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MECHANICAL TESTING OF FIBRE-REINFORCED POLYMER MATRIX COMPOSITES AT CRYOGENIC TEMPERATURES (-165 °C)

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Approved on behalf of NPLML by
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EXECUTIVE SUMMARY

This report details a programme of work undertaken to investigate the tensile and compressive properties of carbon and glass thermoset and thermoplastic fibre-reinforced polymer (FRP) composites at cryogenic temperatures; down to -165 °C (108 K) the boiling temperature of liquified natural gas (LNG) at atmospheric pressure. Tension and compression tests were carried out in general accordance with ISO 527-4 [1] and ISO 14126 [2], respectively.

The document presents the outcomes of the second stage of work to develop capabilities for mechanical testing of FRP composites at cryogenic temperatures within the National Measurement System (NMS) project “Polymer Composites Metrology in Support of Regulations, Codes and Standards (RCS) Infrastructure”, undertaken by the Advanced Engineering Materials (AEM) Group at the National Physical Laboratory (NPL). The project’s key objectives are to develop capability suitable for investigating the mechanical properties at cryogenic temperatures of composite materials used in liquified natural gas (LNG) and liquid hydrogen (LH_2) distribution and storage applications.

The insights provided in this report have been entirely generated by NPL, alongside thorough relevant published literature and existing standards review.

1 INTRODUCTION

Due to their excellent properties, such as light weight, high specific strength and stiffness, excellent corrosion resistance, low thermal expansion and designability freedom; fibre-reinforced polymer (FRP) composites have been extensively studied, developed, and used in high-performance engineering applications since the 1940s.

In recent years, due to the emerging growth of industry sectors focussed on climate-neutral energy sources; the research, development, and application of FRP composites in the cryogenic liquid storage and distribution fields has risen dramatically. The use of FRPs has been deemed essential to reduce fossil fuel reliance, consumption, and CO_2 emissions, vital materials towards achieving the Net-Zero goal set by the UK Government [3, 4]. Relevant studies report that replacing metallic materials with carbon fibre-reinforced polymer (CFRP) composite can reduce cryogenic tank weights by 30% [5].

The selection of suitable materials for cryogenic storage and distribution applications is a challenging task. Thermal and mechanical properties such as ductility, low coefficient of thermal expansion (CTE), low thermal conductivity, low permeability as well as low cost are to be highly considered in the material selection criteria stage. However, other structural requirements, such as energy absorption, fabricability, inspectability, reparability and compatibility with other parts will also play an important role in the future of cryogenic tank development and manufacture [6].

In order to be used in liquid cryogenic storage and distributions applications, materials should maintain excellent mechanical, physical and thermal performance at very low temperatures. Literature defines the field of cryogenics as relating to temperatures below -150 °C, where the boiling points of gases such as natural gas (LNG), oxygen (LOx), nitrogen (LN_2), hydrogen (LH_2), and helium (LHe) occur, as presented in Table 1 [7]. Liquefied natural gas (LNG) is natural gas, predominantly methane, converted to liquid form at -162 °C for ease of storage or distribution [8].

FRP composite materials, when exposed to extreme temperatures, can exhibit significant changes in their properties. Under cryogenic cycling from room temperature to cryogenic temperatures, thermal stresses are induced by the mismatch of coefficients of thermal expansion (CTEs) of the constituents, leading to the creation of microcracks that degrade the mechanical properties of the material [4, 6, 9]. Therefore, the performance of any candidate material for cryogenic applications must be fully characterised in a similar environment, by cooling to the desired temperature using common inert cryogenic fluids such as LN_2 or LHe, to ensure structural requirements are satisfactorily met under these extreme conditions. In the long term, it is also expected that once the performance of candidate materials for cryogenic applications is extensively investigated, standardised, and qualified, further investigations on the effects linked to chemical interactions will be required, as proposed by the Aerospace Technology Institute in its Fly Zero Advanced Materials report [3].

The adoption of FRP composites in applications exposed to cryogenic temperatures and/or cryogenic gases and fluids, represents high technical risks due to the lack of availability of sufficiently reliable sources of engineering design data or universally accepted standard test methods published to date. Cryogenic data published so far on FRP composites have resulted in remarkable inconsistencies with regard to strength and stiffness values [7, 9, 10, 11, 12, 13]. Therefore, the development of bespoke, complex, costly and immature technologies and standards to allow the industry to fully understand the behaviour of FRP composite materials under cryogenic environment is considered of utmost importance.

This report presents the capability requirements, development details, measurement procedure and results generated for the characterisation of the mechanical performance of FRP composite materials at cryogenic temperatures (-165 °C). In this study, the mechanical properties of FRP composites with different resin, fibre and layup compositions were investigated in order to better understand their behaviour when exposed to cryogenic temperatures, typical values shown in Table 1, with the future aim of investigating their feasibility as candidate materials for cryogenic applications, and addressing additional challenges related to experimental testing.

Table 1. Commonly used cryogenic fluids and example applications.

Fluid	Boiling point		Example applications
	°C	K	
Liquefied Natural Gas (LNG)	-162	112	Road transport, power generation, mining vehicles, industrial plants, railroad, and industrial and commercial boilers [8].
Liquid Oxygen (LOx)	-183	90	Liquid oxygen used as a propellant by advanced vehicles like the American Falcon 9 and Long March 5 rockets [5].
Liquid Nitrogen (LN_2)	-195.8	77	Most used cryogenic liquid due to safety reasons. Cryogenic preservation, coolant for superconductors, low temperature cold source, medical cryotherapy, cooking, etc.
Liquid Hydrogen (LH_2)	-252.9	20	Hydrogen-based fuel cell systems for transportation [14, 15].
Liquid Helium (LHe)	-268.9	4.2	Low temperature cold source, medical cryotherapy and Magnetic Resonance Imaging (MRI), semiconductor processing, etc.

2 EXPERIMENTAL

2.1 MATERIAL SYSTEMS

This work has investigated the mechanical performance - tensile and compressive - of FRP materials at cryogenic temperatures at -165 °C, approximately the boiling temperature of liquid natural gas (LNG) at atmospheric pressure. The materials chosen for the study have been identified as potential candidates for cryogenic liquid storage and distribution applications [3, 4], including well-established and commonly used CFRP and glass fibre-reinforced polymer (GFRP) materials, and a thermoplastic composite system. Details of the materials used for the study can be found in Table 2. Due to confidentiality agreements, further information on materials and manufacturing processing conditions have been withheld.

Table 2. Details of materials investigated in this work.

Panel ID	Test type	Material	Fibre	Resin	Layup
FKR	Tension	CFRP	CF	Epoxy	Woven
1AAZZ	Tension	GFRP	GF	Epoxy	UD
1AIUW	Tension	GFRP	GF	Epoxy	UD
2AIUW	Tension	GFRP	GF	Epoxy	±45°
AJO	Tension	Thermoplastic	Thermoplastic	Thermoplastic	UD
2ADZM	Compression	CFRP	CF	Epoxy	UD
1AEAJ	Compression	GFRP	GF	Epoxy	UD

Note – CF = carbon fibre, GF = glass fibre and UD = unidirectional.

2.2 SPECIMEN PREPARATION

2.2.1 Tensile Properties (ISO 527-4 [1])

Flat tension specimens were machined from supplied materials using a CompCut 500 diamond grit coated saw to a size of 250 mm x 25 mm (Table 3) and prepared following the principles of ISO 527-4 [1]. It should be noted that it was not possible to extract specimens from thermoplastic composites with a width of 25 mm, as recommended in [1], due to the limited width (~18 mm) of the profiles provided.

Strips of 50 mm x 22 mm x 2 mm thick Tufnol® 10G40 woven glass epoxy end-tabs (cut at 45° to the warp fibre direction) were bonded to the ends on both sides of each specimen using Araldite® 2012 two-part epoxy adhesive, recommended for extreme low temperatures. In addition, some specimens (1AIUW and 2AIUW) had end-tabs bonded using 3M ScotchWeld® EC- 9323 two-part epoxy adhesive, recommended for use at room temperature conditions, in order to assess the adhesive suitability at cryogenic temperatures.

Measurements of thickness and width were carried out at three positions along the length of each specimen.

2.2.2 Compressive Properties (ISO 14126 [2])

CFRP and GFRP compression specimens were prepared according to the Type B1 specimen geometry detailed in ISO 14126 [2]. Panels of 2 mm thick Tufnol® 10G/40 woven glass epoxy end-tab material (cut at 45° to the warp fibre direction) were bonded to the panels using 3M Scotchweld® EC-9323 two-part epoxy adhesive. Once the adhesive had cured, individual specimens were cut to width with a CompCut 500 diamond grit coated saw using water as a coolant. The nominal dimensions for the carbon specimens were 110 mm long x 10 mm wide by 2.5 mm thick and for the glass specimens the nominal dimensions were 110 mm long x 10 mm wide x 2.9 mm thick, as presented in Table 3. Care was taken to ensure that the pairs of end-tabs were well aligned and that a 10 mm long gauge length was created between them. The specimens were machined slightly oversized in the width and length dimensions so that specimens could be ground to appropriate tolerances (Table 3) in the NPL Engineering workshop, thus ensuring that the specimen edges were parallel, and the ends were square.

It should be noted that the thickness and width of the thermoplastic material was not compliant with the dimensions specified for the Type B1 coupon geometry, and as such no thermoplastic compression specimens were prepared for testing.

Table 3. Tension and compression FRP standards used and associated specimen sizes.

Standard number	Specimen dimensions		
	Length (mm)	Width (mm)	Thickness (mm)
BS EN ISO 527-4:2021 [1] Plastics — Determination of tensile properties Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites	≥ 250	25 ± 0.5 or 50 ± 0.5	2 to 10
BS EN ISO 14126:1999 [2] Fibre-reinforced plastic composites — Determination of compressive properties in the in-plane direction	110 ± 1	10 ± 1	2 ± 0.2 or 10 ± 0.2

2.3 TEST SET-UPS

2.3.1 Environmental Test Chamber

In this study, a universal test machine fitted with an environmental chamber was used to carry out the mechanical tests at cryogenic temperatures, as presented in Figure 1. The environmental chamber used, Instron model 3119-007, was reprogrammed to provide extensive temperature testing capabilities (+200 °C to -170 °C) for evaluating material properties under non-ambient conditions. The desired temperature, approximately -165 °C, was achieved by evaporating LN_2 pumped into the environmental chamber by means of a 300 litre cryogenic LN_2 dewar, as seen in Figure 2.

Calibrated Pico data loggers with 10 type-T thermocouples were used to verify and monitor the temperature distribution across different locations within the environmental chamber (Figure 3), in general accordance with guidelines described in EN 60068 [16]. The Pico loggers and associated probes were calibrated at NPL over the temperature range -196 °C to 0 °C in agreement with the International Temperature Scale of 1990.

