SHORT CARBON-FIBER-REINFORCED PEEK COMPOSITE CHARACTERIZATION FOR THE SIMULATION OF 3D PRINTED HONEYCOMB SANDWICH PANELS

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ABSTRACT

The purpose of this study is characterization of 3D printable material called PEEK (polyetheretherketone) containing 20% of short carbon fiber reinforcement. The presence of short carbon fibers in the filament causes significant anisotropy since the fibers contribute more to the mechanical properties in the direction of the filament path. This study evaluates the results of tension, compression and shear tests conducted in the three principal directions (X, Y and Z where fiber direction is Y and printing layer direction is Z) to determine fiber impact on mechanical properties. Tensile data for PEEK and reinforced PEEK exists for specimens using alternating (+45/-45) degree layers, but no data is present for properties in any other directions. This data will be implemented to verify that specimens used in this study are made with acceptable quality. A set of +/- 45 degree specimens will be tested in prior to X,Y,Z tests and printing parameters will be modified until the +/-45 degree specimens demonstrate tensile behavior consistent with the data present in literature.

This preliminary step revealed multiple issues that arise during additive manufacturing of reinforced polymers. The initial tensile data, namely axial stress at failure, was significantly lower than reference values (about 46%) and evaluation of the microstructure (via CT and SEM imaging) showed multiple types of defects. Before proceeding with the rest of characterization testing, this study will examine how the multiple parameters that can be modified during additive manufacturing impact fabrication of reinforced polymers.

1 INTRODUCTION

Countries around the world are preparing to send people to the Moon, which will then serve as a stepping stone to go to Mars. One of the main challenges of lunar exploration is dealing with the effects of large temperature variations to which equipment is subjected. Temperature rapidly drops from 100 ˚C to -200 ˚C as lunar night falls, and the night lasts two Earth weeks. The focus of the project is to design the structure of a lunar rover able to withstand this harsh environment. The specific objective of this research project is to investigate the structural performance of a thermoplastic sandwich composite made by 3D printing. Polyetheretherketone (PEEK) reinforced by short carbon fibers (SCFs) is a 3D printable composite with properties that make it viable for the rover frame due its excellent thermal insulation properties and the possibility to forego a mix of adhesives and resins, which inevitably leads to coefficient of thermal expansion mismatch, thanks to 3D printing.

As there is no possibility of implementing upgrades on a structure once it is launched, it is imperative to test the structure in all foreseeable conditions. However, it is impossible to simultaneously reproduce low gravity (usually done in a pool, with a heavy fluid surrounding the structure) and vacuum, which prescribes an absence of all fluids. For this reason, reliable simulations are extremely important. While more traditional composites have been sent in space and there is some heritage regarding their behavior, 3D printed polymers do not benefit from that heritage. Moreover, their structural properties are highly dependent on the printing parameters. It is therefore extremely important to have reliable simulations of the 3D printed material to allow its use on a space mission.

Prior to simulation, mechanical testing is conducted to characterize SCF reinforced PEEK by experimentally establishing its material properties. During fused filament fabrication (FFF), the polymer filament is melted and extruded in a specific path that allows a gradual fabrication of a shape one layer at a time. Due to the nature of this fabrication method, a perfectly monolithic structure cannot be created. As can be seen in Figure 1, continuous extrusion of polymer creates voids between different layers of the structure. As a result, even when the structure is printed at 100% infill, it is not truly monolithic nor is it homogeneous. For this reason, behavior displayed during in plane compression (along the fiber orientation) and out of plane compression (perpendicular to fiber orientation) will be different. Same is true for tensile and shear properties. This anisotropy becomes much more impactful when the material has reinforcement additives (such as carbon fiber or glass fiber).

