

INVESTIGATION OF THE MECHANICAL PROPERTIES OF CARBON AND GLASS FIBRES EXPOSED TO CRYOGENIC TEMPERATURES AND CRYOGENIC CYCLING

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Keywords: Single fibre testing, Cryogenic, Carbon fibre, Glass fibre

Abstract

The need for lightweight storage vessels has grown in recent years with the potential utilisation of liquid hydrogen as a fuel source in aircraft. Fibre-reinforced polymer vessels have been recognised as a potential solution due to their exceptional mechanical properties and lightweight nature. However, due to the cryogenic temperatures endured when storing liquid hydrogen, the composite material will be potentially exposed to temperatures considerably below the glass transition temperature. Thus, fundamental studies are required to understand the effects this will have on the mechanical properties of the fibre, matrix, and fibre-matrix interface in addition to the effects of natural convection, cryogenic shock, and cryogenic cycling between refuelling. This paper presents a methodology and findings from mechanical testing and surface analysis of individual fibres before and after cryogenic fatigue. Results for glass fibre reveal fluctuations in mean diameter and tensile strength but remain within error unless a film former is present. With a film former in the glass fibre size an increase in diameter and decrease in tensile strength is observed after one cryogenic cycle which stabilises with further cycling. It is concluded that cryogenic cycling does not significantly affect the fibre diameter and tensile strength of carbon fibre by the method used in this paper.

1. Introduction

A variety of industries are currently exploring the potential utilization of liquid hydrogen (LH₂) as a pivotal energy source for the future. Given the great potential of LH₂ as an energy vector, there arises a significant need for regulations governing pressurised vessels and fatigue testing of composites that could be used to store LH₂ [1-3]. These vessels, potentially manufactured from fibre-reinforced polymer composites, will be exposed to cryogenic environments over an extended period with little knowledge of the effects on the materials known. The effects of cycling between ambient and cryogenic temperatures on the fundamental fibre-matrix interface of a composite is a little-known yet crucial parameter for ensuring the integrity and reliability of LH₂ pressurised vessels over their lifespan.

The properties of composites arise from an amalgamation of the characteristics of the fibre and the matrix alongside the ability to transfer stresses across the fibre-matrix interface [4]. The reinforcing fibres have a critical role in providing strength and stiffness to composites. These fibres bear the majority of applied load, while the matrix binds the fibres together, leading to uniform stress distribution and protection. The mechanical properties of the fibres significantly influence the overall performance of the material. Given the critical influence these constituents have in determining the long-term

performance of fibre-reinforced polymer composites, there is a need for fundamental investigations into the effect of exposing such materials to cryogenic environments and cryogenic cycling to understand the resultant effect on these crucial parameters [5-7].

As an initial step, it is first necessary to understand the effects on the mechanical properties of single fibres that materialise after exposure to cryogenic conditions. Currently, there has been a seldom amount of research into the material properties of the fibres whilst under cryogenic conditions [5, 7-9] but investigations of the effect of cryogenic cycling have been extremely limited. Given the scale and nature of the testing to be conducted, and its sensitivity to changes in material properties, at either a fibre or interface level, it is thus essential to gain an understanding of the characteristics and trends that will vary solely in individual fibres prior to investigating the changes to the fibre-matrix interface collectively.

Therefore, in the present work the impact of cryogenic shock and cryogenic cycling on the mechanical properties of individual carbon and glass fibres was investigated with subsequent analysis of the fibre surface. Subsequently, this will serve as a prerequisite for further investigations into the fibre-matrix interface.

