CRYOGENIC TEMPERATURE EFFECTS ON THE MECHANICAL PROPERTIES
OF CARBON, ARAMID, AND PBO FIBERS

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This study examines the effects of cryogenic temperatures on the mechanical properties of carbon, aramid, and poly(p-phenylene-2, 6-benzobisoxazole) (PBO) fibers. Although the mechanical properties are documented for these fibers at ambient and elevated temperatures, there is an absence of data in the open literature for how these fibers behave at very low temperatures. To evaluate the mechanical properties, the ASTM standard method for testing at ambient temperature was used as a baseline. The low temperature tests were conducted inside a double walled cryogenic chamber to evaluate the fiber performance at 100K. Fiber properties at low temperatures displayed differences from room temperature properties in the form of increased ultimate tensile strength (UTS), decreased in elongation to failure, and increased Young’s Modulus. The change in properties due to the effect of temperature was more pronounced in fibers with a higher degree of crystallinity.
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CHAPTER 1
INTRODUCTION

Carbon and synthetic fibers are used in the production of continuous fiber reinforced polymeric composites. These structures are designed so that the load is carried by the continuous fibers. The role of the polymer matrix is to transfer this load between the fibers and provide protection from the operating environment. Depending on the particular application of the composite, the fibers are commonly selected based on either high modulus, or high tensile strength, or a combination of the two. Because there are many applications with different structural needs, there is a large assortment of fibers with their own unique mechanical properties. Although many applications for continuous fiber reinforced polymers are at room temperature (298K), there is also increased interest for these materials at cryogenic temperatures (<123K) [1]. An application for components at these temperatures is composite overwrapped pressure vessels (COPV). These vessels are used to store a variety of liquids such as: liquid hydrogen (LH₂) at 20K, liquid nitrogen (LN₂) at 77K, liquid oxygen (LOX) at 90K, and liquefied natural gas at 109K. All of which fall in the cryogenic temperature range. Thus the properties of both matrix and fibers as a function of temperature are required by design engineers to characterize the behavior of polymeric composites at the various operational conditions.

This research evaluates the effects of temperature on the mechanical properties of three different categories of structural fibers: carbon, aramid, and poly(p-phenylene-2, 6-
benzobisoxazole) or PBO. Properties were measured with uniaxial tensile tests for each of the four fibers; T1000 [2] (carbon), IM7 [3] (carbon), Kevlar® 49 [4] (aramid), and Zylon AS [5] (PBO). Two types of carbon fiber were selected to evaluate the response of different microstructures to cryogenic temperatures. The tensile testing was conducted at two temperatures, ambient (298K) and cryogenic (100K). The initial ambient tests were conducted and the results compared with the published vendor properties to validate the test procedures. Then each fiber type was tested at cryogenic temperature (100K). A comparison was made between the data sets to determine the effects of cryogenic temperature. In addition, the microstructure of each fiber was characterized using X-ray diffraction (XRD) to determine the degree of the crystallinity of the microstructure for correlation with the trends in mechanical behavior as a function of temperature.

An overview of the microstructure of the three types of fibers and reported ambient temperature mechanical properties are discussed in Chapter 2. It was found that fibers with higher percentages of crystallinity will experience an increase in the elastic modulus as the unit cell contracts. Less of a change was found in fibers with a higher amorphous content. The change in properties is due to the fact that the atoms move closer together within the crystal structure, improving properties. Fibers with a higher percent of crystallinity will have more atoms moving closer together, thus the properties will be more affected than a fiber with less crystallinity.

Chapter 3 summarizes the single fiber/filament tension test procedure used to determine the fiber’s mechanical properties at ambient and cryogenic temperatures.
Chapter 4 discusses the experimental results from this study, with a summary in Chapter 5.
CHAPTER 2
MECHANICAL PROPERTIES OF STRUCTURAL FIBERS

2.1 Carbon Fiber

Carbon fiber is typically produced from by one of two precursors; pitch-based or Polyacrylonitrile (PAN)-based. While pitch-based fibers manufactured from petroleum asphaltene or coal tar, display a high Young’s Modulus, the lower ultimate tensile strength (UTS) makes them less desirable in structural applications [6]. PAN-based carbon fibers display a higher UTS along with a high Young’s Modulus and are therefore the most commonly used in high strength structural fiber-reinforced composites. Two PAN-based vendor products are evaluated in this study.