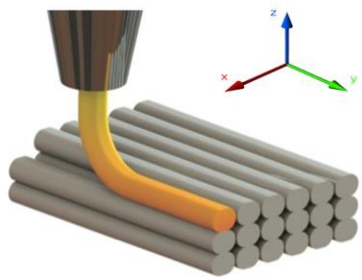

Figure 1. FFF fabrication of a specimen where all filament is aligned [1]

In Figure 1, all filament paths point in the Y direction. Therefore, the Y direction is referred to as the 0^o direction. Consequentially, the X axis corresponds to the 90^o direction and the Z axis is the out-of-plane direction. It is assumed that Y direction will benefit more from the carbon fiber reinforcement than X and Z (since X and Z are only as strong as the polymer to polymer fusion between filament passes).

2 EXPERIMENTAL METHODS

2.1 Material

Material used in this study is PEEK reinforced by 20% short carbon fibers (SCF or CF). The material is supplied by 3DXTECH who claim an ultimate tensile strength of 126 MPa and a tensile modulus of 10.1 GPa [2]. For comparison Table 1, also provides properties for pure PEEK without carbon fibers [3] and PEEK with 10% carbon fiber content [4].

Table 1. Mechanical properties of PEEK and reinforced PEEK supplied by 3DXTECH (±45º raster orientation)[2]–[4]

Property	Pure PEEK	PEEK 10% CF	PEEK 20% CF
Ultimate Tensile Strength [MPa]	100	105	126
Modulus of Elasticity [Gpa]	3.72	8.1	10.1
Elongation at break [%]	28	3	1.9
Flexural Strength [Mpa]	130	136	145
Flexural Modulus {Gpa]	2.7	8.3	11.2

As can be seen from the properties, increasing the carbon fiber content increases strength (in tension and flexion) and also makes the material stiffer. Prior to fabrication, the material undergoes a dehydration procedure to eliminate printing defects caused by moisture evaporating from the filament during heating.

2.2 Processing

Two series of specimens were printed. The first series of specimens were printed on an AON 3D printer. Parameters were selected based on recommendations provided by 3DXTECH for PEEK with 20% CF [2]. On their website, the company makes suggestions for nozzle, bed, and air temperatures as well as the minimum optimal nozzle diameter. However, 3DXTECH does not specify a suggested print speed. Therefore, a speed was selected based on what was considered a reasonable printing time. The summary of print settings is listed in Table 2.

Table 2. Printing Parameters for the first set of specimens

Parameter	Value
Nozzle Temperature	415 °C
Bed Temperature	140 °C
Air Temperature	120 °C
Nozzle Size	0.6 mm
Layer Hight	0.25 mm
Print Speed	60 mm/s

As will be discussed in the result section, the quality of the first batch of specimen was not satisfactory (Tensile stress at failure was lower than anticipated). Therefore, additional specimens were printed using different parameters and a different printer.

The new specimens were manufactured on an APIUM P220 printer which is designed specifically for high temperature polymers like PEEK. The print speed was reduced to 25mm/s. In addition, the following changes were implemented to improve the quality of the specimens.

- Brim around the dogbone to prevent thermal warping (see Figure 2)
- Perimeter layer to avoid stress concentrations (see Figure 2)
- Reduction in print speed (from 60 mm/s to 25 mm/s, see Table 3)
- Increase in print temperature (from 420°C to 485°C, see Table 3)
- Change form Type II to Type I dogbone to increase the cross-section area of the neck

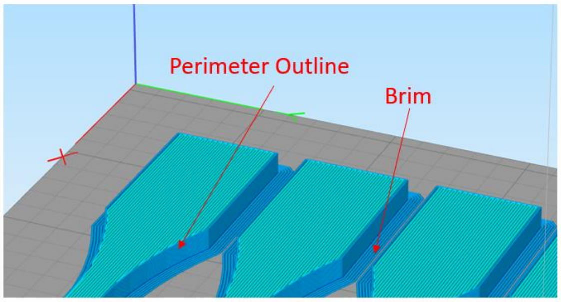

Figure 2: Simplify3D representation of brim and perimeter (or 'wall') outline features

Table 3. Printing parameters for the second set of tests

Parameter	Value
Nozzle Temperature	485 °C
Bed Temperature	130 °C
Air Temperature	N/A
Nozzle Size	0.4mm
Layer Hight	0.2mm
Print Speed	25mm/s

2.3 Mechanical testing and analysis

Tensile tests were performed according to the ASTM standard D638 [5]. The test speed was adjusted so that failure occurs within 3min to 5min. A Digital Image Correlation (DIC) system called ARAMIS is used to create a virtual mesh over the specimen and track deformation at every element of that mesh. This enables detection of any stress concentrations (which might be a sign of an early failure due to a structural defect) and accurately measures the stress-strain data of the tests. After testing, computed tomography (CT) scan and scanning electron microscope images were taken to study the microstructure of the specimens.