2. Experimental

2.1. Materials

Three glass fibres with different sizes and two carbon fibres with different sizes were selected to investigate the varying levels of protection to the fibre surfaces:

1. Bare (water-sized) E-glass fibre with an average diameter of 17.5 μm supplied by Owens Corning
2. 3-Aminopropyltrimethoxysilane (APTMS) sized E-glass fibre with an average diameter of 17.5 μm supplied by Owens Corning
3. Fully sized commercial Advantex E-CR-glass fibre SE2020 with an average diameter of 17.0 μm supplied by 3B
4. T700S FOE 12K carbon fibre with an average diameter of 7.0 μm supplied by Toray
5. T700S 50C 12K carbon fibre with an average diameter of 7.0 μm supplied by Toray

The fibres were cut into 30 cm long bundles from larger rovings to facilitate sample preparation. Experimental work was carried out using liquid nitrogen, allowing 77 K to be reached, as a cryogen due to safety concerns associated with hydrogen.

2.2. Cryogenic Cycling of Fibres

The cryogenic cycling of fibres consisted of immersing a fibre bundle directly into a vessel containing liquid nitrogen for one minute to allow equilibrium at 77 K to be reached, before removing the sample and heating by natural convection for one minute to allow the samples to reach equilibrium at room temperature. This process could be repeated for the desired number of cryogenic cycles using fresh cuttings from the rovings.

In addition to one-minute cryogenic cycling a single thirty-minute cryogenic cycle was conducted on all glass fibre samples used. This involved immersing the fibres in liquid nitrogen using the same procedure as previously stated except for an extended hold time at 77 K of thirty minutes before being removed and allowed to warm to room temperature by natural convection.

2.3. Single Fibre Tensile Testing

Single fibres were tensile tested according to ASTM C1557-20 (standard test method for tensile strength and Young's modulus of fibres) on 250 g/m² paper card tensile testing templates with a gauge length of 20 mm. Double-sided tape was positioned on the testing template approximately 1 mm away from the end of the template. Individual fibres were then carefully and randomly extracted from fibre bundles

and placed along the vertical axis of the template onto the double-sided tape. Loctite Power Gel Super Glue was applied to the fibre at the edge of the gauge hole to securely fasten the single fibre in place, before testing the glue was allowed to set for 24 hours. Measurements of the fibre diameter were determined using a Leitz Ergolux optical microscope at 500x magnification and analysed with ImageJ analysis software. A Testometric M250-2.5CT tensile tester equipped with a 5 N load cell utilising WinTest Analysis version 4.2.12 was used to perform the tensile tests. A rate of 0.3 mm/min was used and the tests were performed at room temperature with relative humidity varying between 35 and 65%. At least 60 samples were measured and tested for each fibre type and experimental condition with the mean value reported along with 95% confidence limits.

3. Results

3.1. Glass Fibre Diameter Observations

Microscopy and subsequent measurements revealed a decrease in average fibre diameter for water and APTMS-sized E-glass fibres with the exception of APTMS-sized fibres after ten cryogenic cycles as shown in Figure 1. This outlier to the downward trend is potentially due to the variability in diameter originating from the fibre manufacturing process [10] and in addition, the sample size represents only a small fraction of the fibre roving. As a result, it is unclear if the APTMS-sized diameter changes are attributable to cryogenic cycling or simply reflect variations in diameter throughout the roving. The water-sized fibre exhibited a clear decrease in diameter post-cryogenic cycling but remains within the error range of the control sample in all but one of the conditions in which a decrease by a maximum of only one micron was observed. Suggesting that the variation is just due to an error in the fibre diameter throughout the roving and cryogenic cycling does not significantly affect water-sized E-glass. These findings necessitate further analysis at precise locations along the fibre before and after cycling to investigate the effect of cryogenic temperatures on specific areas rather than relying solely on average fibre diameter measurements.

The fully sized SE2020 glass fibre displays a clear increase in diameter after one cryogenic cycle which persists in further cycles but does not appear to deviate any further out width error. This change is highly likely to be due to water uptake between the fibre surface and film former, which has frozen and expanded, subsequently remaining trapped at a saturated level after the cycle. This clear trend aligns with changes in tensile strength, as illustrated in Figure 3, indicating a correlated effect which will be discussed later in this paper.