PAN is a copolymer created primarily from the monomer acrylonitrile (AN) with about 6-9% of other monomers. The AN repeating unit, illustrated in Figure 2.1, is [(CH$_2$CHCN)$_n$] [7].

![Chemical Structure of Acrylonitrile (AN) - Figure 2.1](image)

Chemical Structure of Acrylonitrile (AN)
Free radical polymerization occurs to form the PAN precursor from the AN. This is done via a process called wet-spinning illustrated in Figure 2.2. During this process a solution consisting of 10-30%, by weight, of the PAN copolymer is dissolved into solvents such as sodium thiocyanate, nitric acid, or dimethylacetamide. This solution is pumped through a filter to remove contaminants. From the filter, the solution then is extruded through spinnerettes creating numerous PAN fibrils. By passing through the capillaries of the spinnerette, the solidifying polymer orients chains parallel to the direction of the longitudinal axis of the fibril, the direction of flow. They are then drawn from the spinnerette into a coagulation bath containing various solutions. These solutions help prevent entanglement of the polymer, increase orientation, and help prevent contamination reducing fiber defects. The fibrils then undergo a stretching process in which the orientations of the chains are further enhanced. The stretching process also assists in producing adequate mechanical properties in the final carbon fiber [8].

At this point PAN is still a linear polymer that must undergo a stabilization process to insure that the orientation of the fibril microstructure remains intact during the
higher temperatures of the carbonization process. During stabilization, the structures in the fibrils are cross-linked to create a type of ladder structure. The fibers are subjected to an oxidation process in which they are heated in air to temperatures reaching 400°C [9]. The incorporation of oxygen molecules from the air causes a rearrangement of the carbon atoms in the microstructure. During this step, cyclization and dehydrogenation also take place. To restrict relaxation of the structure, tension is applied to the strands. The cyclization process is highly exothermic as the double bond of a nitrile group is formed from the triple bond. The nitrogen of the nitrile group bonds with the carbon forming a closed ring structure as illustrated in Figure 2.3 [6].

![Figure 2.3](image)

**Figure 2.3**

Bonding of Nitrogen to form a Closed Ring Structure

Cyclization is conducted to ensure a slow release of heat that prevents disorientation and possible melting within the structure of the fiber. Because loss of orientation in the fiber structure has a large effect on the UTS and modulus of the final fiber, this step is carefully controlled to ensure optimal mechanical properties.

Stabilization is considered the most important step in the manufacturing process because it determines the final structure of the fiber, which in turn affects the ultimate mechanical properties [10, 11, and 12].
Once the fibers are stabilized and capable of withstanding higher temperatures, they are subjected to a process known as carbonization. Here, the fibers are heated to temperatures between 1,000 - 1,500°C [6]. When the fibers are heated they lose their non-carbon atoms forming various volatile gases during expulsion. Due to the loss of these atoms, the mass of the fibers is decreased from 55-60% with a corresponding reduction in fiber diameter [10]. The wet-spun fiber has diameter of ~35 microns, with the final fiber diameter ranging from 5-10 microns. After the excess atoms are removed from the fiber, the remaining carbon atoms form tightly bonded carbon crystals. These crystals are in the form of well-defined hexagonal networks as shown in Figure 2.4.

![Figure 2.4](image)

**Figure 2.4**

Carbonized Hexagonal Networks

Typically in commercial processes, the fibers are carbonized at ~1000°C and then heat treated at ~1300°C to produce high strength fibers [6]. The temperature of the heat treatment plays an enormous role in the balance between high UTS and high Young’s Modulus of the carbon fiber. A lower heat treatment temperature means that some of the hexagonal networks are still mingled together resulting in an amorphous structure, while higher temperatures cause the sheets of hexagonal unit cells to unravel. The closer to
2000°C that the fibers are heated, the lower the atomic ratios of nitrogen to carbon, and this ratio has been inversely linked to tensile strength [9]. Heating above 2000°C reduces the nitrogen to carbon ratios, but increases the fibers modulus. The reduction in UTS due to this phenomenon can be minimized by applying tension during heat treatment [10]. As the heat treatment temperature increases, the fiber becomes more graphitic, more crystalline, and more brittle. The unit cell of graphite is shown in figure 2.5

Figure 2.5
Graphite Unit Cell [13]

Thus, the mechanical properties of carbon fibers are determined throughout the manufacturing process in which the microstructure evolution is controlled. The mechanical properties are determined by three factors; orientation, crystallinity, and defects [9].