Several trials were run prior to the required mechanical tests in order to monitor the cooling efficiency and temperature lag within the environmental chamber. As seen in Figure 4Table 5, a significant temperature difference was observed at different locations within the chamber, most notably between the thermocouples placed in top (TC 1 - 5) and bottom (TC 6 - 10) positions, due to the nature of liquid nitrogen displacing warm air upwards as it evaporates at the bottom of the chamber.

In the literature this effect is often disregarded, however, this could potentially lead to a considerable temperature gradient, and therefore stress and strain gradients over the length of the specimen, which can induce material failure [7, 16]. Therefore, monitoring the temperature of the jig and specimen throughout the test duration is of paramount importance to ensure the temperature remains at the desired level and is constant. For the work detailed in this report, the temperature distribution was also monitored during the mechanical tests, not only in different locations within the chamber but also on the jigs and samples prior to starting the tests to ensure samples were at the desired temperature before loading. Approximately 90 mins after starting the cool down to temperature with evaporating LN_2, tensile samples reached -165 °C, whereas between 90-120 mins was required to cool down compression samples due to the heat capacity of the testing rig.

Figure 1. Instron universal 250 kN test machine fitted with environmental chamber.

Figure 2. 300 L liquid Nitrogen dewar.

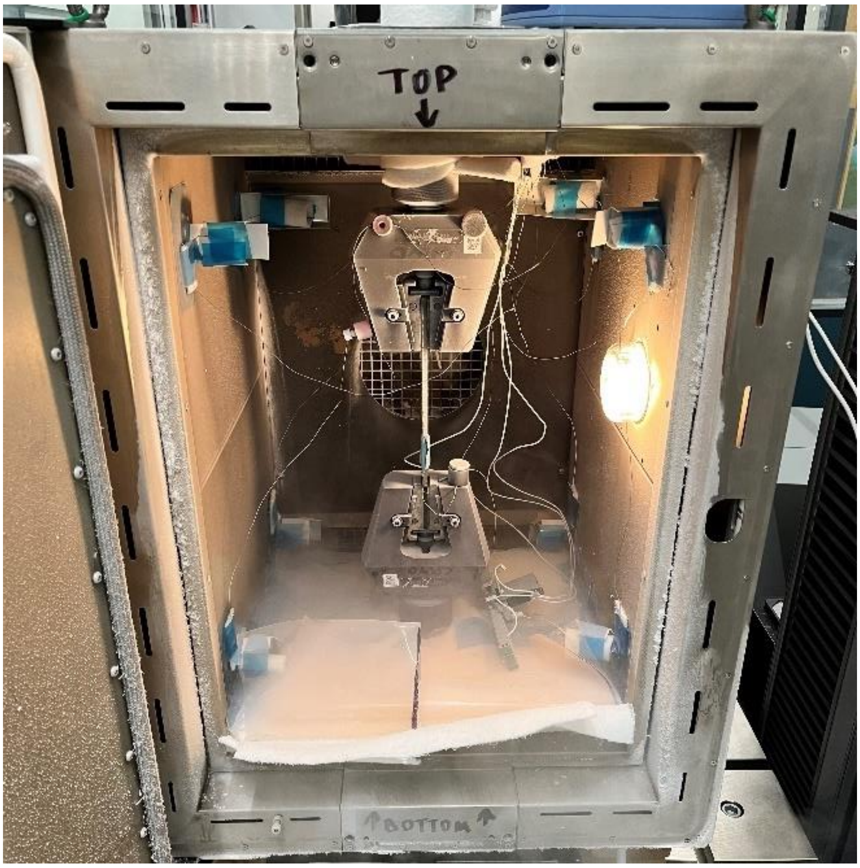

Figure 3. Temperature monitoring across different locations.

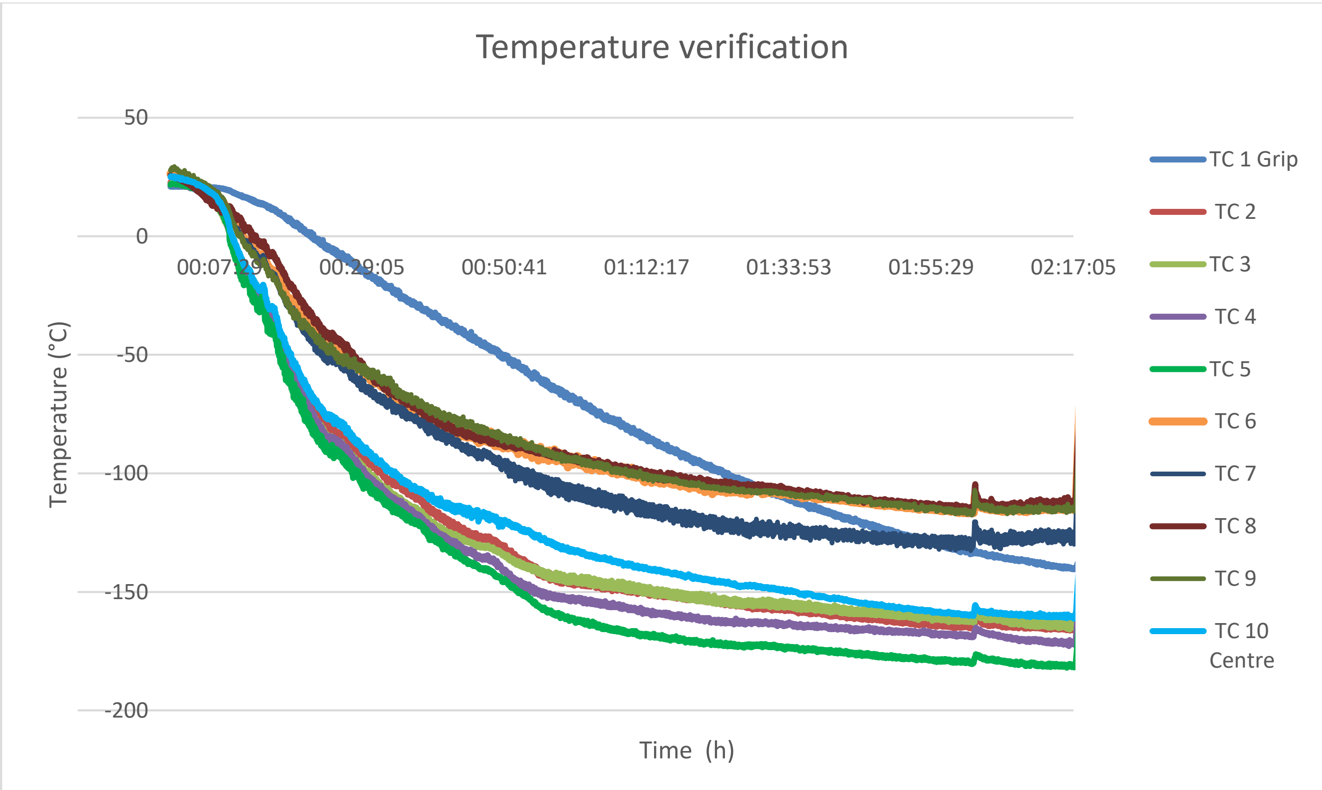

Figure 4. Example of temperature verification trial plot .

2.3.2 Tensile Properties (ISO 527-4 [1])

Tension tests at -165 ºC were conducted following the principles of the method described in ISO 527-4 [1] using an Instron model 5985 universal test machine fitted with a ±250 kN load cell.

As shown in Figure 5 and 6, the grips and loading bars were inserted into the environmental chamber and the gaps between them were sealed with insulating lagging material. Tensile specimens were gripped using a pair of mechanical wedge action grips fitted with serrated grip faces. Molykote® D-321 R anti-friction coating lubricant suited for cryogenic temperatures was used in order to improve lubrication, and hence, gripping at extreme temperatures.

Strain was measured on opposing faces of the tensile specimens using clip-on extensometers and strain gauges suited for cryogenic temperatures. For specimens tested at -165 °C, 3 mm biaxial strain gauges (Tokyo Sokki Kenkyujo Co. Ltd. Type: CFCA-3-350-11-6FA2LT, gauge factor 2.11, gauge resistance 350 Ohm) were bonded to either side of each coupon using EA-2A epoxy adhesive for cryogenic use. A Wheatstone half bridge circuit was used to compensate for the thermal strains induced by the thermal contraction of gauges when their temperature changes from room temperature (RT) to -165 °C.

Epsilon biaxial model 3560-BIA-050M-005-LHT extensometer was used for CFRP and GFRP tensile specimens, whereas Epsilon axial model 3542-050M-050-LHT was used for thermoplastic tensile specimens, since it is better suited for films or thin specimens and provides a full scale measuring range of +50%/-10% strain. Extensometers were all verified in accordance with ASTM E83 [17] and NPL internal procedures.

Load, crosshead displacement and strain were continuously recorded throughout each test using a National Instruments data logger with NPL designed logging software (Logit). Instron Bluehill Universal software was used to control the test machine. The modulus values were calculated over the strain range 0.05-0.25% (500-2500 $\mu\varepsilon$), from the average longitudinal strains measured on opposite faces. Tensile strength was calculated using the maximum load divided by the cross-sectional area of the specimen.

Prior to initiating cooling of the environmental chamber, specimens were positioned in the mechanical wedge grips. The grips were tightened and a pre-load was applied to the specimen prior to the grips being tightened again. The pre-load was removed from the specimen and the specimen protect function of the test machine was applied to limit any load increase to below 150 N during cool down.

Once the target temperature (-165 °C ± 3 °C) was reached on the specimen, after approximately 90 mins, specimen protect was disengaged, any pre-load on the specimen was removed and the specimen was loaded at a crosshead speed of 2 mm/min until failure.

When using extensometers, tests were paused when 0.3% strain was reached in order to remove the extensometer to avoid damage during specimen failure. Once the extensometer was removed, testing was re-started and continued until failure.

After each test, the moisture that formed within the environmental chamber during the times when the door opened, exposing the test set-up to warm moist air, was eliminated by heating the chamber up to +50 °C for approximately 1 hour, and using a hot air gun afterwards to heat and dry any areas with remaining moisture, such as the lower grips.