3 RESULTS

3.1 Results for the first set of specimens

3.1.1 Tensile test results

Tensile tests were done using a Type II dogbone specimens. The specimens were tested in tension with the direction of filament orientation being orthogonal to direction of loading (referred to as 90° specimens). It is expected that, since all filaments and fibers are orthogonal to the loading, the specimen will only be as strong as the PEEK bond between the filament paths. The results are presented in Figure 3.

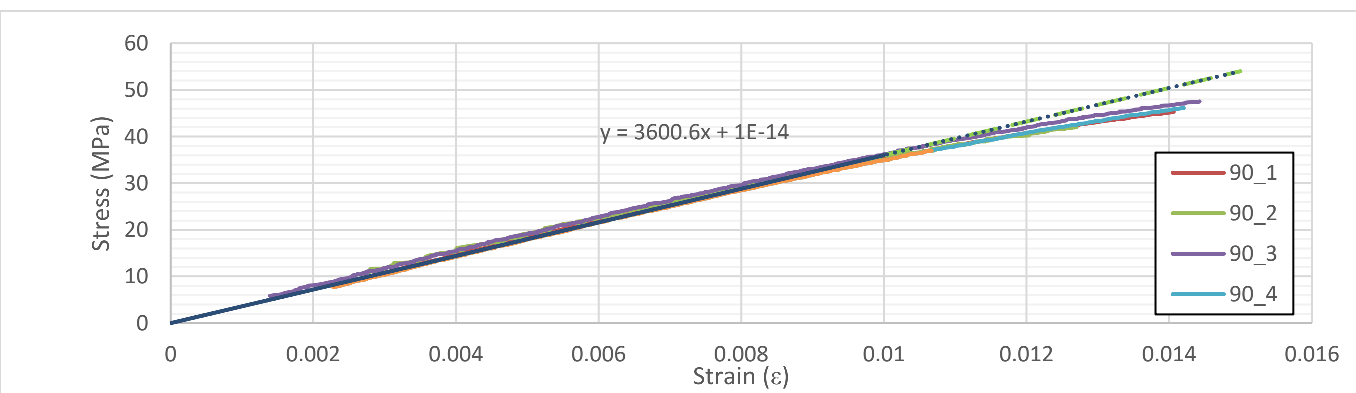

Figure 3. Axial Stress vs Strain Curve for 90 degree specimens.

The stress-strain curves show that failure occurred at a low stress of around 46 MPa (when pure PEEK should have failed at 100 MPa in ±45°orientation). However, the results are very consistent since all specimens failed at the same load level. The elastic modulus is measured to be 3.6 GPa. This is close to the value of pure PEEK (3.72 GPa according to data presented in Table 1). The strain at failure of 1.4 % is reasonable since PEEK with 20% carbon fiber is expected to have a failure strain of 1.9 % when the filament is oriented in a ±45° stack (see Table 1).

Next, a set of tests was conducted with specimens having the same ±45° raster orientation as the tests used for the data sheets by 3DXTECH. If the results for these tests are similar to values provided by 3DXTECH, it will demonstrate that the quality of fabrication is appropriate. A set of five Type II dogbones were used for this test. The results are indicated in Figure 4.

