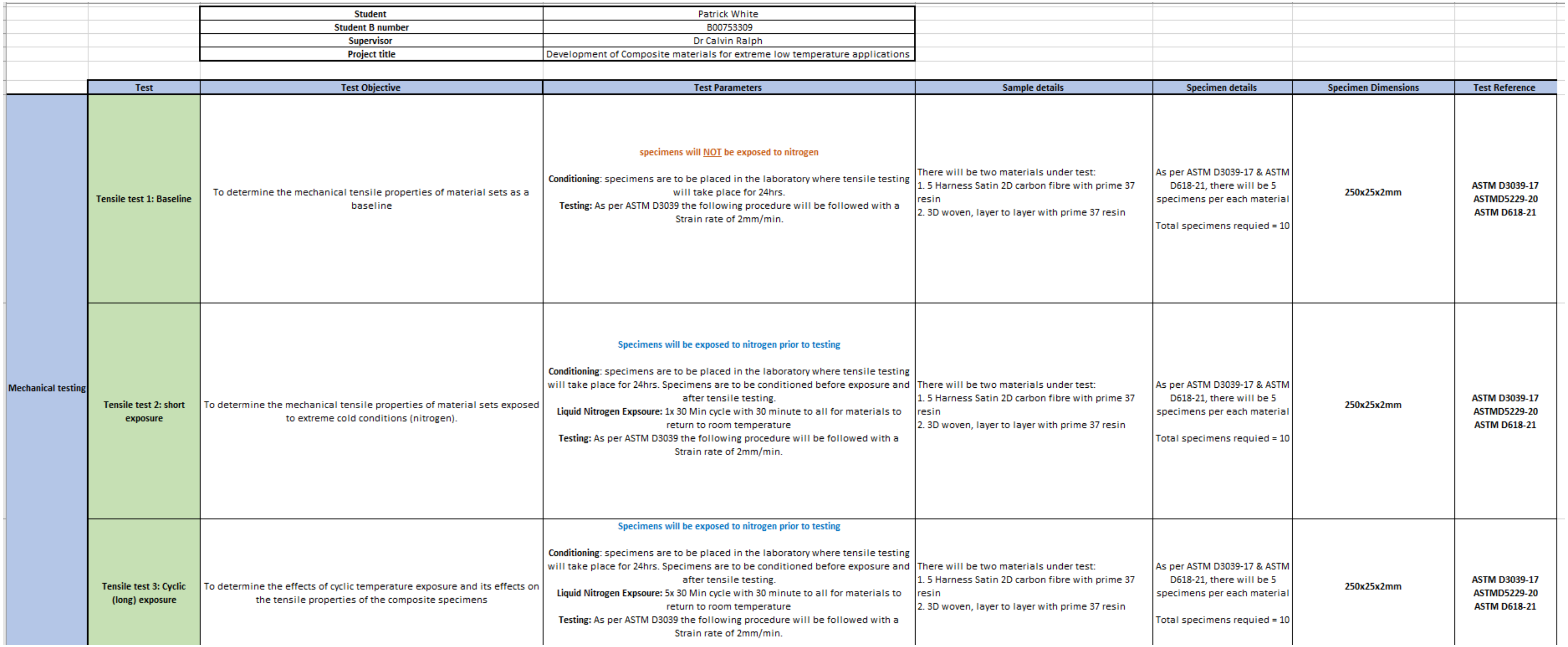
Ulster University

Key	
◆	Milestone
⬟	Deliverable

Start date	Mon, 1/30/2023
Display Week	1

Milestone/Deliverable	TASK	PROGRESS	START	END
	Literature review			
	Research of relavent literature	100%	1/30/23	2/13/23
	Reading of literature	100%	1/30/23	2/13/23
◆	Determining associated headings related to the task	100%	2/2/23	2/13/23
	Contact supervisor to evaluate the headings and relance to the task	100%	2/14/23	2/14/23
	Start writing up literature report	100%	2/14/23	2/28/23
	Meeting with supervisor to evelaute current progress	100%	2/22/23	2/22/23
	Finial evaluation with supervisor of assignment 1 before submission	100%	2/28/23	3/3/23
⬟	**Assignment 1 submission**		**3/3/23**	**3/3/23**
	Experimentation			
	Meeting with supervisior for evaluation of current progress	100%	3/3/23	3/15/23
◆	Determination of sample size, number and testing procedures	100%	3/15/23	3/29/23
	Sample conditioning and exposure	100%	3/29/23	4/6/23
	Sample testing-Mehanical, thermoanalysis, microscopy, DSC, etc	100%	4/6/23	4/20/23
◆	Evaluation of tests	100%	4/6/23	4/20/23
	Poster Presentation			
	Meeting with supervisor to summarise progress	100%	4/9/23	4/9/23
	Start drawing up of presentation	100%	4/10/23	4/14/23
	Finial evaluation with supervisor of presentation before submission	100%	4/15/23	4/25/23
⬟	**Poster Presntation Submission**		4/26/23	4/26/23
	Report Write up			
	Start final report write up	100%	3/15/23	5/5/23
	Evaluation of current progress, meeting with supervisor 1	100%	3/27/23	3/27/23
	Evaluation of current progress, meeting with supervisor 2	100%	4/3/23	4/3/23
	Evaluation of current progress, meeting with supervisor 3	100%	4/17/23	4/17/23
	Evaluation of current progress, meeting with supervisor 4	100%	5/2/23	5/2/23
◆ ⬟	**Report Submission**		5/5/23	5/5/23

Appendix A2: Project test plan



Student	Patrick White
Student B number	B00753309
Supervisor	Dr Calvin Ralph
Project title	Development of Composite materials for extreme low temperature applications

	Test	Test Objective	Test Parameters	Sample details	Specimen details	Specimen Dimensions	Test Reference
