

Mechanical Property Testing of Thermoset and Thermoplastic Composites for Cryotank Applications

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Abstract

Lightweight cryogenic propellant storage solutions with zero or near zero boil-off represent a critical need for NASA in both aeronautics and space technology missions. Applications for composite cryogen storage tanks range from hydrogen powered aircraft to long-duration in-space and on-surface missions. Over the past several decades, NASA and industry partners have supported several notable composite cryotank development programs documenting lessons learned with respect to materials and manufacturing. This paper specifically reports the results of material screening efforts funded by both the Aeronautics Research Mission Directorate and the Space Technology Mission Directorate to evaluate thermoset and thermoplastic composites for cryogen storage. Although the end applications differ, the fundamental material requirements across the two projects are the same. This paper details characterization of candidate thermoplastic and thermoset composite materials for cryogen storage, with test data generated (1) at -196°C and (2) following 100 thermal cycles between room temperature (21°C) and -196°C.

Introduction

Both the United States and Europe have established strategies for achieving net-zero carbon emissions in air transportation over the next several decades. The US National Clean Hydrogen Strategy and Roadmap presents a framework for achieving large-scale production and use of clean hydrogen, resulting in the development of strategic programs on hydrogen propulsion for the aviation industry.[1] Similarly, lightweight composite cryotanks can enable opportunities in space such as on-orbit or lunar propellant depots, in-space propulsion systems, and long-duration spacecraft. NASA's Commercially-viable Hydrogen Aircraft for Robust Growth in Efficiency (CHARGE) project addresses the multi-faceted challenges associated with implementing cryogenic fuel storage systems for aircraft propulsion [2] and the Composite Technology for Exploration Applications (CTE-A) project assessed composite materials for long term cryogen storage on the lunar surface. The project teams combine a diverse set of skills including aircraft architecture modelling and optimization, advanced material science, and engineering of high performance cryogenic systems. This paper will detail mechanical test data generated within the CHARGE and CTE-A projects.

Materials and manufacturing development for composite cryotank applications has a long history within the aerospace community, beginning with the National Aerospace Plane (NASP) in 1982. NASP was a Defense Advanced Research Projects Agency (DARPA)-funded feasibility study for a single stage to orbit (SSTO) spaceplane where the tank was required to hold pressurized cryogenic fluid while also withstanding aerothermal heating. To meet the challenge, the McDonnell Douglas Corporation (MDC) evaluated a carbon fiber/thermoplastic cryotank

concept, however the high processing temperature, tooling, and scale-up costs for manufacturing the thermoplastic tank provided a major barrier to development. MDC shifted to a carbon fiber/epoxy tank and since that time, composite cryotank material selection has relied heavily on thermosetting materials due the relatively lower processing temperatures and development of toughened epoxies to mitigate matrix microcracking.[3]

Microcracking within the composite matrix is the primary pathway for cryogen leakage through the tank wall. In 2013, NASA's Composite Cryotank Technology Development (CCTD) project successfully demonstrated the manufacture, thermal cycling, and burst test of two composite cryotanks for liquid hydrogen (LH2) storage.[4] The material used in this project was IM7/5320-1 which is a toughened epoxy and the CCTD program evaluated incorporation of thin ply prepreg to reduce microcracking. Photomicroscopy images of biaxially strained and thermally cycled panels showed greater than thirty cracks per inch for panels fabricated with standard, 5.3 mil thick carbon fiber/epoxy prepreg whereas less than five cracks were found in panels made with 2.6 mil thick carbon fiber/epoxy prepreg. The CCTD project furthered this manufacturing approach beyond panel tests and demonstrated that microcracking of thermoset composites could be reduced through incorporation of thin-ply in the cryotank wall.[3]

Recent advances in manufacturing and improvements to prepreg quality have renewed interest in carbon fiber/ thermoplastic composites for cryotank structures. The inherent toughness of thermoplastics offers the potential for reduced microcrack density with cold temperature storage. While less commonly investigated than carbon fiber/epoxy, literature is available to provide permeation, microcracking, and mechanical property data for carbon fiber/ thermoplastic systems.[5-6]

Development of materials for hydrogen propulsion for aviation presents unique challenges relative to space propulsion including much longer service life (5000-15,000 hours for commercial aviation versus 1-20 hours for space propulsion).[7] Due to the large number of fill/drain cycles required of tank materials in aviation, material screening in the CHARGE project included thermally shocking test coupons in liquid nitrogen (LN2) (-195°C / -320°F). for up to one hundred cycles and testing those coupons in static and fatigue tests.