The degree of orientation in the fiber refers to how well the graphite layer planes are in alignment with the longitudinal axis of the fiber. Corresponding to an increase in orientation of the layer planes is a reported increase in the modulus [13]. As the increase
in orientation increases the Young’s Modulus, a corresponding decrease is also observed in the UTS [9].

Crystallinity in the fiber is a combination of the size and shape of the crystallites as well as the crystalline perfection. The theoretical parallel spacing between graphite layer planes is 3.35 Angstoms. How closely packed the layers in the fiber become is referred to as degree of crystalline perfection. In addition to orientation, Young’s modulus is also related to crystallite size (Lc and La) and crystallite shape (La/Lc), where Lc is the crystallite thickness and La is the length parallel to the fiber axis [14]. And like orientation, crystallinity also affects longitudinal tensile UTS. As crystallinity increases, the tensile modulus increases while tensile UTS decreases due to the degree of graphitization as the fiber become more brittle. As the carbon turns more and more to graphite, the basal planes within the microstructure becomes less entangled and are able to slip past one another more easily. This is because the covalent bonding between atoms in the hexagonal arrays is strong, while the secondary van der Waals bonds between the graphite layers is weak. To ensure some degree of ductility, carbon fiber can only be at a maximum of 50% crystalline. For the fiber to be able to bend and be flexible, random amorphous regions are needed throughout the structure. Figure 2.6 illustrates semi-crystallinity with the outer layers being oriented, while the inner layers are more entangled.
Defects in the fiber also have a strong impact on the UTS of the fiber. Contaminants in the polymer get trapped with the networks and then are vaporized due to the high temperatures of the various processes creating voids. The effect on UTS does not result because of the voids created by the flaws, but rather to crack propagation from extensive crystalline walls around the defects which are created from catalytic graphitization [13]. Defects in the fiber can be controlled by reducing impurities in the precursor and prevention of contamination throughout the manufacturing process.

### 2.2 Aramid Fiber

Aramid fiber is another name for aromatic polyamide fibers. Kevlar fibers fall in the aramid category due to the fact that the repeating unit in its polymer chain is an aromatic polyamide [15] whose repeating unit is shown in Figure 2.7.

---

Figure 2.6

Representation of PAN-based Fiber Structure [13]
The backbone of this chemical structure is the benzene ring \( [\text{C}_6\text{H}_6] \). This is a compound formed from a ring of carbon atoms that have alternating double and single bonds. Because of the para-orientation of the ring, the structure of the polymer chain is very rigid and rod-like. These chains form sheets that are held together in the transverse direction by hydrogen bonds as shown in Figure 2.8. These sheets coincide with the ‘y’ and ‘z’ directions (or ‘b’ and ‘c’ lattice parameters) of the fiber crystalline structure similar to a monoclinic unit cell [16].

The manufacturing process of these fibers begins with the synthesis of the liquid crystal polymer poly(p-phenylene terephthalamide) (PPTA). This is a compound made
from the monomers para-phenylenediamine and terephthaloyl chloride. The filaments are formed by spinning the polymer through spinnerettes. When the polymer solution is passed through the spinnerettes, the resulting shear forces acting on them cause the rigid rod-like chains to fully orient in the direction of the shear. This gives the fiber randomly oriented domains of highly oriented polymer chains. Due to slow relaxation, the molecular structure is almost completely preserved in the as-spun fiber [4]. The as-spun fibers are also subjected to stretching, which results in even greater chain orientation along the fiber axis enhancing the tensile properties. This stretching process is described in terms of draw ratio, or ratio of initial diameter to final diameter. Increasing the draw ratio gives the fibers a higher degree of alignment and a higher degree of crystallinity [17]. The percentage of crystallinity and the crystal structure parameters have been linked to the fiber’s mechanical properties. It has been reported that increases in crystallinity and ‘z’ axis (or ‘c’ lattice) spacing correlate to an increasing Young’s modulus with corresponding decreases in UTS and strain to failure [16].