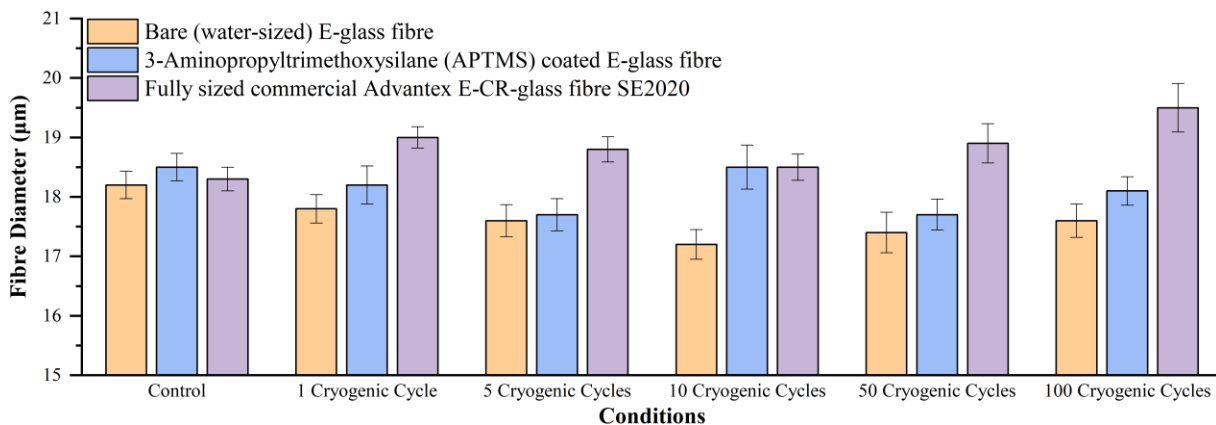


Figure 1: Variation in glass fibre diameter after reported number of cryogenic cycles

The trends described for each of the glass fibre samples tested hold consistent when cryogenic cycling is increased from one one-minute cycle to a single thirty-minute cycle as depicted in Figure 2 with both

the water and APTMS-sized fibres exhibiting diameter variations within error, while the SE2020-sized fibre displayed the clear increase that was previously described and maintained after an extended period. Hence, it is inferred that this increase reaches saturation within a minute of cryogenic exposure.

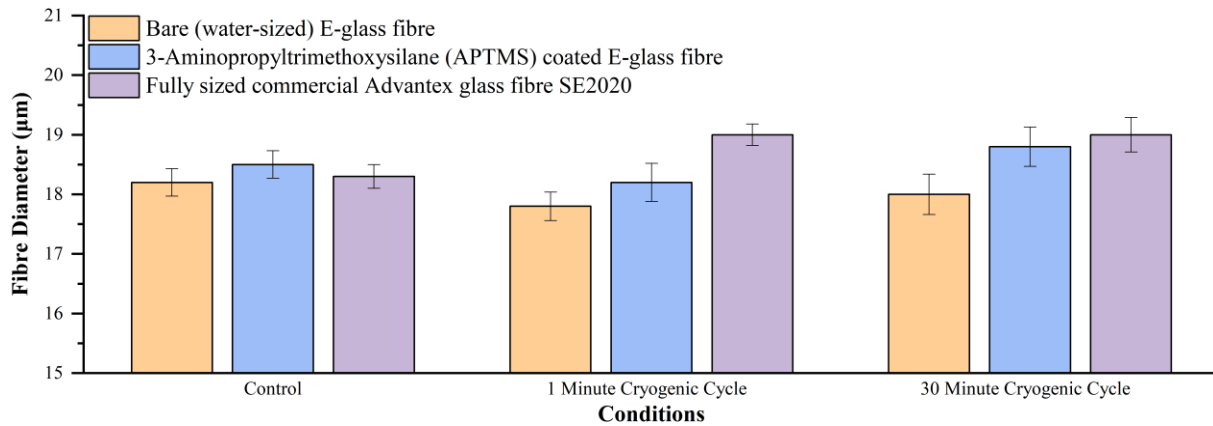


Figure 2: Variation in glass fibre diameter with varying time held at cryogenic temperatures