Two sets of data will be presented in this paper. The first includes coupon test data collected at 21°C (70°F), -101°C (-150°F), and -195°C (-320°F). This data was generated from as-manufactured test coupons for the purpose of collecting baseline data for model development and cryotank design. The second dataset was generated from coupons that had experienced one hundred thermal cycles from 21°C to -195°C, then tested at room temperature. Liquid nitrogen was used for preliminary screening due to the higher costs associated with testing in liquid hydrogen.

Experimental

Materials: The purpose of the materials effort within the CHARGE project was to evaluate a thermosetting (TSC) and thermoplastic (TPC) composite material for a composite cryotank application. The materials selected include T1100/3960 toughened epoxy prepreg, 192 gsm and 34% resin content, and T1100/TC1225 low-melt polyaryletherketone (LM-PAEK) prepreg, 145 gsm and 34% resin content. Both procured from Toray Advanced Composites.

Conditioning: LN2 was selected for thermal cycling and the low temperature for mechanical tests during material screening for both projects to reduce programmatic costs. Thermal cycling proceeded by submersion of individual test specimens in LN2, held for 5 minutes, removal from the LN2 bath, then thermal equilibration to room temperature over 10 minutes. This process was repeated for 100 total cycles.

Coefficient of Thermal Expansion (CTE): Thermal expansion was measured according to ASTM Standard E289-17 with a Michelson laser interferometer system under vacuum with liquid nitrogen cooling, over the temperature range -170°C to 50°C at a 1°C /min ramp rate. Data were acquired as coupon strain in parts per million (ppm) as a function of temperature, with strain defined as zero at 20°C. Each coupon was measured on both cooling and heating across multiple cycles, with the samples left undisturbed in the measurement chamber under vacuum between tests. Strains are fitted to a linear function of temperature and CTE is presented as a constant: $CTE = A \pm \delta$, where δ is the average over all temperature points of the standard deviation in CTE between replicate measurements.

Mechanical Tests: Coupon tests were performed based on ASTM standards as detailed in Table 1. Test temperature, pre-conditioning, and test location are included.

Table 1: Mechanical tests performed within the CHARGE and CTE-A projects.

Abbr.	Test	ASTM	Layup	Test Temperature	Test Location
0T	Lamina Tension	D3039	[0] ₆	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
90T	Lamina Tension	D3039	[90] ₆	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
0C	Lamina Compression	D6641	[0] ₁₄	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
90C	Lamina Compression	D6641	[90] ₁₄	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
IPS	In-plane Shear	D3518	[+45/-45] _{4s}	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
UNT	Unnotched Laminate Tension	D3039	[45/0/-45/90] _{2s}	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
UNC	Unnotched Laminate Comp.	D6641	[45/0/-45/90] _{3s}	21°C, -101°C, -195°C	NIAR
				21°C following LN2 cycles (50x and 100x)	NASA GRC
OHT	Open Hole Tension	D5766	[45/0/-45/90] _{2s}	21°C, -101°C, -195°C	NIAR
OHC	Open Hole Compression	D6484	[45/0/-45/90] _{3s}	21°C, -101°C, -195°C	NIAR

Results and Discussion

The mechanical properties of composites tested at cryogenic temperature are influenced by physical and thermal characteristics of the fiber and matrix and their interfacial interactions. Multiple material phenomena contribute to composite strength, modulus, fatigue, and permeability at cryogenic temperatures but are ultimately driven by thermal expansion of the matrix resin and carbon fiber.[8] It is well established that the CTE of carbon fiber and resin can vary by an order of magnitude, with expansion and contraction of the resin being much larger. In general, contraction of the resin on cooling generates compressive stresses on the fiber, increasing the fiber-matrix interface strength which translates to increased mechanical strength.

The CTE of the fibers, while smaller, is not uniform with carbon fibers typically contracting along the fiber direction but expanding in the transverse direction on cooling.