### 2.3 PBO Fiber

Poly(p-phenylene-2, 6-benzobisoxazole) fiber, or PBO, is a high strength high modulus fiber that goes under the trade name Zylon. Like Kevlar, PBO is also a rigid rod isotropic crystalline polymer. PBO is synthesized from 2,5-diamino-1,3-benzenediol (DABDO) and terephthalic acid (TA) [18] shown in Figure 2.9.
After dissolving the PBO into poly(phosphoric acid) (PPA) to polymerize, the liquid crystal polymer solution is then spun by a process called dry jet-wet spinning. The polymer passes through a spinnerette into air and then into a coagulation bath. The conditions of this coagulation bath can greatly affect the fiber’s structure. After the fiber is washed and dried, it is heat-treated under tension. High molecular orientation, and ultimately modulus, is dependent on this step. The structural model of PBO can be found in Figure 2.10.
Although the fibers do contain defects such as chain ends, chain bends, and voids, they exhibit a high degree of order and orientation. The degree of crystallinity of PBO fibers can approach 100%. Like Kevlar, the crystal structure of these fibers has been determined to be monoclinic [18] as shown in Figure 2.11.
The tensile properties of these fibers depend heavily on polymeric molecular weight, manufacturing techniques, as well as post-processing conditions [21]. The unit cell dimensions for the ‘c’ lattice parameter have been found to increase with heat-treatment. This suggests that because the improved properties correlate with post-processing parameters, such as heat treatment temperature and amount of tension applied, that properties will be dependent on crystal size and degree of crystallinity [21].
CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Test Sample Preparation

Tensile tests were conducted on single, visibly undamaged fibers extracted at random from the fiber tow and secured to a piece of cardstock. Figure 3.1 illustrates the cardstock mounting tab with dimensions recommended by ASTM D 3379-75 [22]. A 25.4mm gage length was used which was within the ASTM guidelines of 20 to 30mm.

![Typical Single-filament Mounting Method][22]

Figure 3.1

Typical Single-filament Mounting Method [22]

Once the single fiber was extracted, it was centered over the tab slot of the mounting tab and secured with Loctite® “6-minute” epoxy. The epoxy was allowed to cure fully for at ambient conditions.
3.2 Fiber Diameter Measurement

3.2.1 Measurements Using Optical Microscopy

Individual fiber diameters were measured along the longitudinal direction and digitally recorded using a Leica DMI 5000M optical microscope OM. Measurements were made in Image-Pro Express [23] to determine the fiber diameter. A total of 12 measurements were taken for each fiber sample and the mean calculated for each type of fiber.

To ensure that the fiber’s sizing did not affect fiber diameter readings, T1000 fibers were impregnated into a matrix of Epon 828 which was metallographically prepared. The cross-sectional area of the composite was photographed and measurements recorded.

3.2.2 Measurements Using Scanning Electron Microscopy

Because of the resolution concern for the micron range diameter fibers, scanning electron microscopy (SEM) measurements were also recorded. Three to four fibers from each category were mounted to stubs using double sided carbon tape. Multiple measurements were taken for each fiber and averaged. Measurement accuracy was calibrated prior to use using the SEM Magnification Standard Reference Material 484a [24]. Resolution of this standard is 0.083 µm. Because of low electrical conductivity, resulting in charging effects from the uncoated fibers, accurate dimensions of Kevlar and Zylon specimens could not be obtained.
3.3 Ambient Tensile Testing

The fiber tensile test procedure at ambient temperature was in accordance with ASTM standard D 3379-75 [22]. Tensile testing was conducted using an Instron model 5869 EM load frame with a 50N load cell. The load cell was electronically calibrated before each test session. Because the fiber specimens were fragile, the use of a strain gage or extensometer was impractical and the strain was obtained from the cross-head displacement assuming the 10kip load frame machine compliance was negligible. For ambient temperature tests, the specimen was placed in single fiber grips mounted to the load frame as illustrated in Figure 3.2. The sides of the mounting tab were cut away prior to the test to allow the uniaxial load to be passed through the single fiber. The load and displacement were zeroed prior to each test. Tests were conducted at a constant cross-head speed of 0.254mm/min to provide specimen fracture within 1 minute per ASTM D3379-75 [22].
3.4 Cryogenic Temperature Testing

Because no standard test method was found for testing single fibers at low temperatures, the test standard for ambient temperature was used as a baseline to evaluate the effects of cryogenic temperature. Testing the single fiber directly in a LN$_2$ bath was not possible due to the small loads and displacements required to fracture the specimen. As the LN$_2$ was introduced into the round cryostat, the boiling effect, which occurs when LN$_2$ reaches room temperature, causes loads sufficient to fracture the delicate fiber [25]. To alleviate this, a dual-walled cryostat was constructed as shown in Figure 3.3. The specimen is placed inside the inner chamber of the cryostat while the outer chamber is filled with LN$_2$. This provides a test atmosphere for the fiber of 100 +/- 5K as measured with a type K thermocouple.
After the LN$_2$ was introduced into the outer cylinder of the cryostat, a 15 minute hold time was used to ensure thermal equilibrium for the environment. The load and displacement were set to zero prior to the start of the test. The cross-head speed was identical to the cross-head speed applied in ambient temperature testing.