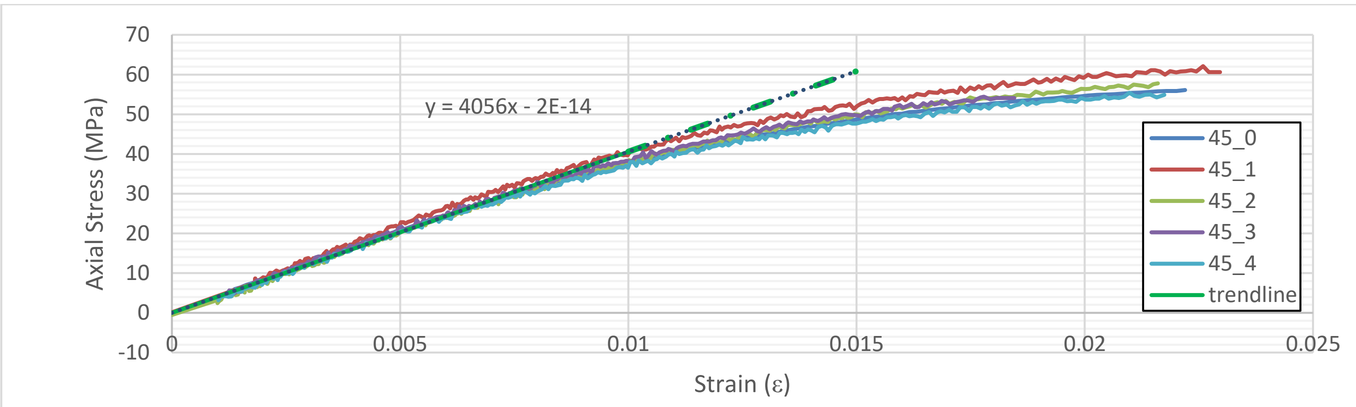

Figure 4. Axial Stress vs Strain Curve for +/-45 degree specimens.

The axial stress data has proven to greatly differ from the reference values provided by 3DXTECH, as can be seen in Figure 4. The specimens broke at around 55 MPa when they were supposed to withstand up to 120MPa. Also, the specimens were supposed to have a modulus of elasticity of around 10.1 GPa, not 4.01 GPa.

Such low values suggest that there are defects in the structure. So, it is possible that the fibers are not contributing effectively due to some defects.

3.1.2 Microstructure

SEM imaging was performed on the specimens. Specimens at raster orientation of 0°, 90° and ±45° were examined. The results can be seen in Figure 5.

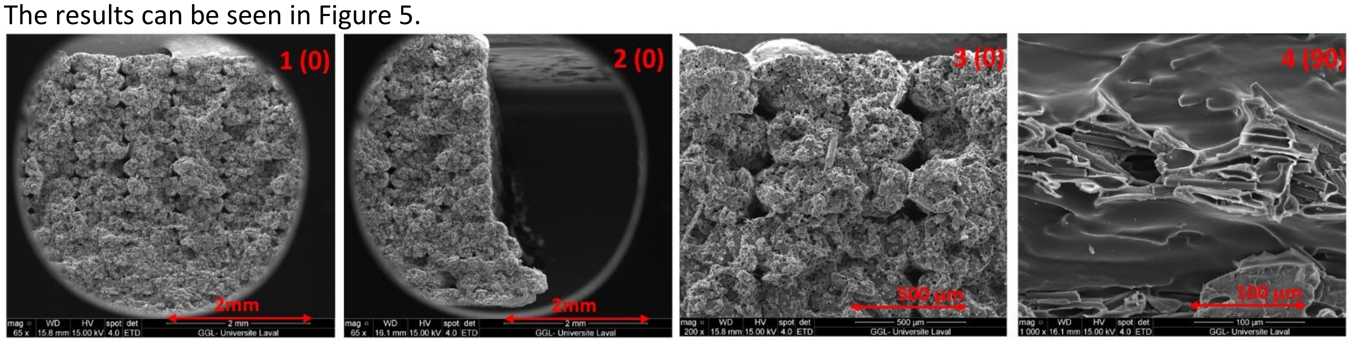

Figure 5. SEM results for 0° specimen (subfigure 1, 2, 3) and 90° specimen (subfigure 4).

From the SEM images, it can be seen that there are large porosities within the structure both between the filament paths and also within the filament. As can be seen in the Figure 5.1, the number of porosities between filament paths increases as layers progress higher (so layers that were deposited further from the heated print bed during fabrication). It is possible that the heat from the build plate aids with avoiding porosity by affecting the cooling rate of the filament, but this needs to be verified.