Because CTE drives composite behavior at cryogenic temperature and is isotropic in nature, it was important to measure the CTE along each fiber direction. In this work, CTE data was collected from -175°C to 50°C and the results demonstrate the influence of measurement direction, with respect to fiber orientation, on the material CTE. The coupon fiber orientation with respect to the test direction is shown in figure 1.

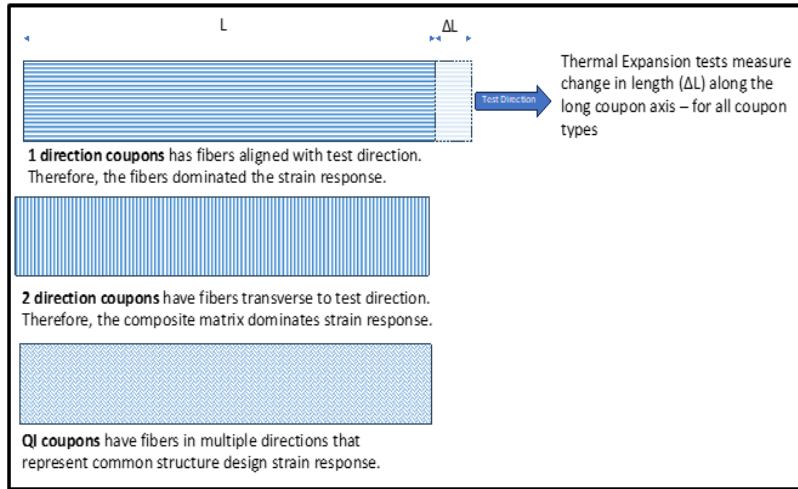


Figure 1. Thermal Expansion Coupons Fiber

Coupons were measured in the 1-direction, along the fiber length of a uni-directional fiber orientation, 2-direction, transverse to the fiber direction of a uni-directional fiber orientation, and across a quasi-isotropic (QI) fiber orientation. The lower temperature 2-direction CTE data could alternatively be used to back out the matrix CTE or matrix Young's modulus at the low temperatures. Data for both candidate thermoplastic and thermoset composites are shown in Table 2.

Table 2. CTE data for candidate thermoplastic and thermoset materials.

Thermoplastic (T1100/TC1225)		
Lay-up	Test Direction	CTE(1)(ppm/°C)
[0] ₂₆	1	0.09 ± 0.06
		0.4 ± 0.2
[90] ₂₆	2	44 ± 1
		45 ± 1
[45/0/-45/90] _{3s}	Q/I	2.6 ± 0.2
		2.5 ± 0.2
Thermoset (T1100/3960)		
Lay-up	Test Direction	CTE(1)(ppm/°C)
[0] ₂₆	1	0.39 ± 0.04
		0.13 ± 0.04
[90] ₂₆	2	44 ± 1
		45 ± 1

[45/0/-45/90] _{3s}	Q/I	2.6 ± 0.2
		2.5 ± 0.2

The data represents expansion of the composite system and can be used to predict strain due to CTE mismatch at the fiber-matrix interface. CTE induced thermal strains at the interface can lead to considerable changes in composite structure and properties, particularly when exposed to repeated thermal cycling, with potholing, delamination, and microcracking being among the most common.[9] Overall, the CTE of the thermoset and thermoplastic composites measured in this study was similar and unlikely to cause considerable difference in microcracking between the two candidate materials.

Matrix microcracking is a key consideration because it is the leading path for cryogen permeation in a composite and even this small-scale damage can grow with repeated cycling and lead to composite failure. Photomicrographs of the thermoplastic and thermoset are shown in figure 2. Microcracking was not observed in the TPC or the TSC coupons, which were exposed to 100 cycles to LN2 temperature (-196°C).