3.5 Data Reduction Methodology

3.5.1 Ultimate Tensile Stress Calculation

A typical load versus displacement curve is presented in Figure 3.4. The UTS for each specimen was calculated using equation (3-1) based on the maximum measured load (F). This load was divided by the area (A), which was calculated using the vendor’s reported fiber diameter.
Due to the delicate nature of the fiber, no preload was applied prior to initiation of the test.

### 3.5.2 % Strain to Failure Calculation

The cross-head displacement was recorded from the load frame displacement normalized to the initial gage length to determine strain as shown in equation 3.2.

\[
\varepsilon = \frac{\Delta L}{L} \quad (3-2)
\]

Where \( \Delta L \) represents displacement with specimen slack removed and zeroed and \( L \) represents initial gage length. The point of strain at fiber fracture determined the % strain to failure.
3.5.3 Modulus Calculation

Machine compliance was neglected in calculating modulus, and the cross-head displacement was used in equation (3-3).

\[ E = \frac{\sigma}{\varepsilon} \]  \hfill (3-3)

Where \( \sigma \) represents the normalized force applied to the fiber (3-1) and \( \varepsilon \) represents the resulting normalized elongation (3-2). The reported secant modulus was graphically obtained for each tested sample by measuring the slope of the stress vs. strain curve. The range used was consistent within a given type of fiber tested, but varied from data set to data set.

3.5.4 Determination of Valid Data Points

The number of samples tested was in accordance with the design basis B set forth by MIL-HDBK-17-F [26]. The handbook specifies 18 “good” data points to be averaged for each fiber property (UTS, % strain to failure, and Young’s Modulus) at both ambient and cryogenic temperatures. Values for each property were averaged with the mean for each sample defined in equation (3-4).

\[ X_{bar} := \frac{1}{N} \left( \sum_{i} X_i \right) \]  \hfill (3-4)

Where \( X_{bar} \) is the mean, \( N \) is the total number of data points for a given test, and \( X_i \) is the individual property reading.

\[ S_X := \left[ \frac{1}{N-1} \sum_{i} (X_i - X_{bar})^2 \right]^{1/2} \]  \hfill (3-5)
Where $S_x$ is the standard deviation, $N$ is the number of specimens tested, $X_i$ is the individual reading, and $X_{\text{bar}}$ is the property sample mean.

Outliers in the sample populations were excluded and mean and sample deviations were recalculated. Validity of “good” data points were determined by Chauvenet’s criterion for rejecting a reading, which gives a specific deviation limit for a number of data points tested [27].

### 3.6 X-Ray Diffraction

To characterize fiber crystallinity, XRD was used as suggested by the MIL-Standard Handbook [27]. The measurements were made using a Rigaku Ultima III X-ray diffraction system with a graphite monochromator and Cu-\(k\alpha\) X-rays. Double sided cellophane tape was applied to the glass specimen slides and a tow of each fiber type was wrapped around to obtain complete coverage of the slide. The fibers were aligned at 0° and 90° in relation to the beam source direction for the T1000 fibers. Because no difference in data was found between the 0° and 90° orientations, a 90° relative orientation was used for all fibers investigated. This is illustrated in Figure 3.5. A step scan was made with a step width of 0.4° and a dwell of 10 seconds over a 2θ scan range of 3-59°. 2θ being the angle that the x-ray beam is rotated about the specimen. The range of the Ultima III is 3° - 156°.
Figure 3.5

(a) Fiber Sample (b) Sample Mounted into Ultima III
Table 4.1 summarizes the measured fiber diameters. The values for these diameters were found to be different than the values reported by the vendor. This is because fiber diameter is not physically measured by vendors, rather an estimation of cross-sectional area of a tow is calculated from the yield of sample tows and tow density and a fiber diameter extracted. The resolution of the optical microscopy (OM) images is limited by the 300-700nm wavelength of visible light. Thus the optical resolution of structural features is in the range of 0.6-1.4\(\mu\)m [6, 26]. Higher resolution images can be obtained using an SEM, although these did not differ greatly from the OM images. Similar diameters were obtained from the mounted and polished cross-sectional specimens which suggest the fiber sizing is not the cause of the discrepancy. It is not known how the combinations of amorphous and crystalline content affect the effective diameters.
Table 4.1