Mechanical testing	**Tensile test 1: Baseline**	To determine the mechanical tensile properties of material sets as a baseline	specimens will NOT be exposed to nitrogen **Conditioning**: specimens are to be placed in the laboratory where tensile testing will take place for 24hrs. **Testing:** As per ASTM D3039 the following procedure will be followed with a Strain rate of 2mm/min.	There will be two materials under test: 1. 5 Harness Satin 2D carbon fibre with prime 37 resin 2. 3D woven, layer to layer with prime 37 resin	As per ASTM D3039-17 & ASTM D618-21, there will be 5 specimens per each material Total specimens requied = 10	**250x25x2mm**	**ASTM D3039-17** **ASTMD5229-20** **ASTM D618-21**
	Tensile test 2: short exposure	To determine the mechanical tensile properties of material sets exposed to extreme cold conditions (nitrogen).	Specimens will be exposed to nitrogen prior to testing **Conditioning**: specimens are to be placed in the laboratory where tensile testing will take place for 24hrs. Specimens are to be conditioned before exposure and after tensile testing. **Liquid Nitrogen Expsoure:** 1x 30 Min cycle with 30 minute to all for materials to return to room temperature **Testing:** As per ASTM D3039 the following procedure will be followed with a Strain rate of 2mm/min.	There will be two materials under test: 1. 5 Harness Satin 2D carbon fibre with prime 37 resin 2. 3D woven, layer to layer with prime 37 resin	As per ASTM D3039-17 & ASTM D618-21, there will be 5 specimens per each material Total specimens requied = 10	**250x25x2mm**	**ASTM D3039-17** **ASTMD5229-20** **ASTM D618-21**
	Tensile test 3: Cyclic (long) exposure	To determine the effects of cyclic temperature exposure and its effects on the tensile properties of the composite specimens	Specimens will be exposed to nitrogen prior to testing **Conditioning**: specimens are to be placed in the laboratory where tensile testing will take place for 24hrs. Specimens are to be conditioned before exposure and after tensile testing. **Liquid Nitrogen Expsoure:** 5x 30 Min cycle with 30 minute to all for materials to return to room temperature **Testing:** As per ASTM D3039 the following procedure will be followed with a Strain rate of 2mm/min.	There will be two materials under test: 1. 5 Harness Satin 2D carbon fibre with prime 37 resin 2. 3D woven, layer to layer with prime 37 resin	As per ASTM D3039-17 & ASTM D618-21, there will be 5 specimens per each material Total specimens requied = 10	**250x25x2mm**	**ASTM D3039-17** **ASTMD5229-20** **ASTM D618-21**