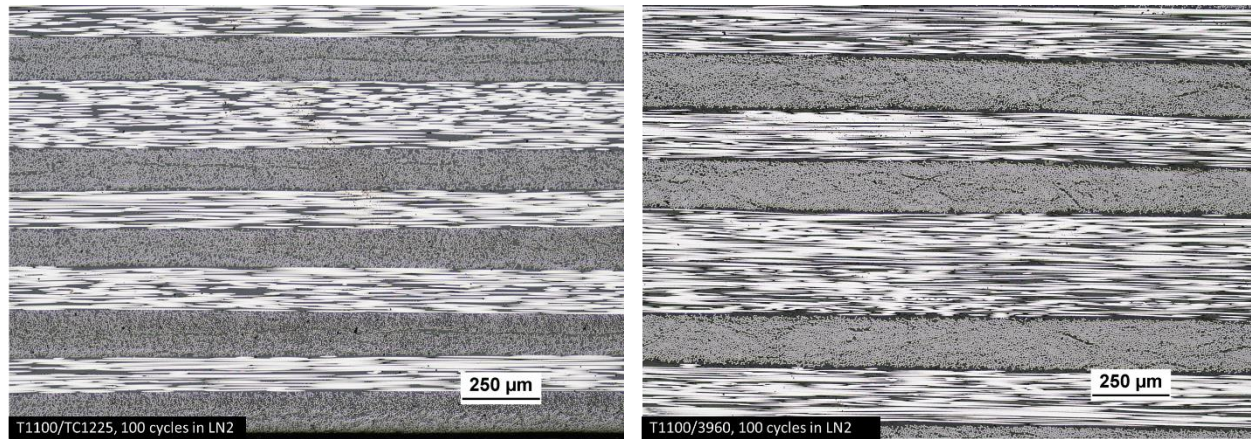


Figure 2: Photomicrographs of the TPC (left) and TSC (right) following 100 LN2 to room temperature thermal cycles.

Mechanical Tests

Two coupon conditions were considered for mechanical testing, (1) testing at LN2 temperature(-196°C) and (2) thermal cycling to LN2 temperature, then testing at room temperature. Cold temperature tests were selected to provide strength and stiffness data at a temperature that approaches operating temperature. While valuable, this test represents only one half of a first thermal cycle, in which case the resin contracts around the fiber and the test is performed. Alternatively, repeated expansion and contraction from thermal cycling causes molecular chains to pack more tightly resulting in increased intermolecular forces; the net effect being increased matrix stiffness.[10] A reduction of both free volume and molecular motion diminishes mechanisms for stress relaxation and can lead to microcracking. Both sets of data are useful in analyzing composite properties for cryogen storage.

RT and Cold Temperature Test Data

The first set of data generated measured a series of coupons at 21°C (70°F), -101°C (-150°F), and -195°C (-320°F). The purpose of this dataset was to evaluate the effect of temperature on material strength and modulus. Tension, compression, and in-plane shear data for the TPC is plotted in figures 3-5.

In general, minimal effect on mechanical property data was observed for the TPC when tested at over this temperature range, with compression slightly increasing at -196°C, and both tensile strength and in-plane shear strength decreasing at LN2 temperature.

Tensile test data at from 21°C to -196°C shows a decrease in tensile strength. This opposes of trends typically reported in the literature [8]. In general, contraction of the resin at cold temperature, and reduced molecular movement result in both increased fiber-matrix strength and increased molecular interaction between polymer chains. The net effect tends to be an increase in tensile strength and modulus a low temperature.