3.1.1. Glass Fibre Tensile Testing

Single fibre tensile testing of all three glass fibres revealed large variations in tensile strength after varying the number of cryogenic cycles whilst remaining within the error margins of the control values as illustrated in Figure 3. It is suspected that the fluctuation in mean value for water and APTMS-sized fibre arises from insufficient levels of protection potentially allowing the formation of defects and cracks during the lifecycle of these fibres. Whilst the samples with the film former are expected to still have cracks and defects the level of which should be significantly lower due to the enhanced level of protection provided by the film former. Therefore, suggesting that the variation in tensile strength could be linked to the increase in fibre diameter supporting the proposal that a saturated level of moisture has been up taken between the fibre and size after one cryogenic cycle. Additionally, while all the SE2020-sized glass fibre values are within the error range of the control value of 1.7 GPa, every sample subjected to cryogenic cycling exhibits a mean value at least 0.1 GPa lower than the control. This could be correlated to the significant increase that could be seen in the fibre diameter measurements after one cryogenic cycle.

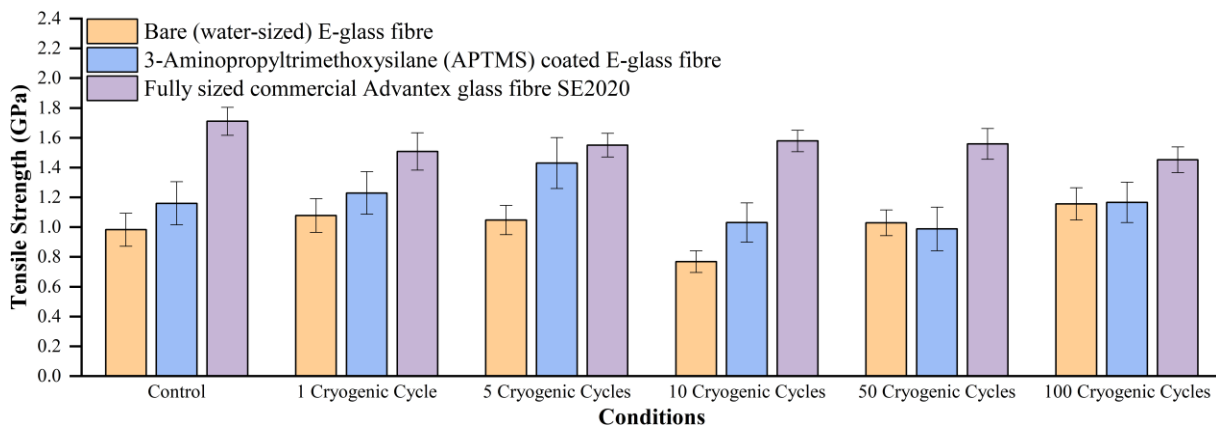


Figure 3: Variation in tensile strength of glass fibres after reported number of cryogenic cycles

Increasing the hold time for cryogenic cycling from one minute to thirty minutes results in an increased mean tensile strength for all three sample types. Specifically, the water-sized fibre increases by 36 %,

the APTMS by 10 % and the SE2020 by 4 % from the control as depicted in Figure 4. Intriguingly, while the water and APTMS-sized fibres display an increase from the one-minute cycle to the thirty-minute cycle, the SE2020-sized fibre displays a drop after one-minute cycling but an increase from the control after a thirty-minute cycle.

These changes in tensile strength imply that glass fibres may undergo morphological changes over an extended period at cryogenic temperatures, resulting in increased tensile strength [11]. However, further analysis would be required with a larger number of samples and over a much larger period to confirm whether this trend reflects genuine variations in mean tensile strength and is not just a deviation throughout the glass fibre rovings. Such work is planned for future research.