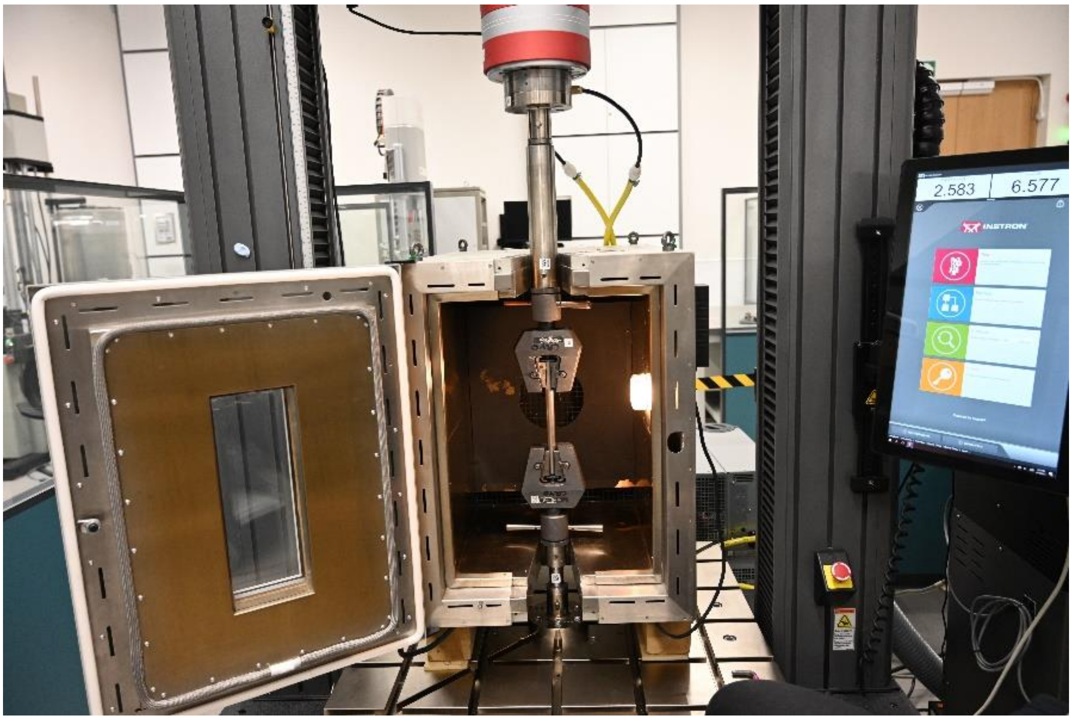

Figure 5. Tensile set-up.

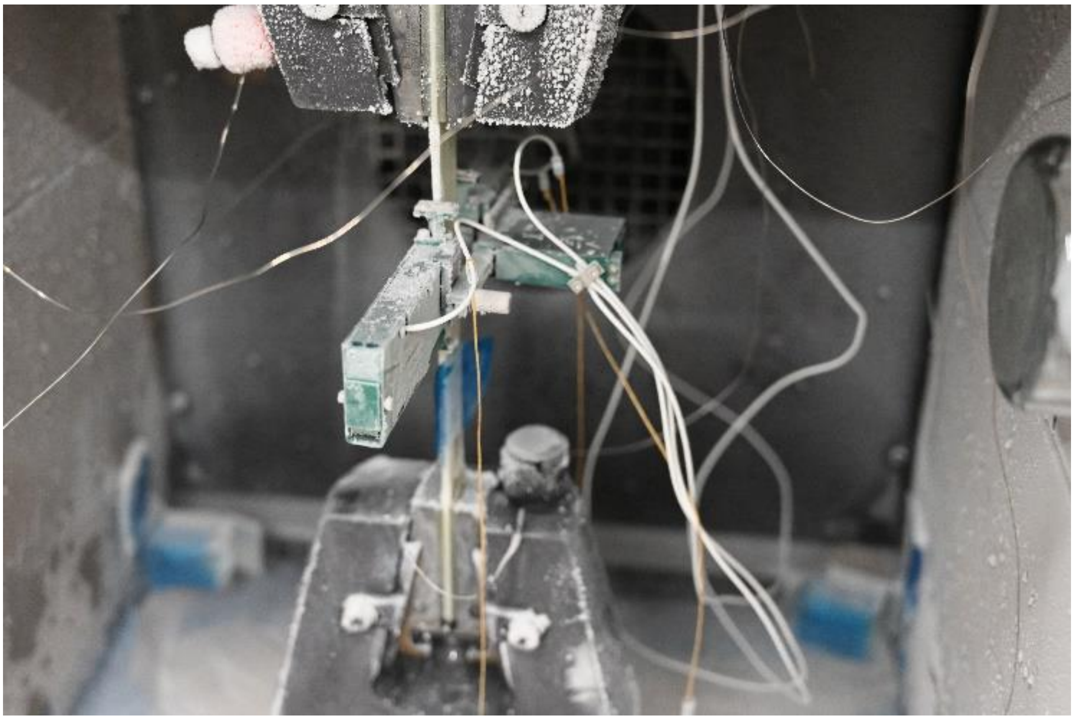

Figure 6. Close up view of the tension wedge grips and biaxial extensometer on a GFRP specimen after testing.

2.3.3 Compressive Properties (ISO 14126 [2])

Compression tests were conducted in general accordance with Method 2 (combined loading) of ISO 14126 [2]. Tests were performed using a four-pillar die set combined loading compression jig mounted inside the environmental chamber. A ground steel bar was used to align the end-loading blocks of the compression jig. The environmental chamber was mounted on an Instron 5985 screw-driven machine fitted with a ± 250 kN load cell. Liquid nitrogen was used to cool down the chamber to -165 °C (see Figure 7).

For all compression specimens tested at -165 °C, 1 mm biaxial strain gauges (Tokyo Sokki Kenkyujo Co. Ltd. Type: CFCA-1-350-11-6FA2LT, gauge factor 2.11, gauge resistance 350 Ohm) were bonded to either side of each coupon using EA-2A epoxy adhesive for cryogenic use.

Specimens were positioned into the bottom loading block and the integral lead wire strain gauges were connected to the strain data logging equipment, previously calibrated for low temperature testing. After checking that the gauges were connected correctly, the crosshead was lowered until a slight compressive load (~30-40 N) was introduced to the specimen. The inner and outer sets of bolts on each loading block were then torqued to 5 Nm and 10 Nm, respectively. A further check was made to ensure that the strain gauges were reading correctly before the conditioning chamber was left to stabilise at -165 °C over 90-120 minutes. Specimens were loaded at a crosshead speed of 1 mm/min until failure.

Load, crosshead displacement and strain were continuously recorded throughout each test using a National Instruments data logger with NPL designed logging software (Logit). Instron Bluehill Universal software was used to control the test machine. The modulus and Poisson's ratio was calculated, where possible, over the strain range 0.05-0.25% (500-2500 $\mu\varepsilon$).

Figure 7. View of the compression set-up after testing.

3 RESULTS AND DISCUSSION

3.1 TENSION

The tensile properties of CFRP, GFRP and thermoplastic specimens were investigated at - 165 °C, results are presented in Tables Table 4 to Table 8. Where possible, historical data generated by NPL on the same materials at other temperatures, or additional data generated at RT for this investigation, have been added to the summary tables to better assess and understand the material mechanical performance at -165 °C. At least 3 specimens were tested for each material to enable the mean, standard deviation and coefficient of variation to be calculated.

The load versus displacement and stress versus strain traces, along with images of the failed tensile specimens tested for this study are shown in Figure 8 to 20.

Table 4 shows the longitudinal tensile results for the CFRP woven composite specimens. In order to evaluate the relative mechanical performance at -165 °C, three specimens extracted from the panel FKR were also tested at RT.

All specimens tested at -165 °C showed a significant reduction in maximum load in comparison to the specimens tested at RT. Specimen FKR002 showed a more significant reduction in load compared to the other specimens shown in Figure 8. This was thought to be due to a common phenomenon when testing at cryogenic temperatures (CT) where moisture trapped between grip-faces causes the specimen to slide from the grips. It was also observed that the end-tabs clearly show signs of de-bonding in Figure 10. This typically occurs because shear stress is induced due to the different CTEs between the tab material and the specimen.

All the woven CFRP specimens tested at -165 °C exhibited a lower tensile strength than measured at room temperature, around a 20% reduction. *Kumagai et al* also experienced reductions in tensile strength of CFRP woven material at cryogenic temperatures (77K) [18]. However, the stiffness results showed little change; a marginal increase of ~3% at -165 °C compared to room temperature results.

Poisson's ratio was successfully measured on all the specimens. Results showed an increase of approximately 50% between RT and -165 °C. A possible explanation to this phenomenon, provided by *Sápi and Butler* [7], could be due to relative changes in longitudinal (*E1*) and transverse (*E2*) elastic moduli. If the longitudinal elastic modulus is more susceptible to decreasing temperature, then the difference between *E1* and *E2* will also increase. As a result, the longitudinal Poisson's ratio becomes higher.

The displacement at failure results show that the longitudinal elongation of the CFRP woven specimens decreases with decrease in temperature. This is thought to be due to the resin increasing in stiffness and losing its ductility [7, 18]. All specimens tested at RT and -165 °C failed at the end of the tab region (stress concentration at the end of the grip), with the exception of specimen FKR004, which failed in the gauge area.

All cryogenic temperature results, except Poisson's ratio and displacement, show very minimal scatter (< 5%). The high level of repeatability observed from the low coefficients of variation further indicate optimal specimen preparation and compatibility of the CFRP and end-tab adhesive for cryogenic conditions.

From these results, the longitudinal tensile stiffness of the woven CFRP material tested showed only a slight increase at -165 ºC compared to room temperature, whilst the longitudinal tensile strength showed a significant reduction as reported by other authors in the literature [7, 10, 13].

Table 4. Tensile properties of panel FKR in the 0° direction.

Specimen ID	T (°C)	Strain measurement by	Max. load (kN)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's ratio	Displacement to failure (mm)	Comments
FKR003, 008 & 009	RT	Biaxial extensometer	53.2 ± 0.5	489.1 ± 5.3	47.67 ± 1.08	0.1 ± 0.0	5.47 ± 0.33	Extensometer removed at 0.3 % strain
FKR002	-165 °C	Biaxial extensometer	38.3	355.7	50.63	0.1	2.40	Extensometer removed at 0.3 % strain
FKR004	-165 °C	Biaxial extensometer	41.6	388.6	49.22	0.2	3.23	Extensometer removed at 0.3 % strain
FKR005	-165 °C	Biaxial extensometer	43.4	395.6	50.15	0.1	3.50	Extensometer removed at 0.3 % strain
FKR006	-165 °C	Biaxial extensometer	42.9	395.6	50.45	0.2	3.32	Extensometer removed at 0.3 % strain
FKR007	-165 °C	Biaxial extensometer	-	-	49.39	0.1	-	Extensometer removed at 0.3 % strain
		Cryogenic strain gauges	41.9	387.6	50.81	0.1	3.57	-
		Mean	**41.6**	**384.6**	**50.11**	**0.1**	**3.20**	**-**
		Std.Dev.	**2.0**	**16.6**	**0.66**	**0.0**	**0.47**	**-**
		Coeff. Var (%)	**4.8**	**4.3**	**1.32**	**22.9**	**14.66**	**-**

Note – Statistical summary calculated only from data generated at -165 °C.