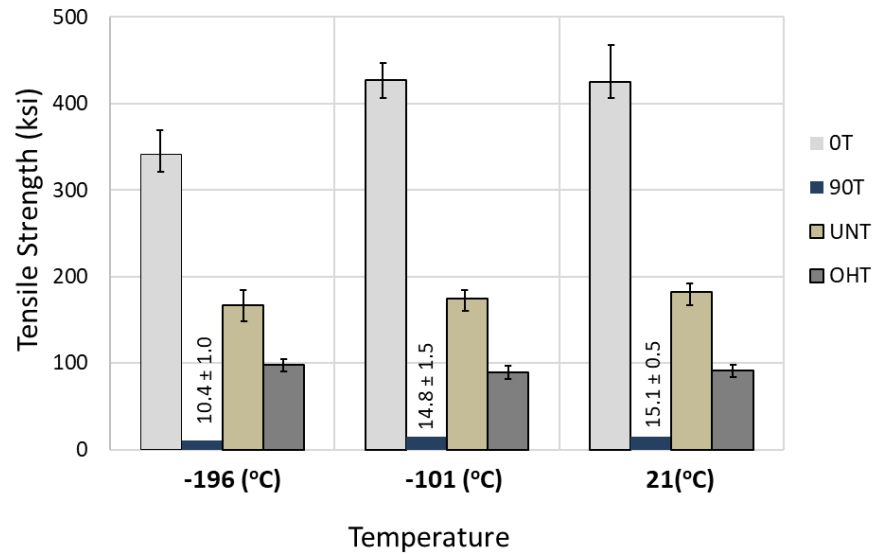


Figure 3: Tensile strength of T1100/TC1225 measured at -196°C, -101°C, and 21°C.

Tensile modulus, Table 3, tends to increase with decreasing test temperature. This is consistent with the literature and due to resin contraction resulting in greater intermolecular interaction and restricted chain movement.

Table 3: Tensile modulus for T1100/TC1225 measured at decreasing test temperature.

Temp	0T	CoV (%)	90T	CoV (%)	UNT	CoV (%)	OHT	CoV (%)
-196°C	25.1 ↑	1	1.7 ↑	1.7	9 ↑	3	9.3 ↑	1.9
-101°C	24.1 ↑	1.6	1.7 ↑	11.8	8.8 ↑	3.6	9.2 ↑	4.2
21°C	24.7 ↑	2.5	1.4 ↑	1.2	8.7 ↑	2.7	9 ↑	2.4

The increase in compression strength, figure 4, is attributed to a reduction in polymer chain mobility with decreasing temperatures leading to increased intermolecular forces and reduced

stress relaxation relative to room temperature. In addition, the greater CTE of the resin as compared to the carbon fiber leads to resin shrinking around the fibers. In a compression test, the matrix supports the fiber and reduces failure from fiber buckling. Therefore, an increase in resin strength and stiffness often translates to an increase in compression strength and modulus of the composite.

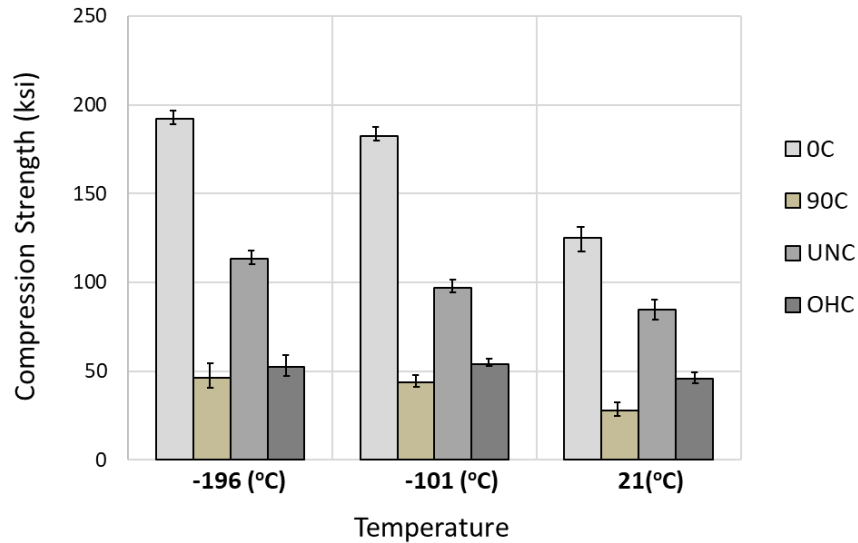


Figure 4: Compression strength of T1100/TC1225 measured at -196°C, -101°C, and 21°C.

The modulus values for compression tested coupons are listed in Table 4. Modulus tends to increase with decreasing test temperature for 0C, 90C, and UNC tested coupons. Only the OHC tests lead to a reduction in modulus at cold temperature.

Table 4: Compression modulus for T1100/TC1225 measured at decreasing test temperature.