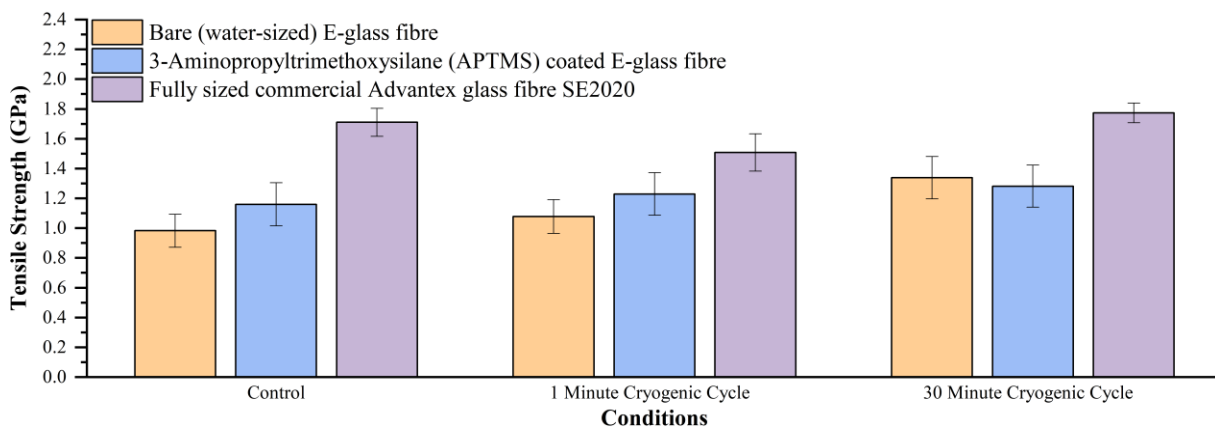


Figure 4: Variation in tensile strength of glass fibres with varying time held at cryogenic temperatures

3.2. Carbon Fibre Diameter Observations

Microscopy followed by fibre diameter measurements revealed a near-negligible increase in mean fibre diameter after ten cryogenic cycles, amounting to less than 0.01 microns as shown in Figure 5. This suggests that cryogenic cycling exerts no discernible effect on the tested samples after ten cryogenic cycles and that the variation in measurements is just as a result of deviation in the measured bundles.

As discussed by Sápi and Butler [12], the crystallinity content and molecular orientation in carbon fibre are typically close to peak values post-manufacturing, thus it is unlikely any changes to these properties would be noticeable in diameter measurements after exposure to cryogenic temperatures which is in agreement with the experimental observations illustrated in Figure 6.

Notably, Zhang et al [13] concluded that quenching carbon fibres has no significant effect on these properties. However, if the temperature is reduced at a controlled cooling rate down to 77 K a small increase in crystallinity, a decrease in crystallite size and shrinkage of the fibre diameter are observed. Hence, further analysis is warranted to determine if quenching and temperature-controlled methods over multiple cycles replicate the effects described by Zhang et al [13] for a single cycle with a 12-hour hold time.

Furthermore, given the much smaller dataset collected for carbon fibre and the observed high levels of variability in the mean values of the glass fibre diameter measurements, additional analysis with a higher number of cycles is imperative to ensure clarity in observations of carbon fibre behaviour.

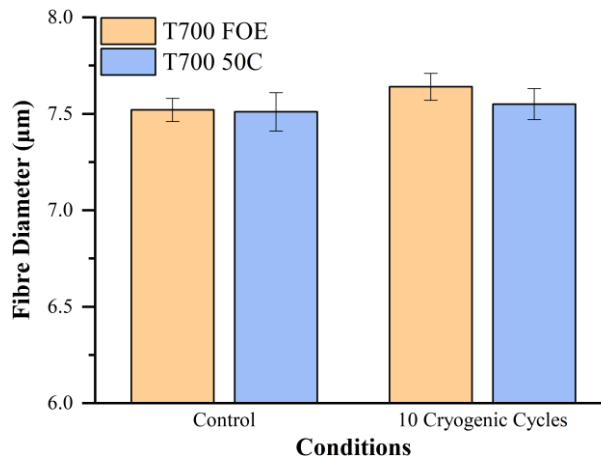


Figure 5: Variation in carbon fibre diameter between control and after ten cryogenic cycles