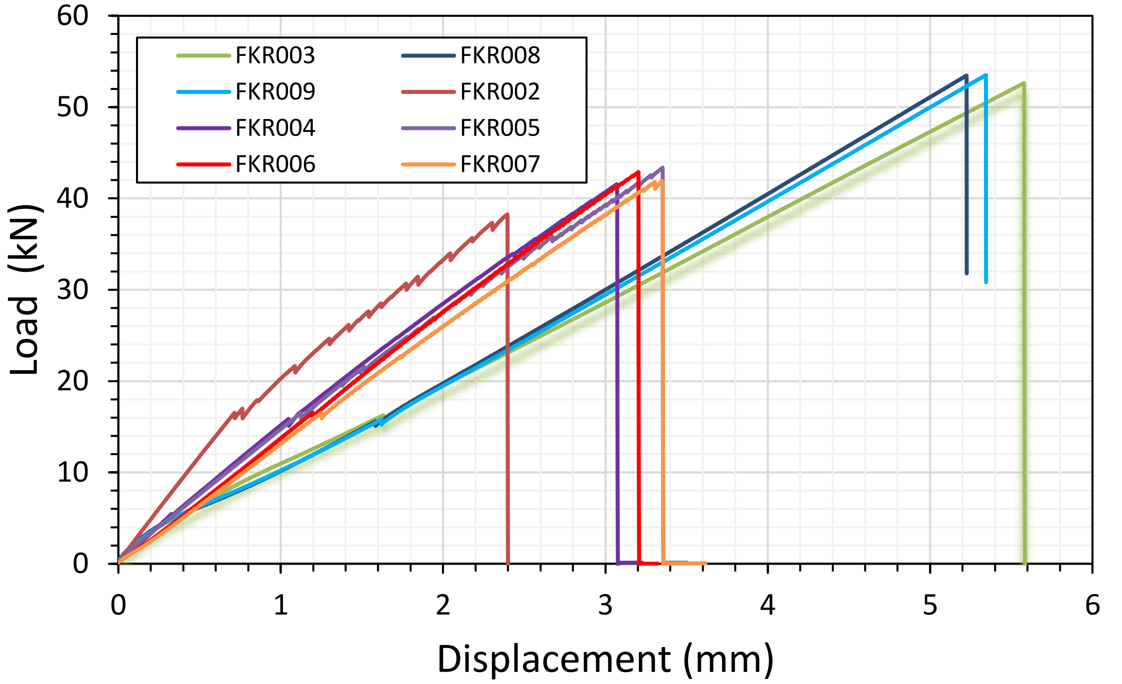

Figure 8. Load versus displacement plot for panel FKR. Specimens FKR003, 008 and 009 were tested at RT and FKR002, 004-007 at -165 °C.

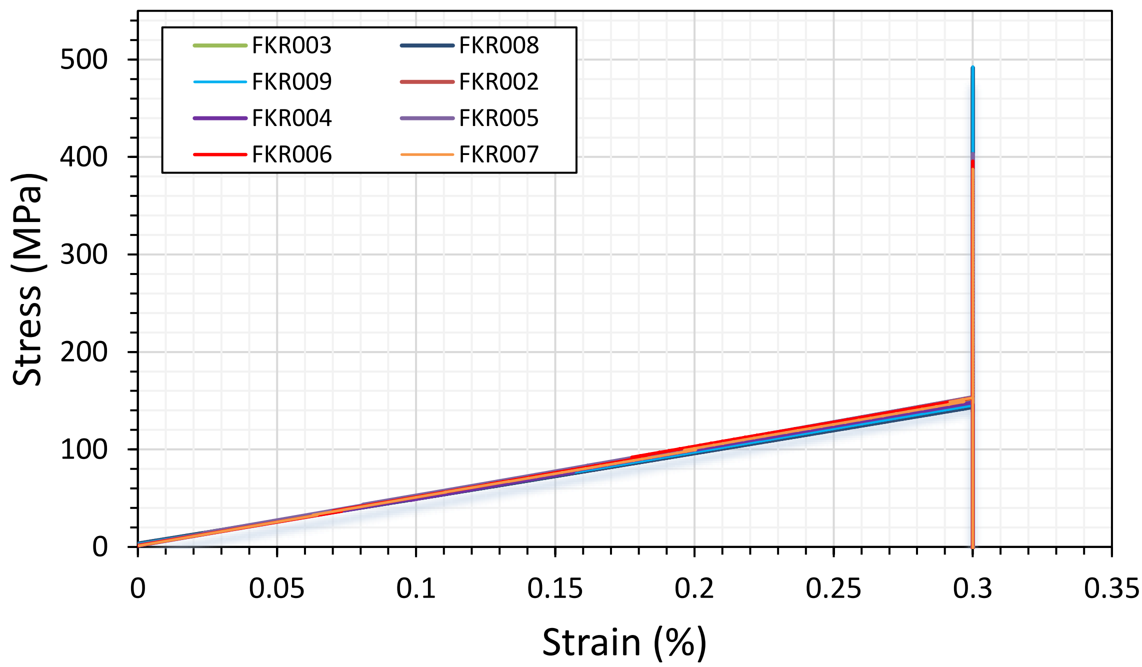

Figure 9. Stress versus strain plot (up to 0.3% strain) for panel FKR. Specimens FKR003, 008 and 009 were tested at RT and FKR002, 004-007 at -165 °C.

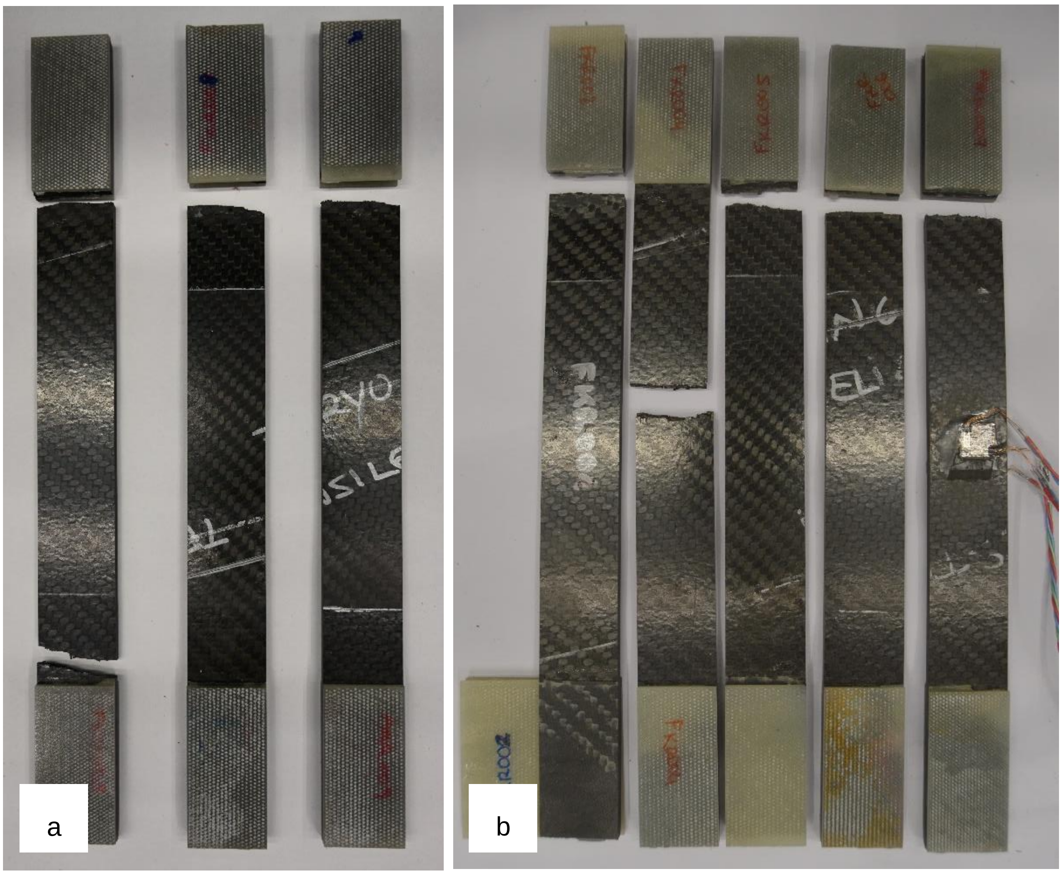

Figure 10. Failed specimens for batch FKR: a) tested at RT and b) tested at -165 °C.

Table 5 presents the longitudinal tensile results for the GFRP composite specimens extracted from the UD laminate 1AAZZ. Three specimens were also tested at RT to compare the mechanical performance at RT to -165 °C. Load versus displacement plots are shown in Figure 11 and stress verus strain plots up to 0.3% are shown in Figure 12. The failure modes for all specimens are shown in Figure 14 (-165 °C).

All RT specimens failed between the grips via extensive longitudinal splitting and fibre fracture. However, for all but one specimen (1AAZZ004) the tests at -165 °C were unsuccessful due to end-tab de-bonding (Figure 14), as evidenced by several load drops in the load versus displacement plots shown in Figure 11. Specimen 1AAZZ004 failed via longitudinal splitting between the grips but the failure mode was far less extensive than for specimens tested at RT. As only one specimen failed in an acceptable manner at -165 °C, it is not possible to draw any conclusions concerning failure properties compared to values measured at RT.

The stiffness results did not show a significant change at -165 °C in comparison to RT, as although the mean value measured at -165 °C was slightly greater than that at RT, the greater level of scatter at -165 °C did not indicate a clear distinction between the two sets of results .

Poisson's ratio was successfully measured on all specimens. Results show no difference from RT to -165 °C, however as for the stiffness results, the higher level of scatter observed does not indicate a clear distinction between the two sets of results.

Table 5. Tensile properties of panel 1AAZZ in the 0° direction.