Fiber Diameter Comparisons

<table>
<thead>
<tr>
<th>Fiber ID</th>
<th>Vendor Diameter (µm)</th>
<th>Optical Microscope (µm)</th>
<th>T1000/Epon 828 (µm)</th>
<th>SEM (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1000GB [2]</td>
<td>5</td>
<td>5.5± 0.2</td>
<td>5.4 ± 0.4</td>
<td>5.5± 0.3</td>
</tr>
<tr>
<td>IM7 [3]</td>
<td>5.2</td>
<td>5.3± 0.1</td>
<td>NA</td>
<td>4.9 ± 0.1</td>
</tr>
<tr>
<td>Kevlar 49 [17]</td>
<td>12</td>
<td>12.6± 0.5</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Zylon AS [17]</td>
<td>12</td>
<td>11.9± 0.7</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

The differences in fiber diameter between measured and reported are less than 0.5µm. However, due to the small scale of these specimens, this difference results in very large differences in the calculated properties. Variations in diameter as small as 0.5µm can skew the modulus calculation by ~69GPa. Table 4.2 summarizes the published vendor data for the mechanical properties of each of the fibers included in this study. The vendors’ data were obtained using tow testing of fiber bundles that provides an effective diameter possibly related to percent crystallinity.

Table 4.2

Vendor Published Properties

<table>
<thead>
<tr>
<th>Fiber ID</th>
<th>UTS (MPa)</th>
<th>E (GPa)</th>
<th>ε failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1000Gb [6]</td>
<td>6370</td>
<td>294</td>
<td>2.2</td>
</tr>
<tr>
<td>IM7 [7]</td>
<td>5520</td>
<td>276</td>
<td>2.0</td>
</tr>
<tr>
<td>Kevlar 49 [17]</td>
<td>3000</td>
<td>112</td>
<td>2.4</td>
</tr>
<tr>
<td>Zylon AS [17]</td>
<td>5800</td>
<td>180</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Table 4.3

Single Fiber Properties at Ambient Temperature

<table>
<thead>
<tr>
<th>Fiber ID</th>
<th>UTS (MPa)</th>
<th>CV (%)</th>
<th>N</th>
<th>E (GPa)</th>
<th>CV (%)</th>
<th>N</th>
<th>E failure (%)</th>
<th>CV (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1000GB</td>
<td>5373 ± 1624</td>
<td>30.2</td>
<td>18</td>
<td>297 ± 24</td>
<td>8.1</td>
<td>18</td>
<td>2.34 ± 0.40</td>
<td>17.1</td>
<td>18</td>
</tr>
<tr>
<td>IM7</td>
<td>3501 ± 708</td>
<td>20.2</td>
<td>17</td>
<td>245 ± 21</td>
<td>8.6</td>
<td>17</td>
<td>1.50 ± 0.33</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>3347 ± 523</td>
<td>15.6</td>
<td>18</td>
<td>105 ± 10</td>
<td>9.5</td>
<td>18</td>
<td>3.59 ± 0.18</td>
<td>6.5</td>
<td>18</td>
</tr>
<tr>
<td>Zylon AS</td>
<td>2886 ± 861</td>
<td>29.8</td>
<td>18</td>
<td>148 ± 29</td>
<td>19.6</td>
<td>18</td>
<td>2.08 ± 0.53</td>
<td>25.5</td>
<td>18</td>
</tr>
</tbody>
</table>

*N=Number of data points

**CV=Coefficient of Variation

Table 4.3 summarizes the results from ambient temperature testing in this study performed on single fiber samples. This data is represented as the mean value with standard deviation. Close agreement between Young’s Modulus (E) values in Tables 4.2 and 4.3 were used to validate the testing method and data analysis techniques. Values between the vendor’s published data and this study are very similar for the modulus and elongation to failure. However, a large variation is noted in the UTS of the IM7 and Zylon fibers relative to the reported values.