Physical testing	**Thermal analysis**	To evaluate the thermal conductivity performance of composite specimens	**Conditioning:** specimens are to be placed in the laboratory where tensile testing will take place for 24hrs. Specimens are to be conditioned before exposure and after tensile testing. **Liquid Nitrogen containment:** Composite plaques will have a 80x40x25mm box section adhered to its surface by Araldite. 3x 3 min exposure cyclics with 30 minute to all for materials to return to room temperature. Testing: No standards for reference, however the procedure is as follows: •Place the thermocouple on the bottom side of the composite specimen, securing it with a generous amount of high-temperature tape (Figure 37). •Turn on the thermocouple temperature gauge and record the temperature. •Place the specimen in the fume cupboard on top of the two 40X40mm wooden blocks, ensuring that the thermocouple is not in contact with the wood or fume cupboard (Figure 38). •A video recording of the stopwatch and thermocouple readout meter is started. •Pour a small amount of liquid Nitrogen into the box steel, allowing the composite and steel to lower in temperature for 10 seconds. •The stopwatch is started at the same time as the first pour is finished. •After 10 seconds, more liquid Nitrogen is poured into the box section. The level of liquid Nitrogen should be close to the top. •78X38X25 polystyrene foam block is then placed on top of the steel box section to limit Nitrogen loss due to evaporation. •The test is allowed to run for three minutes, ensuring the camera used for videoing the stopwatch and thermocouple readout is being recorded in focus. After three minutes, the recording and stopwatch can the stopped.	There will be 1 specimen per material under test: 1. 5 Harness Satin 2D carbon fibre with prime 37 resin 2. 3D woven, layer to layer with prime 37 resin	Total specimens requied = 2	**139x54x2mm**	-
Failure analysis tests	**Microscopic analysis**	Determine the mechanisms of failure under cryogenic conditions vs baseline specimens under no mechanical loading conditions. This will be used to evaluate how the composite structure was affected by liquid Nitrogen Exposure.	Three specimens per material. 1 specimen will be analysed per sample set. 2D BL- 2D baseline specimen with no liquid nitrogen exposure. 2D A- 2D short exposure specimen with 1x 30 Min liquid Nitrogen exposure cycle. 2D B- 2D Cyclic exposure specimen with 5x 30 Min liquid Nitrogen exposure cycle. 3D BL- 2D baseline specimen with no liquid nitrogen exposure. 3D A- 2D short exposure specimen with 1x 30 Min liquid Nitrogen exposure cycle. 3D B- 2D Cyclic exposure specimen with 5x 30 Min liquid Nitrogen exposure cycle. Specimens will then be potted in resin for microscopy	There will be one specimen per sample sets per material: 1. Baseline 2D & 3D 2. A, Short exposure 2D & 3D 3. B, Cyclic exposure 2D & 3D	6 specimens in total will be analysed under microscopy Total specimens requied = 6	**30x30x2mm**	-
Failure analysis tests	**CT Analysis**	Determine the mechanisms of failure under cryogenic conditions vs baseline specimens when under mechanical, tensile loading.	After tensile testing, 1 specimen is chosen at random from each sample set, (BL,A,B) from each material (2D & 3D). Specimens chosen at random will be cut to an approximate size of 10x10mm for micro CT scanning.	There will be one specimen per sample sets per material: 1. Baseline 2D & 3D 2. A, Short exposure 2D & 3D 3. B, Cyclic exposure 2D & 3D	6 tensile failure specimens will be analysised under micro CT scanning. Total specimens requied = 6	**approx 10x10x2mm**	-