Temp	0C	CoV (%)	90C	CoV (%)	UNC	CoV (%)	OHC	CoV (%)
-196°C	22.8 ↑	4.1	1.7 ↑	3	8.2 ↑	0.3	8.1 ↓	1.4
-101°C	22.1 ↑	1.6	1.5 ↑	1	8.1 ↑	2.5	8.5 ↓	1.6
21°C	21.8 ↓	0.8	1.4 ↓	1.8	7.9 ↓	2.7	8.9 ↓	2

Like compression, in-plane shear is a matrix driven property. Unlike compression where an increased resin modulus and fiber-matrix interaction limit failure from fiber buckling, for IPS tests the increased matrix stiffness leads to reduced strain to failure and a reduction in IPS strength, figure 5. The modulus data for IPS tests is provided in Table 5, showing a 38% increase in modulus at -196°C when compared to the room temperature test.

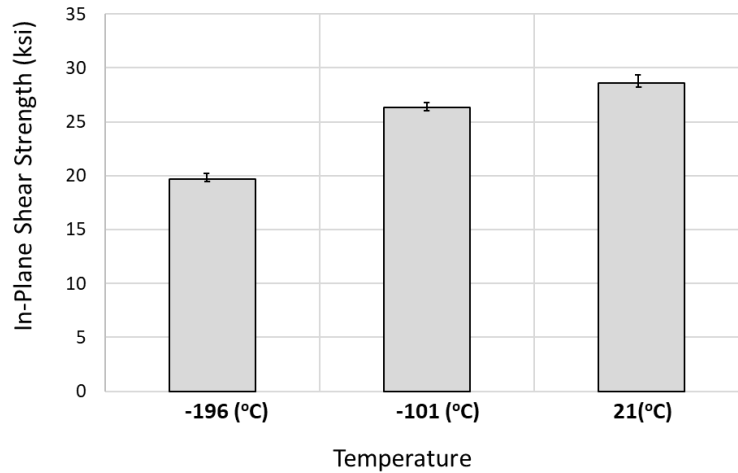


Figure 5: In-plane shear strength of T1100/TC1225 measured at -196°C, -101°C, and 21°C.

Table 5: In-plane shear modulus for T1100/TC1225 measured at decreasing test temperature.

Temp	IPS	CoV (%)
-196°C	0.83	0.34
-101°C	0.75	1.8
21°C	0.6	1.94

The schedule for this project did allow time to test the TSC, however trends in strength and modulus reported for epoxy matrix composites are similar to the TPC findings reported here . Sapi et al report a general increase in tension and compression strength and modulus for epoxy matrix composites tested at cold temperature compared to room temperature. The reported effect on interlaminar shear strength varies, with the effect of temperature being resin specific. [11-15]

Thermally cycled coupon data

Data presented in the previous section is representative of the first half of a single thermal cycle experienced by the material. The second set of data was intended to evaluate the influence of repeated LN2 cycling on mechanical properties.

The tensile strength of LN2 cycled coupons is presented in figure 6. The mean values of the OT TPC increased with thermal cycling, while the strength data for UNT, TPC coupons was constant. The trend of the TPC cycled OT coupons is opposite from data collected at 196°C, where a decrease in tensile strength was measured. The deviation in trend may be due to (1) test temperature, where coupons tested at 196°C may have failed early due to reduced failure strain of the resin at the test temperature, or (2) repeated cycling resulting in increased strength of the fiber matrix interface. It should be noted that cycled coupons and the 196°C coupons were tested in different labs and future work should consolidate mechanical tests to a single facility.

The influence of thermal cycling on the thermosetting material was a small increase in OT and a small decrease in UNT strength. All strength measurements were within the scatter.

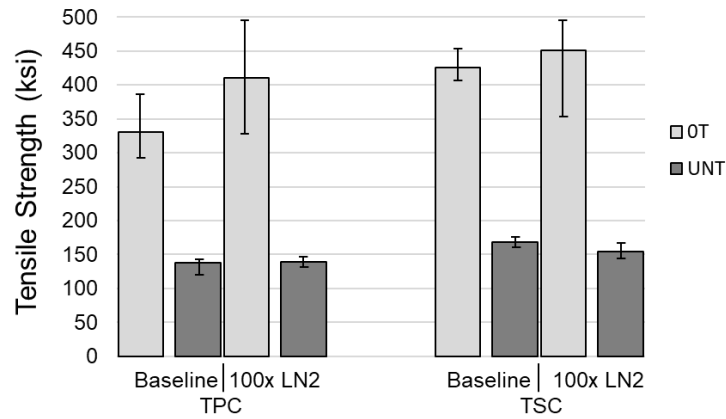


Figure 6: Tensile strength of TPC and TSC baseline and LN2 cycled coupons.