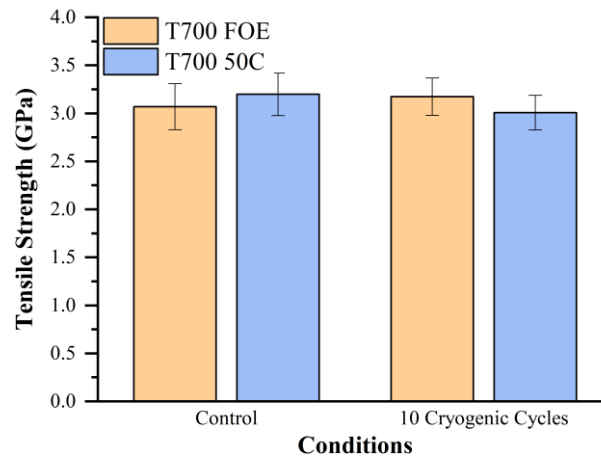


Figure 6: Variation in tensile strength of carbon fibres between control and after ten cryogenic cycles

3.2.1. Carbon Fibre Tensile Testing

Single fibre tensile testing of T700 carbon fibre with two different sizes exhibited opposing trends in mean tensile strength values after ten cryogenic cycles. Due to the small variation from the control for each sample, it is unlikely that the difference in size is accountable for this opposing trend. Instead, this change is likely to be due to experimental error, suggesting that ten cryogenic cycles by quenching have had no effect on the crystallinity and molecular alignment and thus no impact on the tensile strength, similar to the findings discussed previously in section 3.2 regarding diameter measurements.

4. Microscope Observations

After cryogenic cycling, no visible changes were observed with the naked eye to the fibre bundles with the exception of ice formation along the bundles, which rapidly dispersed into water droplets upon heating by natural convection to room temperature. Microscopy at 500x magnification of the single fibre samples revealed no notable changes to the surface of water and APTMS-sized fibres. However, signs of cracking were present in the SE2020-sized fibres, but it remains unclear if this had occurred in the size or the fibre itself, and whether these defects were present before cryogenic cycling. Therefore, further analysis will be required using atomic force and scanning electron microscopy to allow clear conclusions to be drawn.

A small percentage of single fibre samples that were prepared contained anomalies that could be observed during microscopy in both fibrous materials. These anomalies included fuzzing and a notable increase in surface roughness at the fibre edges. Given that these observations occurred throughout all of the test conditions and, in the control this small percentage of samples were excluded from calculated mean values. It is highly probable that these occurrences were due to manual handling of single fibres and potential defects from manufacturing.

5. Conclusions

In this paper, the effect of cryogenic cycling on the average fibre diameter and average tensile strength of both carbon and glass fibres was investigated by microscopy and single-fibre tensile testing. It was observed that cryogenic cycling resulted in a decrease in the average diameter of water-sized E-glass fibres, whilst APTMS-sized E-glass fibres exhibited fluctuations, but both remained within error of the control sample. This suggests that cryogenic cycling does not significantly affect the diameter of water and APTMS-sized glass fibres, with fluctuations likely arising from variations in fibre diameter

throughout the rovings. Conversely, the fully sized SE2020 glass fibre showed a clear increase in diameter after one cryogenic cycle, which could be attributed to water uptake between the fibre surface and the film former. This change occurred rapidly within the first minute at cryogenic temperatures and remained consistent thereafter.