Because the properties in Table 4.2 were obtained in single fiber tow testing, there are expected variations from Table 4.3 [22, 26]. Tow testing incorporates a twist of the fibers during testing, while single fiber testing has zero twist. It has been found that this twist factor plays a role in measuring UTS [5]. The less the twist applied to the fiber, the lower the measurement of UTS. This is because the twist incorporates an internal friction within the tow. This friction allows the load to be distributed along every fiber, thus normalizing the stress among the weaker and strong fibers. This could be the reason in part for differences in UTS for vendor vs. ambient temperature data.
The results from fiber tensile testing at cryogenic temperatures are shown in Table 4.4. The behavior of the synthetic fibers at different temperatures was interesting compared to reported high temperature studies of Kevlar 49 and Zylon in which the fibers demonstrated a tendency to be temperature sensitive with decreasing properties as the temperature increased. The UTS of Kevlar 49 is reported to decrease by approximately 16%, 42% and 71% at higher temperatures of 423K, 523K and 623K respectively [28].

The UTS of Zylon is reported to decrease by a range of 10% to 75% at higher temperatures of 473K to 673K respectively with thermal exposure time [5]. From the measured data it would appear that low temperatures have the opposite effect on the Zylon fibers and carbon fibers, where these fibers displayed an increase in UTS at low temperature. Kevlar fibers, however, saw a slight decrease in UTS. In this study, the UTS at lower temperatures increased in Zylon AS 42.9% while decreasing 5.4% in Kevlar 49. This suggests that scaling properties from high to low temperatures is not always linear. In comparison, both carbon fibers showed an increase in UTS of 27.7% and 4.6% for the T1000 and IM7 fibers, respectively.

Table 4.4

Single Fiber Properties at Cryogenic Temperature

<table>
<thead>
<tr>
<th>Fiber ID</th>
<th>UTS (MPa)</th>
<th>CV (%)</th>
<th>N</th>
<th>E (GPa)</th>
<th>CV (%)</th>
<th>N</th>
<th>ε_failure (%)</th>
<th>CV (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1000GB</td>
<td>6682 ± 1251</td>
<td>18.2</td>
<td>18</td>
<td>321 ± 24</td>
<td>7.5</td>
<td>18</td>
<td>2.21 ± 0.44</td>
<td>19.9</td>
<td>18</td>
</tr>
<tr>
<td>IM7</td>
<td>3662 ± 744</td>
<td>20.3</td>
<td>18</td>
<td>264 ± 23</td>
<td>8.7</td>
<td>18</td>
<td>1.50 ± 0.33</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>3176 ± 603</td>
<td>19</td>
<td>18</td>
<td>112 ± 19</td>
<td>17</td>
<td>18</td>
<td>2.80 ± 0.33</td>
<td>11.8</td>
<td>18</td>
</tr>
<tr>
<td>Zylon AS</td>
<td>4124 ± 1380</td>
<td>33.5</td>
<td>18</td>
<td>139 ± 27</td>
<td>19.4</td>
<td>18</td>
<td>3.79 ± 0.98</td>
<td>25.9</td>
<td>18</td>
</tr>
</tbody>
</table>

*N=Number of data points  
**CV=Coefficient of Variation
Figure 4.1, 4.2, and 4.3 provide a graphic comparison of the effects of temperature on the fiber UTS, % strain to failure, and modulus respectively. Similar increases in properties were found in T1000, IM7, and Zylon. Only the Kevlar 49 exhibited a decrease in UTS and strain to failure at cryogenic temperature.

Figure 4.1
Comparison of Fiber UTS between Ambient and Cryogenic Temperature
Comparison of Fiber Elongation between Ambient and Cryogenic Temperature

Comparison of Fiber Elastic Modulus between Ambient and Cryogenic Temperature
While strain to failure mirrored the trends of the UTS, the modulus for each type of fiber did not as shown in Figure 4.3. The carbon fiber (T1000GB, IM7) modulus increased by amounts of 8.1% and 7.8% respectively. But the synthetic fibers (Kevlar 49, Zylon AS) modulus showed the opposite. The modulus calculated for Kevlar 49 actually increased by 6.7%. The modulus for Zylon AS, on the other hand, showed a decrease of 6.5%. The drop in Zylon modulus at 100K could be the result of the high strain to failure at 100K. There is no data suggesting that the strain to failure would increase or decrease at lower temperatures, but the amount shown at 100K is suspiciously high. The reason for this high increase in strain to failure could be something physical in the testing procedure, such as the fiber sliding out the epoxy or “slip”. A way to verify that this is the cause of the abnormally large increase would be to use different epoxies to anchor the fiber to the mounting tab. The difference in fiber/matrix adhesion should result in more or less slippage, verifying that slip was causing the distortion of data.