Compression strength values, figure 7, of LN2 cycled coupons either increase or remain unchanged, following the trend observed in cold temperature tests.

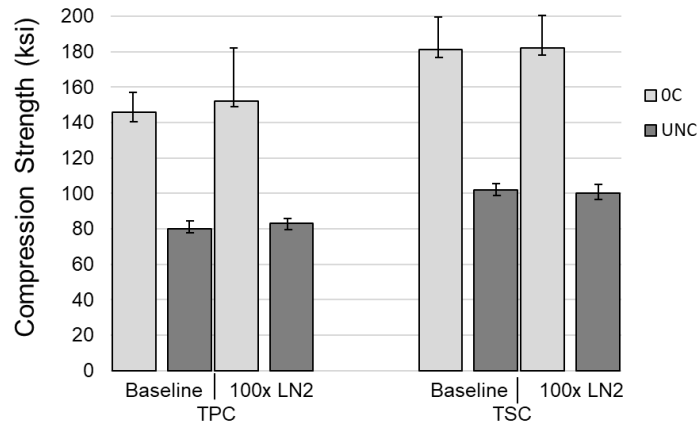


Figure 7: Compression strength of TPC and TSC baseline and LN2 cycled coupons.

The mean IPS strength of baseline and LN2 cycled coupons for the TPC and TSC materials is presented in figure 8. Unlike coupons that were tested at LN2 temperature, the IPS strength of cycled coupons was unchanged relative to the baseline. The cycled coupons were tested at room temperature and therefore the reduction in matrix strain to failure observed during cold temperature testing was not a factor in the strength of the cycled coupons.

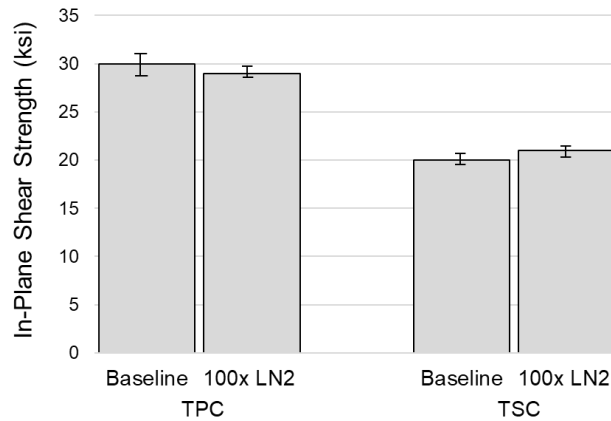


Figure 8: In-plane shear strength of TPC and TSC baseline and LN2 cycled coupons.

A summary of the modulus data for cycled coupons is provided in table 6. Testing cycled coupons at room temperature had little influence on modulus, compared to testing at low temperature. The greatest change on cycling was observed for IPS coupons where modulus was reduced with thermal cycling.

Table 6: Modulus data from baseline and cycled test coupons.

	Condition	OT (Msi)	UNT (Msi)	OC (Msi)	UNC (Msi)	IPS (Msi)
TPC	Baseline	23.7	8.4	22.4	8	0.52
	100x LN2 Cycles	25	8.4	21.8	8.4	0.48
TSC	Baseline	24.9	9	22.2	8.6	0.71
	100x LN2 Cycles	23.9	8.9	21.7	8.5	0.66

Summary

The data presented in this study provided trends in strength and modulus for a TPC and TSC materials when tested from room temperature to -196°C, and following thermal cycles from room temperature to -196°C. Trends in strength and modulus were similar for both materials evaluated. Photomicroscopy following thermal cycling did not show evidence of matrix microcracking following 100 thermal cycles in LN2. While panel data can provide important strength and modulus values as needed for design and model development, further material characterization will be required. We anticipate manufacturing demonstrations to identify manufacturing constraints, in particular for the thermoplastic tank. Leak testing following fill-drain cycles as well as burst test data when combined with coupon data and manufacturing pathfinder information will allow for materials selection for scale-up and further development.

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