Specimen ID	T (°C)	Strain measurement by	Max. load (kN)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's ratio	Displacement to failure (mm)	Comments
1AAZZ006, 008 & 009	RT	Biaxial extensometer	58.2 ± 0.7	1029.6 ± 27.2	48.03 ± 0.86	0.3 ± 0.0	8.53 ± 0.30	Extensometer removed at 0.3 % strain
1AAZZ001	-165 °C	Biaxial extensometer	58.2	-	51.32	0.4	-	Extensometer removed at 0.3 % strain
1AAZZ002	-165 °C	Biaxial extensometer	40.6	-	58.21	0.4	-	Extensometer removed at 0.3 % strain
1AAZZ004	-165 °C	Biaxial extensometer	51.9	931.0	49.80	0.3	5.93	Extensometer removed at 0.3 % strain
1AAZZ005	-165 °C	Biaxial extensometer	71.9	-	44.72	0.3	-	Extensometer removed at 0.3 % strain
		Cryo strain gauges	-	-	46.08	0.3	-	-
1AAZZ007	-165 °C	Biaxial extensometer	53.8	-	52.18	0.3	-	Extensometer removed at 0.3 % strain
		Mean	**55.3**	-	**50.38**	**0.3**	-	**-**
		Std.Dev.	**11.3**	-	**4.82**	**0.0**	-	**-**
		Coeff. Var (%)	**20.5**	-	**9.57**	**15.0**	-	**-**

Note – Statistical summary calculated only on data generated at -165 °C.

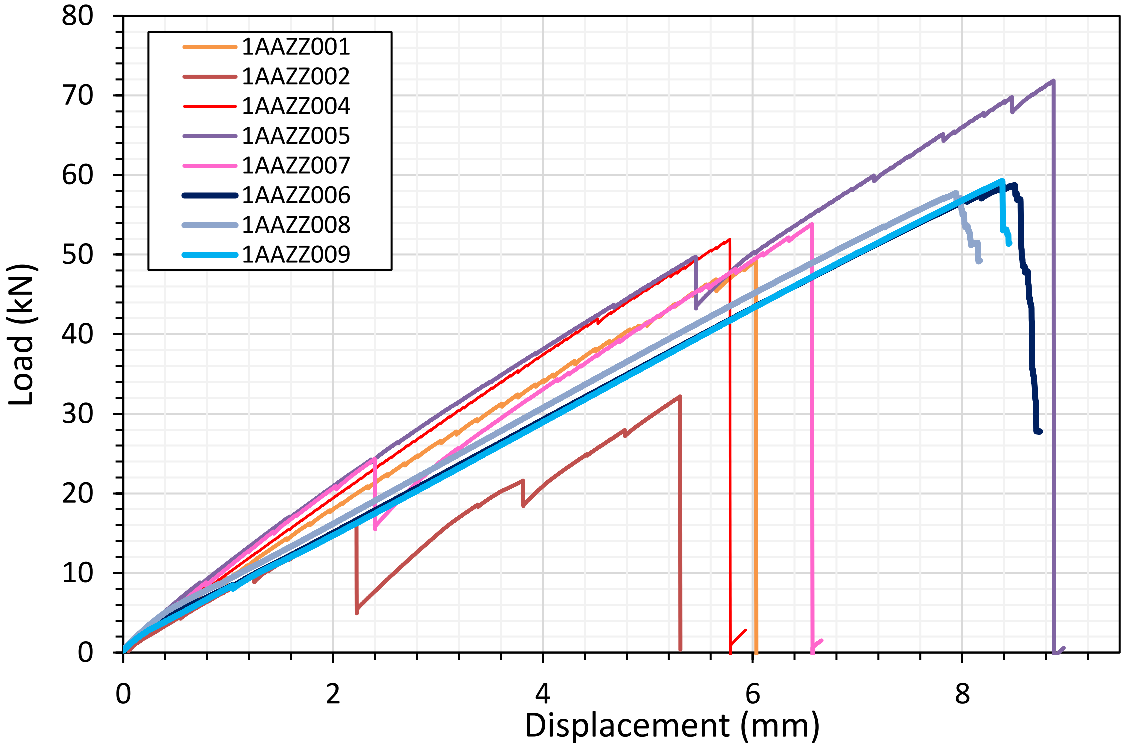

Figure 11. Load versus displacement plot for panel 1AAZZ. Specimens 1AAZZ006, 008 and 009 were tested at RT and 1AAZZ001, 002, 004, 005 and 007 at -165 °C.

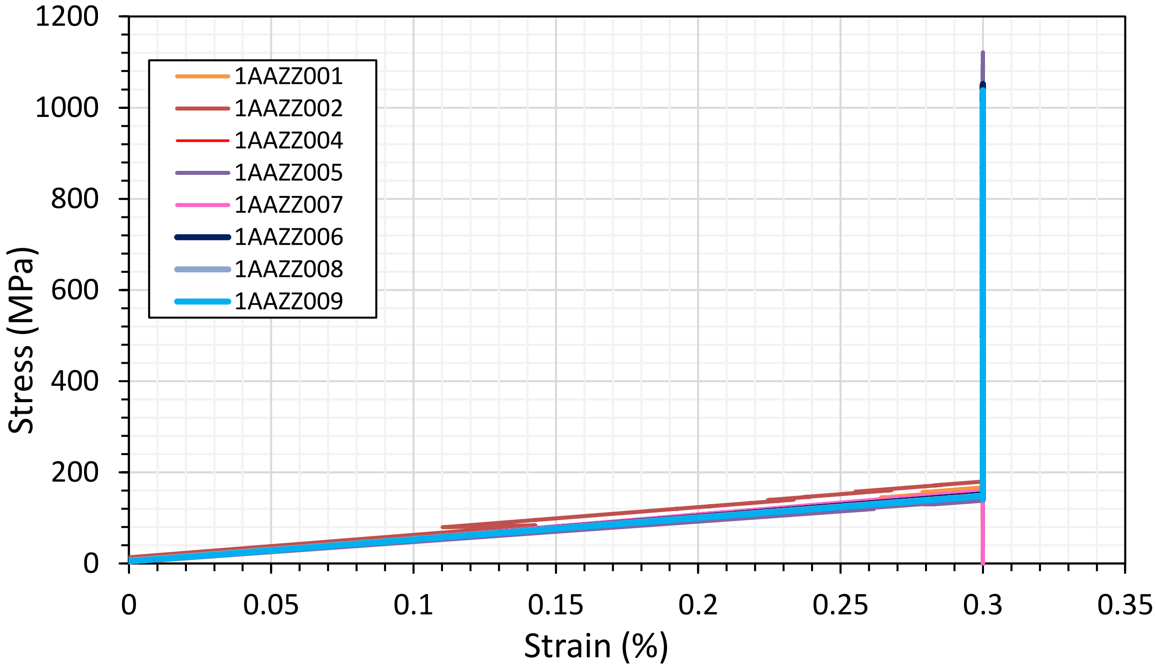

Figure 12. Stress versus strain plot (up to 0.3% strain) for panel 1AAZZ. Specimens 1AAZZ006, 008 and 009 were tested at RT and 1AAZZ001, 002, 004, 005 and 007 at -165 °C.

Figure 13. Failed specimens for batch 1AAZZ tested at RT.

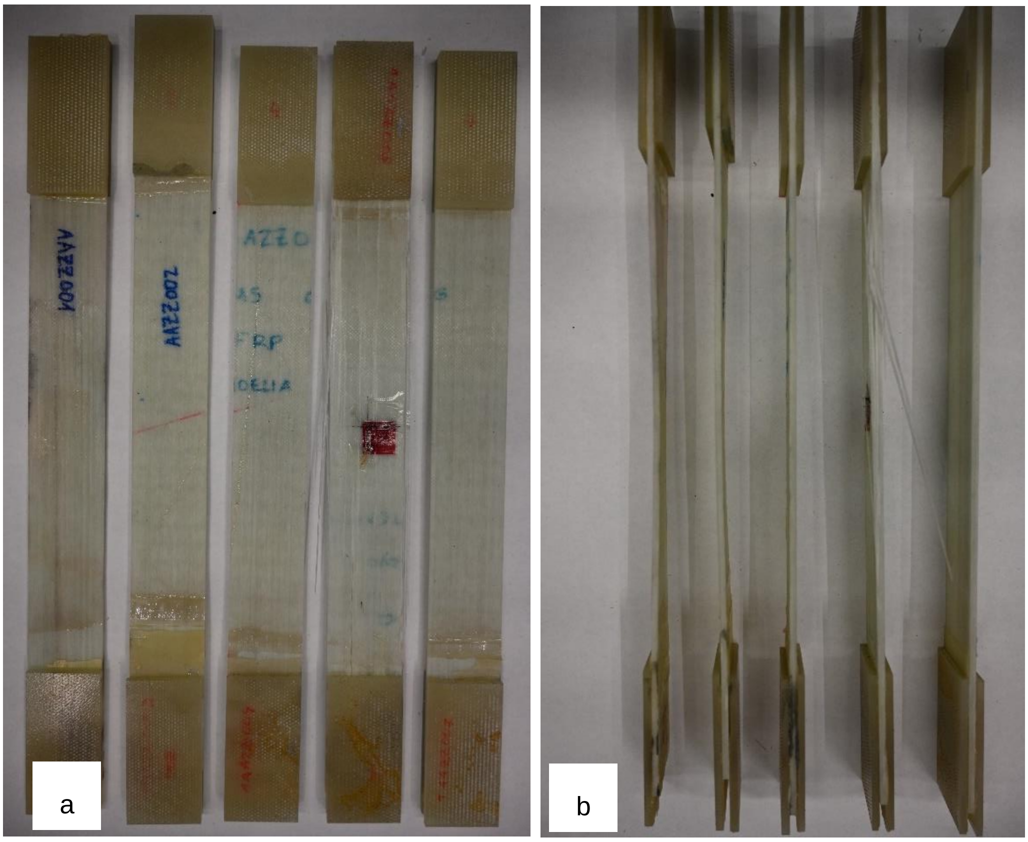

Figure 14. Failed specimens for batch 1AAZZ tested at -165 °C a) top view and c) side view.

Table 6 and 7 presents the tensile results for the GFRP composites specimens extracted from laminate 1AIUW (UD) and 2AIUW (±45°). Historical data generated at RT have been also added to the summary tables to compare the mechanical performance from RT to -165 °C .

In an attempt to reduce the significant scatter presented in the results generated on the previous GFRP material, an alternative end-tab adhesive extensively used by NPL was trialled on 1AIUW and 2AIUW spare specimens in order to erradicate unwanted specimen slippage and end-tab de-bonding at low temperatures.

For the UD material, 1AIUW, where the strength and strain behaviour are dominated by the fibres, these properties show a significant increase with temperature decrease, as reported previously [5, 7, 9, 19]. For specimens 2AIUW004 and 005, failure occurs due to shearing of the ±45º layup, but again both failure strain and tensile strength results increase at -165ºC compared to RT results.

Poisson’s ratio results for both materials, 1AIUW and 2AIUW, decrease with decreasing temperature due to the increased stiffness of the resin, as reported by *Sapi and Butler* [7].