Looking at the data gathered from the X-ray diffraction analysis run on each of the fibers, an explanation of the changes in properties can be related to the extent of crystallinity in the fibers. The comparison of the carbon fibers can be found in Figure 4.4, while data for Kevlar and Zylon are shown in Figures 4.5 and 4.6 respectively.
Figure 4.4
X-Ray Diffraction Data for Carbon Fibers T1000 and IM7

Figure 4.5
X-Ray Diffraction Data for Kevlar 49
Chapter 2 discussed the three factors that determined a fiber’s strength; orientation, crystallinity, and defects. Only one of these factors, crystallinity, would be expected to be affected by temperature. As the temperature of the material lowers, the atoms within each crystalline unit cell move closer together. Since modulus is governed by spacing of these atoms, the closer the atoms, the higher the modulus. So, if a fiber is more crystalline than another, its modulus would be affected to a greater degree. A change in modulus for the T1000 samples was more evident than was the IM7 samples. This difference can be explained by the x-ray diffraction data. From Figure 4.4 it can be seen that the angle of 2θ (between 20° and 30°) in which the peak for the two carbon fibers are about equal. This means that the d-spacing or inter-planar spacing of the fibers are about equal, although the intensity for the fibers is different though. The intensity for T1000 fibers is higher than the IM7 fibers. This means the T1000 fibers have a higher percentage of crystallinity due to the fact that is more crystals in the fiber structure to reflect the x-ray beam. Difference of crystallinity between the fibers can be estimated by

Figure 4.6

X-Ray Diffraction Data for Zylon AS
calculating the areas underneath the peak for each fiber. Using these calculations, we see that the T1000 fibers are more crystalline than the IM7 by 62.0%.

Kevlar and Zylon both see a double peak at 20-25°. Intensity for these peaks was about equal, suggesting that the percentage of crystallinity for the two fibers is about equal. From the peaks, Kevlar is showing to have a greater d-spacing (lower 2 theta value) than the Zylon, giving it a lower modulus. This trend matches vendor and experimental data. However the 100K tensile data doesn’t match expected trend. Since the crystallinity for the two fibers are approximately equal, the behavior of the fibers at 100K should be similar. This was found not to be true since UTS for Zylon increase and Kevlar decreased. Changes in Young’s Modulus for the two fibers differed as well with Kevlar increasing and Zylon decreasing. The difference in Young’s Modulus could be attributed to the extreme increase in strain to failure at 100K in Zylon. This large increase of strain to failure at 100K for Zylon is thought to due to slippage of the fiber in the epoxy during testing.
CHAPTER 5
CONCLUSIONS AND FUTURE WORK

As the need for composites at cryogenic temperatures increases, the behavior and understanding of the composites’ constituents at these temperatures is required. It was found that the various commercial fibers respond differently to temperature changes, such as increases or decreases in properties such as UTS, % strain to failure, and Young’s Modulus. Thus, it cannot be generalized that the mechanical properties of either specific carbon or synthetic fibers will react to temperature change in the same manner. Although there were evident changes in the previously mentioned properties in both carbon fibers tested, the magnitude of change varied. This varying in magnitude, coupled with the x-ray data gathered for the fibers clearly suggest that the percentage of crystallinity of a carbon fiber determines the amount of which its properties will change as a result of temperature. Also, data within the aramid and PBO fibers responded in opposite trends, with certain Kevlar 49 properties decreasing or increasing while the same properties in Zylon showed the opposite for the same properties. Problems with the Zylon fiber test procedure resulted in suspicions of the Zylon data. Thus, the data between Kevlar and Zylon cannot be accurately compared.

With this study as a starting point, an extensive database of various fibers and their mechanical properties at cryogenic temperatures will be constructed to give design engineers the proper tools needed to create structures suitable for any environment, as
well as give insight into proper fiber/resin choices. With the knowledge of how the fibers
and resins behave as a result of temperature change, properties such as % strain to failure
can give designers the knowledge to optimally choose right materials. This test bed can
also serves as a method to evaluate other environmental effects such as irradiation to
evaluate the fibers for in-space applications.

Future studies will address the effect of radiation on the properties of each of the
different fiber types as well. With the data gathered from this study coupled with
radiation effects, a good understanding will be given to how different types of structural
fibers will react in a space environment.
BIBLIOGRAPHY