Single fibre tensile testing of water and APTMS-sized glass fibre showed large variations in tensile strength with no obvious trend. This is concluded to be due to the lack of protection provided by these sizes rather than cryogenic cycling. Fibres with a film former exhibited a drop in average tensile strength after one cryogenic cycle, correlating with the observed increase in diameter. Carbon fibres displayed a negligible change in fibre diameter after ten cryogenic cycles decreasing by less than 0.01 microns and remaining within error margins, indicating that quenching and cycling had no effect under the tested parameters. Similarly, the tensile strength of carbon fibres remained largely unchanged, with only minor fluctuations within error. These observations are likely to be linked to the level of crystallinity and molecular orientation from manufacturing, alongside the quenching process to 77 K. Further analysis will be required using X-ray diffraction and infrared spectroscopy to conclusively assess the changes to crystallinity in carbon fibres. Additionally, atomic force and scanning electron microscopy will be required to monitor changes to the fibre surface as the number of cryogenic cycles is increased. Furthermore, this research could be expanded to investigate cryogenic cycling using liquid helium as a cryogen to broaden understanding at even lower temperatures and the effects of cryogenic cycling on interfacial shear strength.

Acknowledgments

I would like to express my gratitude to Professor Min Zhang and Dr Yudi Xiao for allowing me access to the cryogenic equipment in the Electronic and Electrical Engineering department at the University of Strathclyde, as well as for their continued support in conducting my research.

I am grateful for the financial support provided by the Engineering and Physical Sciences Research Council (EPSRC).

References

1. S. Giannis, N. Salmeron-Perez, and N. Spetsieris. *Challenges in Realising Composite Liquid Hydrogen Cryogenic Storage: A Materials and Standards Perspective*. National Physical Laboratory, 2023.
2. B. Atli-Veltin. *Cryogenic performance of single polymer polypropylene composites*. *Cryogenics*, 90:86-95, 2018.
3. D. Chen, et al. *A Review of the Polymer for Cryogenic Application: Methods, Mechanisms and Perspectives*. *Polymers*, 13(3):320, 2021.
4. R.F. Minty, L. Yang, and J.L. Thomason. *The dependence of interfacial shear strength on temperature and matrix chemistry in glass fibre epoxy composites*. *Composites Part A: Applied Science and Manufacturing*, 164:107303, 2023.
5. C. Hastings and J. Schneider. *Cryogenic temperature effects on the mechanical properties of carbon and synthetic fibers*. In *International SAMPE Technical Conference*, 2007.
6. S. Sethi and B.C. Ray. *Mechanical Behavior of Polymer Composites at Cryogenic Temperatures*. In *Polymers at Cryogenic Temperatures*, Springer Berlin Heidelberg, 59-113, 2013.
7. M. Dyess, et al. *A Systematic Approach to Cryogenic COPV Design*. In *52nd International SAMPE Symposium*, 3-7, 2007.
8. R. Noorda, et al. *Development of COPV's for High Pressure, In-Space, Cryogenic Fuel Storage*. *Sampe Journal*, 44:6-14, 2008.
9. A. Bersani, et al. *Long term elongation of Kevlar-49 single fiber at low temperature*. *Cryogenics*, 54:50-53, 2013.

10. F.R. Jones and N.T. Huff. *The structure and properties of glass fibers*. In *Handbook of Properties of Textile and Technical Fibres (Second Edition)*, Woodhead Publishing, 774, 2018.
11. C.G. Sreenivasa and A.G. Joshi. *Influence of Cryogenic Treatment on Mechanical Behavior of Glass Fiber-Reinforced Plastic Composite Laminate*. In *Polymers at Cryogenic Temperatures*, Springer Berlin Heidelberg, 191-195, 2013.
12. Z. Sápi and R. Butler. *Properties of cryogenic and low temperature composite materials – A review*. *Cryogenics*, 111:103190, 2020.
13. Y. Zhang, et al. *Tensile and interfacial properties of polyacrylonitrile-based carbon fiber after different cryogenic treated condition*. *Composites Part B: Engineering*, 99:358-365, 2016.