Based upon the results generated on laminate 1AIUW (UD) and 2AIUW (±45°) at CT, a greater population is required to draw statistically relevant conclusions. In this case, end-tab adhesive compatibility trials were proven to be successful, since no end-tab debonding was experienced in either case, as seen in Figure 17.

Table 6. Tensile properties of panel 1AIUW in the 0° direction.

Specimen ID	T (°C)	Strain measurement by	Max. load (kN)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's ratio	Displacement to failure (mm)	Comments
1AIUW001-005	RT	Strain gauges	37.8 ± 1.1	355.8 ± 12.9	17.51 ± 0.47	0.5 ± 0.0	5.12 ± 0.37	Historical data
1AIUW006	-165 °C	Biaxial extensometer	49.0	468.9	21.30	0.4	9.19	Extensometer removed at 0.3 % strain

Table 7. Tensile properties of panel 2AIUW in the ±45° direction.

Specimen ID	T (°C)	Strain measurement by	Max. load (kN)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's ratio	Displacement to failure (mm)	Comments
2AIUW001-003	RT	Strain gauges	14.5 ± 0.9	127.9 ± 10.1	9.60 ± 0.66	0.3 ± 0.0	3.82 ± 0.11	Historical data
2AIUW004	-165 °C	Biaxial extensometer	21.2	191.9	12.53	0.2	7.55	Extensometer removed at 0.3 % strain
2AIUW005	-165 °C	Biaxial extensometer	21.8	204.9	13.35	0.2	7.33	Extensometer removed at 0.3 % strain

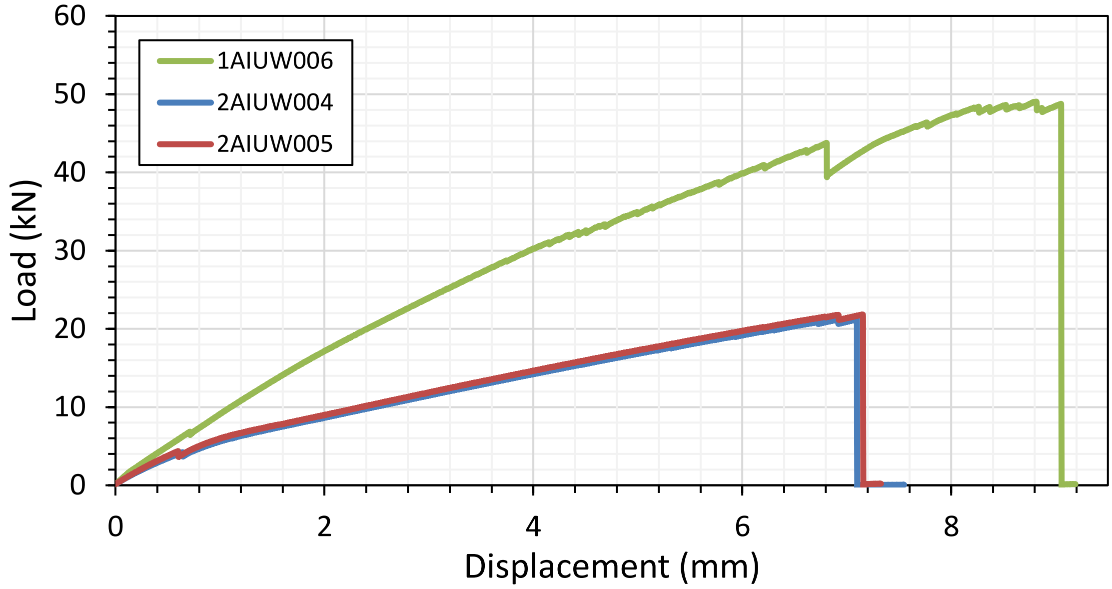

Figure 15. Load versus displacement plot for specimens 1AIUW and 2AIUW at - 165 °C.

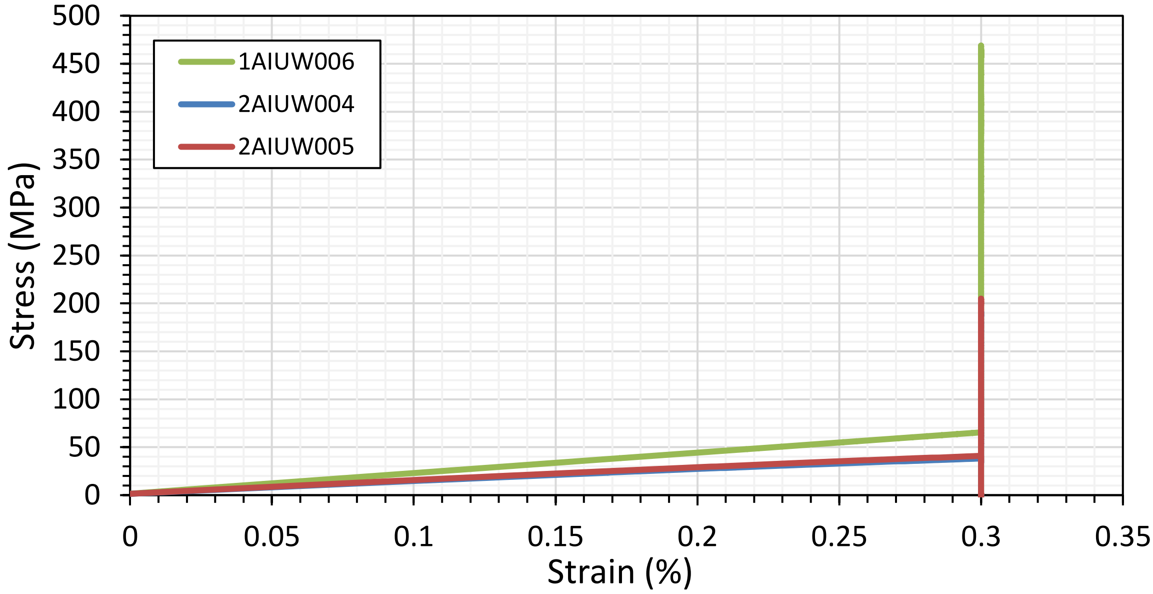

Figure 16. Stress versus strain plot (up to 0.3% strain) for specimens 1AIUW and 2AIUW at - 165 °C.

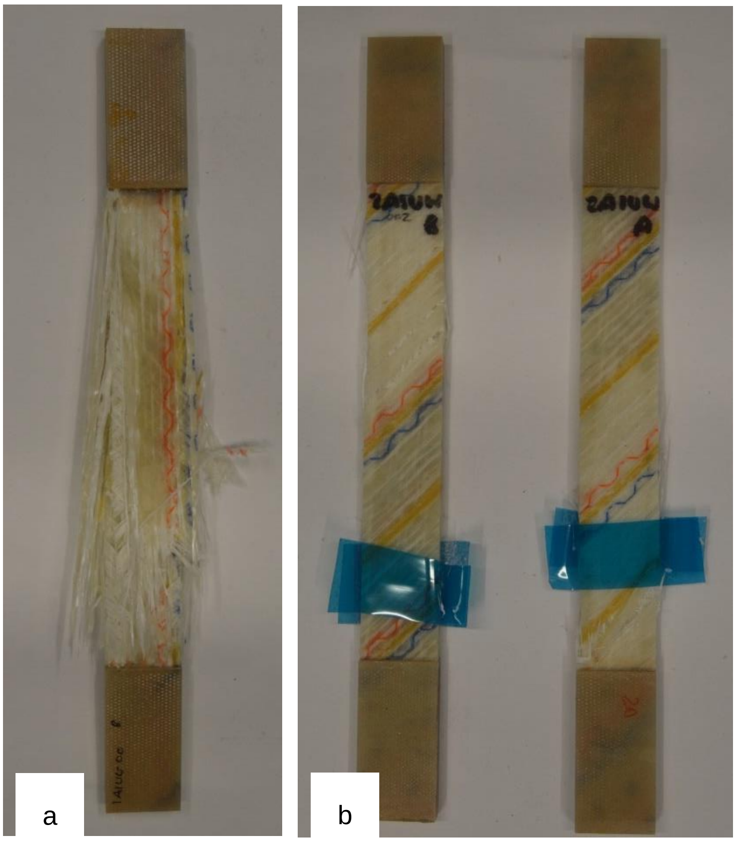

Figure 17. Failed specimens for batch 1AIUW and 2AIUW: a) specimen 1AIUW006 and b) specimens 2AIUW004 and 2AIUW005 all tested at -165 °C.

Table 8 shows the longitudinal tensile results for the thermoplastic composite specimens. In order to compare and evaluate the mechanical performance between RT and -165 °C , three specimens were also tested at RT.

The tensile strength behaviour presented by the thermoplastic specimens tested at RT and -165 °C exhibit a similar average value. As experienced before, specimen AJOQ001 presents a more obvious reduction in maximum load due to its numerous peaks that are likely to be caused by slippage, as displayed in the load vs displacement plot Figure 18.

In addition, the tensile modulus of thermoplastic samples shows a substantial increase with temperature decrease; from an average stiffness of 2.61 GPa at RT to 9.80 GPa at CT.

Displacement to failure results, combined with Figure 18 and 19, show that tensile elongation decreases with temperature decrease, due to the resin becoming more brittle and therefore stiffer. This can be confirmed also by observing failed specimens tested at -165 °C , where all specimens presented no apparent sign of plastic deformation.

From these results, it can be stated that the longitudinal tensile strength remained steady with temperature decrease, whilst stiffness was influenced drastically by low temperature becoming much greater. As previously observed, all RT results show very minimal scatter.

Table 8. Tensile properties of thermoplastic tapes in the 0° direction

Specimen ID	T (°C)	Strain measurement by	Max. load (N)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's ratio	Displacement to failure (mm)	Comments
AJOO002, AJOP002 & AJOQ002	RT	Uniaxial extensometer	2780.3 ± 278.3	126.6 ± 12.6	2.61 ± 0.56	-	29.09 ± 4.29	Extensometer removed at 0.3 % strain
AJON003	-165 °C	Cryogenic strain gauges	3370.3	160.7	10.69	0.2	9.97	-
AJOO001	-165 °C	Uniaxial extensometer	2943.8	122.6	9.01	-	6.61	Extensometer removed at 0.3 % strain
AJOP001	-165 °C	Uniaxial extensometer	2881.3	114.7	-	-	5.91	Extensometer data corrupted
AJOQ001	-165 °C	Uniaxial extensometer	2497.2	118.1	9.70	-	3.77	Extensometer removed at 0.3 % strain
		Mean	**2923.2**	**129.0**	**9.80**	**-**	**6.57**	**-**
		Std.Dev.	**357.5**	**21.4**	**0.84**	**-**	**2.57**	**-**
		Coeff. Var (%)	**12.2**	**16.6**	**8.63**	**-**	**39.17**	**-**

Note – Statistical summary calculated only on data generated at -165 °C.

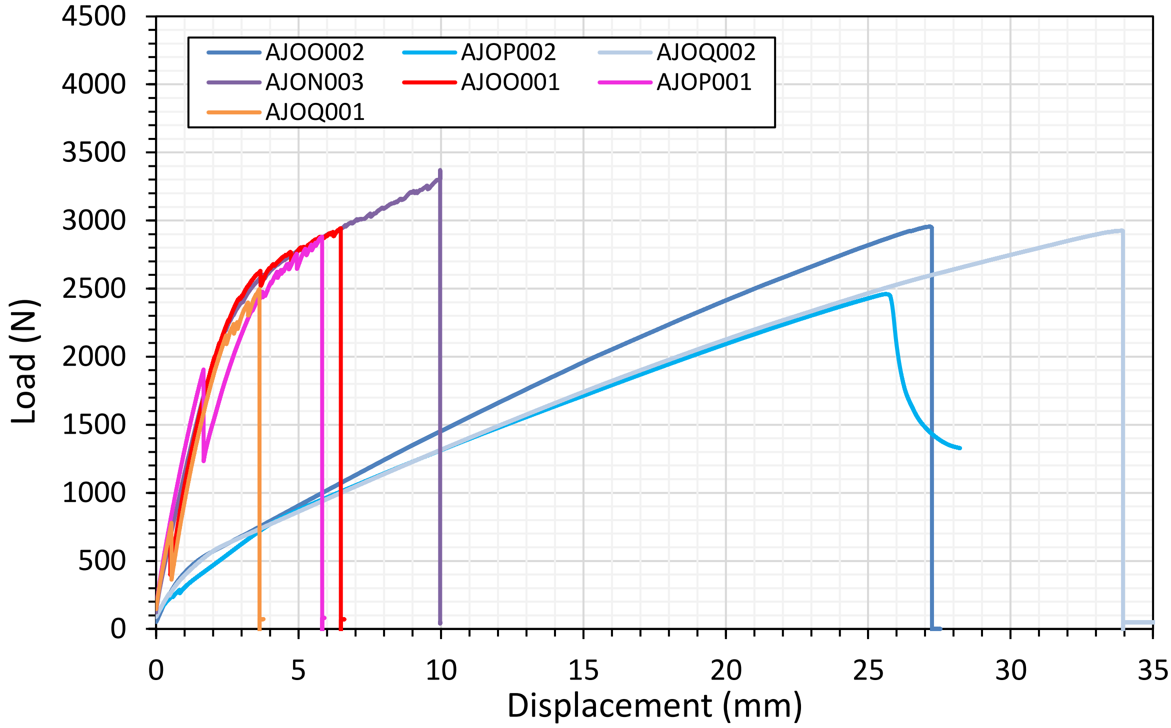

Figure 18. Load versus displacement plot for thermoplastic specimens. Specimens AJOO002, AJOP002 and AJOQ002 were tested at RT and AJON003, AJOO001, AJOP001 and AJOQ001 at - 165 °C.

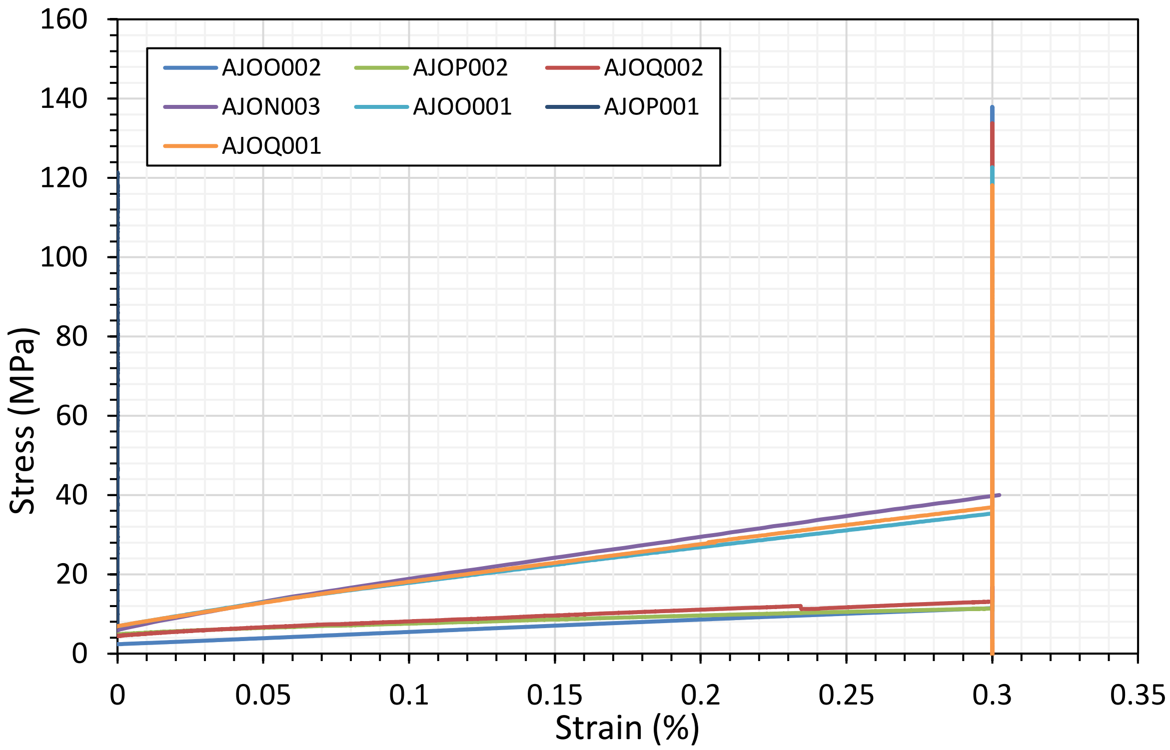

Figure 19. Load versus displacement plot for thermoplastic specimens. Specimens AJOO002, AJOP002 and AJOQ002 were tested at RT and AJON003, AJOO001, AJOP001 and AJOQ001 at - 165 °C.

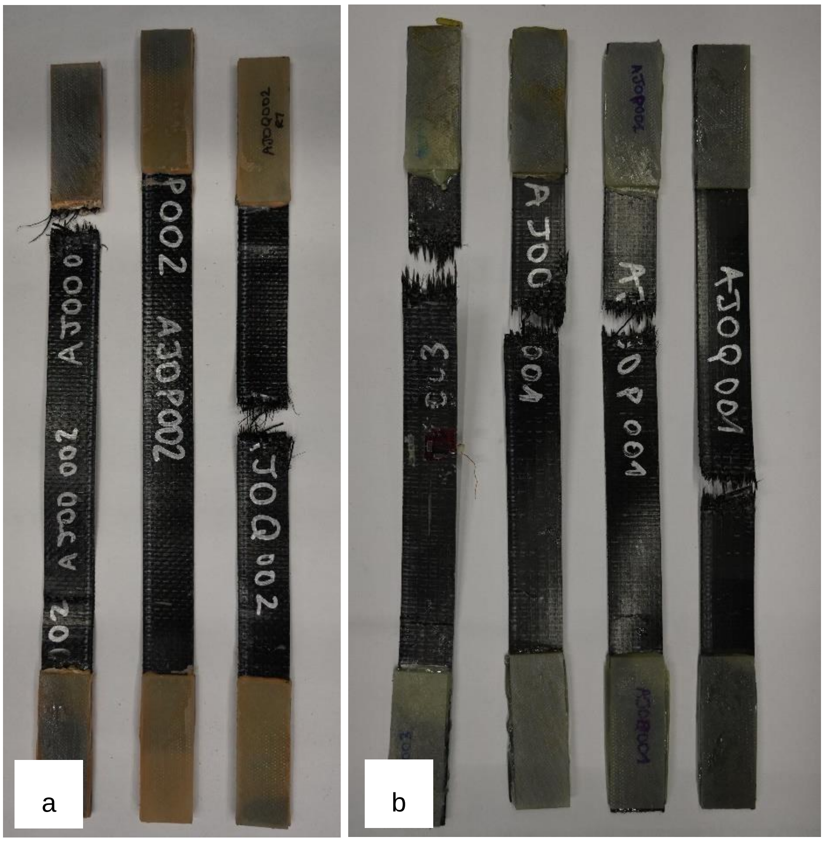

Figure 20. Failed thermoplastic specimens a) tested at RT and b) tested at -165 °C.

For cryogenic applications, the microcracking caused by the CTE mismatch is a topic of concern. According to *Sápi and Butler* [7] a way to mitigate the thermal stresses and microcracking caused by the CTE mismatch between resin and reinforcement and therefore to reach near-zero CTE at cryogenic temperatures can be achieved by using single polymer composites, where both fibre and resin are made of the same thermoplastic material [6, 9]. The results generated in this study prove the benefits of using thermoplastic fibre-thermoplastic resin composites at cryogenic temperatures.

As experienced previously in this study, high coefficients of variation are evident in the results of the thermoplastic composites, both at RT and CT. However, in this case due to the nature of the material provided, it also could be linked to the material.

3.2 COMPRESSION

The compressive properties of CFRP and GFRP generated for the study are presented in Tables 9 and 10. Where possible, historical data generated by NPL on the same materials at other temperatures have been added to the summary tables to better assess and understand the mechanical performance at -165 °C.

The load versus displacement, along with images of the failed specimens tested for this study are shown in Figure 21 and 22.

No strain gauge failures were observed during testing, however, one of the gauge wires of specimen 2ADZM034 was damaged whilst mounting the specimen into the compression die set. Therefore, strain data from that specimen are not available.

Table 9 and 10 display the longitudinal compressive results for the 2ADZM and 1AEAJ composite specimens used in the study.

All compression specimens tested at -165 °C show maximum compressive strength and modulus increases at cryogenic temperatures, due to the increased stiffness of the matrix and increased fibre-resin interfacial strength with decreasing temperature, as stated by Sápi & Butler in their review [7].

In contrast to data reported in [7], the failure strain values generated in this study also increased with decreasing temperature. However, it is thought to be due to an artefact in the behaviour of the bearing pillars of the compression die set at cryogenic temperatures. Moisture trapped within the bearing pillars after long exposure to cryogenic temperatures froze the pillars until a load of 5-10 kN was overcome, as seen in Figure 21, preventing proper characterisation of the compressive performance at cryogenic temperatures.

According to the acceptable failure modes defined in ISO 14126 [2], compression specimens tested at -165 °C present complex failure with de-bonding between fibre and matrix. Fracture surfaces of failed specimens did not show much variation for the composite systems studied, as seen in Figure 22.

Due to practical limitations, such as unsuitable fixture design for cryogenic applications, poor thermal efficiency and large mass of the combined loading die set used for the compression tests, reaching the desired cryogenic temperature was not easily achieved. As a result, the compression set-up used in the study was not deemed entirely fit-for-purpose and further compression rig re-design will be the focus of the following steps of this NMS programme.

Table 9. Compression properties of panel 2ADZM in the 0° direction.

Specimen N°	T (°C)	Strain measurement by	Max. compressive load (kN)	Compressive Strength (MPa)	Compressive Modulus (GPa)	Strain-to-failure (%)	Poisson's ratio	Displacement to failure (mm)	Comments
2ADZM001-010	RT	Strain gauges	29.5 ± 2.4	866.0 ± 83.3	97.77 ± 5.60	0.97 ± 0.10	-	1.25 ± 0.14	Historical data
2ADZM011-021	70°C	Strain gauges	18.3 ± 1.6	555.6 ± 58.5	101.19 ± 8.74	0.58 ± 0.07	-	1.00 ± 0.14	Historical data
2ADZM022-031	-40°C	Strain gauges	35.5 ± 3.3	1091.8 ± 105.0	102.97 ± 5.56	1.37 ± 0.13	-	1.71 ± 0.47	Historical data
2ADZM032	-165 °C	Cryo strain gauges	35.5	1047.1	234.60	4.51	0.8	2.33	-
2ADZM034	-165 °C	Cryo strain gauges	40.9	1144.0	-	-	-	3.24	Strain gauge failed

Table 10. Compression properties of panel 1AEAJ in the 0° direction.

Specimen N°	T (°C)	Strain measurement by	Max. compressive load (kN)	Compressive Strength (MPa)	Compressive Modulus (GPa)	Strain-to-failure (%)	Poisson's ratio	Displacement to failure (mm)	Comments
1AEAJ001-005	RT	Strain gauges	17.9 ± 0.7	770.2 ± 23.6	39.46 ± 0.81	2.01 ± 0.0.4	-	1.49 ± 0.08	Historical data
1AEAJ0015	-165 °C	Cryo strain gauges	29.9	1304.2	51.00	4.73	0.3	3.54	-

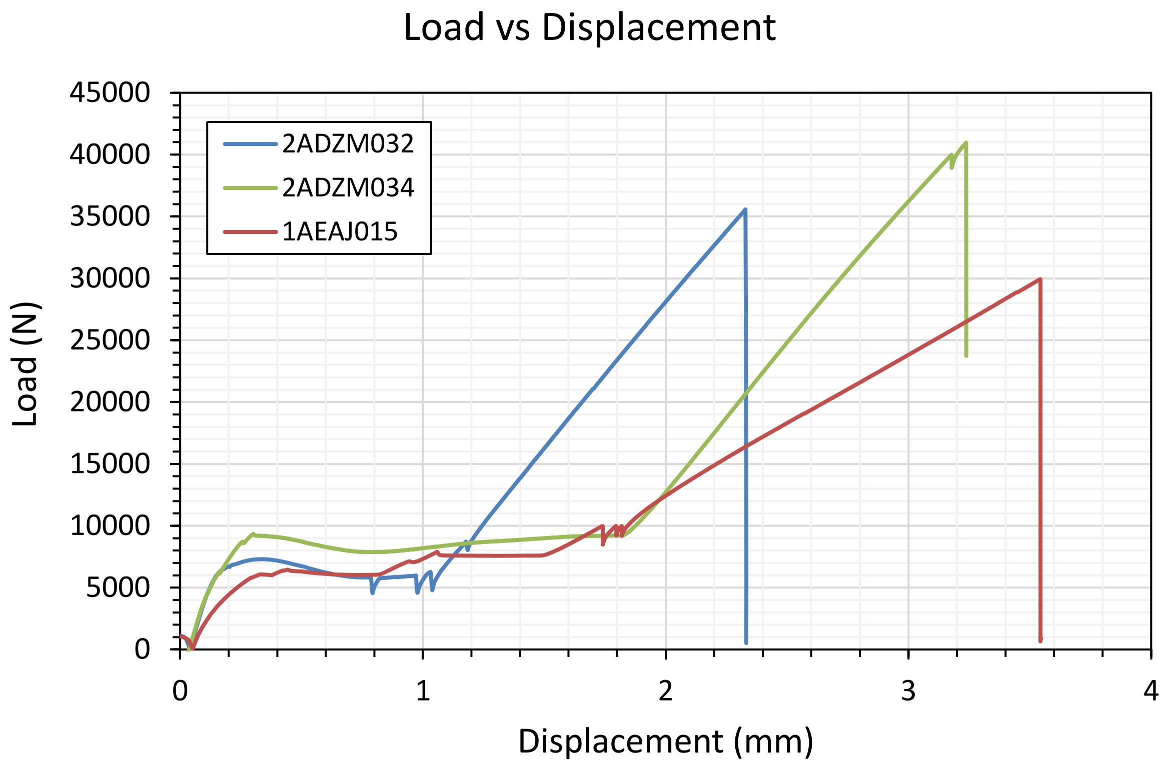

Figure 21. Load versus displacement plot for specimens 2ADZM032, 2ADZM034 and 1AEAJ015 at -165 °C.

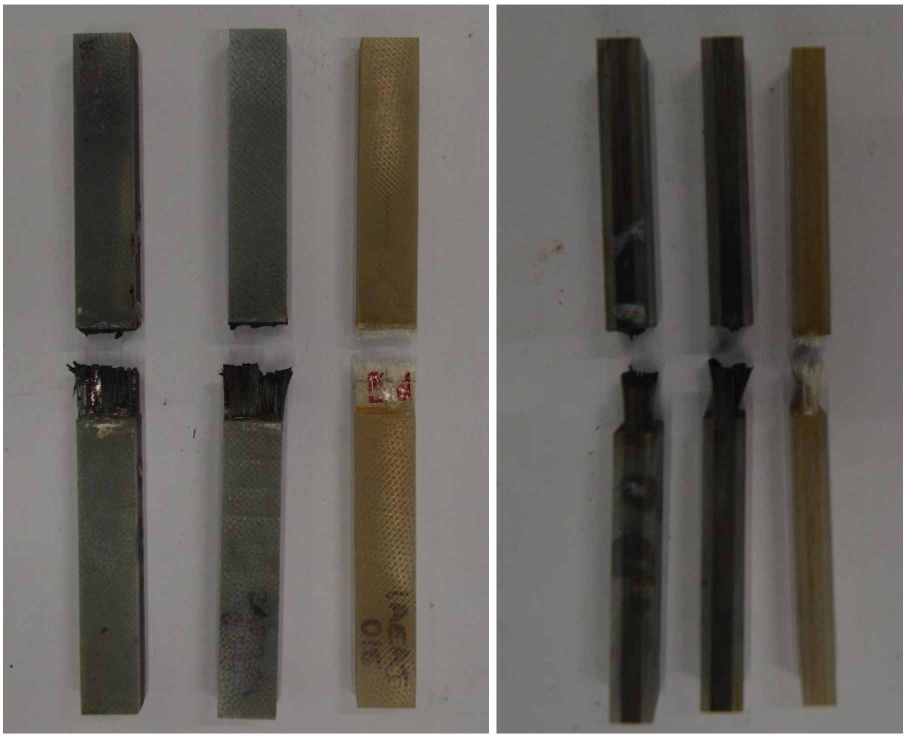

Figure 22. Failed compression specimens ADZM032, ADZM034 and 1AEAJ015 at -165 °C.

4 CONCLUSIONS AND FURTHER WORK

This report has detailed a program of work undertaken to assess the feasibility of performing tension and compression tests at -165 ºC utilising grips and loading rigs typically used for tests at room or elevated test temperatures.

The results generated show that the characterisation of tensile properties of FRP composites at cryogenic temperatures (-165 °C) can be performed with some degree of success. However, the use of wedge-action grips is not particularly suitable for successful load introduction due to seizing of the sliding metallic surfaces at low temperatures and can lead to slippage of the specimen. In addition, de-bonding of end-tabs due to the effect of extremely low temperature on the adhesive used is another issue that can prevent successful tests from being undertaken.

The feasibility of compression testing using a four pillar die-set combined loading rig was assessed, however this rig was found to be problematic due to seizing of the bearings used in the alignment pillars as a result of icing.

The next stage of this work will focus on developing improvements to the measurement techniques for both tension and compression in order to optimise mechanical characterisation at low temperatures. The aim is to develop methodologies that will lead to data consistency and reliability, accelerating the standardisation of testing methods and ultimately the adoption of FRP composites in LNG and LH_2 applications.

Experimental measurement challenges encountered in this study and that will be addressed in the following stages of this project are summarised below:

- Re-design of loading rigs and grips: - The large mass and bulky design of loading rigs, gripping systems that are ineffective at CT and potential damage to the jig after several cycles, cryogenic cooling and loading cycles have proven that re-design of loading rigs and grips will be key issues to address ahead of refining measurements procedures and future standards development. Further investigations are required in order to design and develop the optimal tensile and compressive gripping methods for generating consistent and reliable mechanical properties of FRP composites at cryogenic temperatures.

- Cooling and thermal efficiency: - Significant quantities of LN_2 (75 litres per test) and long cooling periods (90 mins per tensile test and 90-120 mins per compression test) were required in order to achieve the desired temperature. Therefore, improvements are without doubt required to enhance testing efficiency, that will ultimately decrease the overall cost per test. Cooling efficiency is related to the mass of the loading rigs and grips used, but also the efficiency of the thermal insulation of the environmental chamber itself.

- Suitable de-greasing compounds and lubricants: - Part of the investigations that will be carried out in order to develop suitable test rigs for cryogenic testing of FRP composites will include identifying fit-for-purpose de-greasers and lubricants to avoid rigs seizing at low temperatures cycles and to ensure adequate gripping.

- Suitable instrumentation: - Further validation and in-depth comparison of strain instrumentation methods used are essential to ensure data reliability and accuracy. In addition, other instrumentation methods such as Digital Image Correlation (DIC) and acoustic emission will be considered.

- Lack of universal standard test methods applicable to FRP composites: - The lack of guidance to evaluate the performance of FRP composite materials in cryogenic applications is making the process less clear. A key recommendation based on the experimental challenges and high variation in the results generated during this study is to accelerate the publication of universal standards to provide guidance on testing methods, specimen dimensions, apparatus and instrumentation for the successful characterisation of the mechanical properties of FRP composites at cryogenic temperatures for LNG and LH_2 storage and distribution applications.

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