Tomography of one of the ±45° specimens was done to study the internal microstructure. The image provided in Figure 6 shows the results (the color coding was inverted for visibility, so white is solid and black is air). The cross-section image was taken far from the fracture site to avoid misrepresentation of the microstructure by including defects caused by the failure.

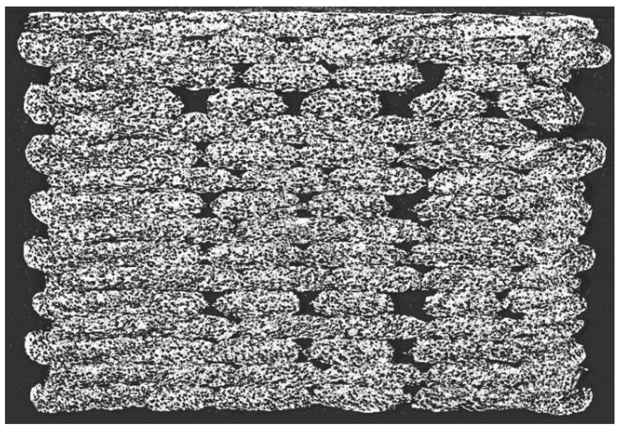

Figure 6. CT scan of +/- 45° specimen

The CT scan showed large gaps between the filament passes. These gaps made the bonding within the layer ineffective and contributed to an early failure. In addition, a large number of micro defects was observed within each filament pass (indicated by the small black specks in the image).

3.1.3 Discussion

The tensile testing data was significantly lower than the reference values provided by the manufacturing company. The material has a stiffness that is consistent with PEEK without carbon fiber reinforcement. The printing parameters used for fabrication were consistent with manufacturing requirements. The main parameter that was not mentioned is the print speed. Review of literature was done to examine printing parameters used in other studies.

A study conducted by Rinaldi et al. [6] looked at structural properties of non reinforced PEEK printed at different orientations and infill layers. For the XY test (same filament orientation setup as for the +/-45 degree test), they have measured the modulus of elasticity and ultimate stress for 100%, 50% and 20% infill. The results were E=3.98 GPa, stress=98.9MPa (100% infill), E=2.27 GPa, stress=68.5MPa (50% infill) and E=2.29 GPa, stress=60.6MPa (20% infill). Therefore, the study was able to recreate the modulus of elasticity and ultimate strength that was stated by 3DXTECH.

Since they were able to get the same values for the XY test as 3DXTECH, it is important to determine what was different between their study and this one. In [6], they explained that the specimens were printed using a nozzle diameter of 0,4 mm, a building platform temperature of 100 °C and a nozzle temperature of 400 °C. The printing speed was set to 20 mm/s. Therefore, aside from slightly lower temperature, the key difference in the manufacturing was printing speed. The samples were printed 3 times slower (60mm/s vs 20mm/s).

Another study by Wang et al. [7] looked at the effects of nozzle temperature, platform temperature, printing speed, and layer thickness. The study looked at a range of printing speeds between 5mm/s and 25mm/s and established that the tensile strength of the print decreases greatly with increase in print speed. The study only explores the range of speeds between 5mm/s and 25mm/s. It can be assumed that the reduced rigidity and tensile strength become worse and greatly impact the print quality at the speed of 60mm/s. Although this study demonstrates the relationship between print speed and tensile strength, it should be noted that even at a very slow print speed of 5mm/min, both pure PEEK and reinforced PEEK were not even able to achieve the ultimate tensile strength of 100MPa.

Based on the literature discussed in this section, it appears that reducing the speed of fabrication should improve the specimen quality. This was done for the manufacturing of the second batch of specimens.

3.2 Results of the second set of specimens

3.2.1 Tensile test results

Tensile testing was done using the same setup as for the first attempt. Type I dogbones were tested in tension until failure. Contrary to expectations, the stress-strain curve of the new specimens was very similar to that of the first set of coupons. Figure 7 shows the stress-strain curves of the old and the new specimens.

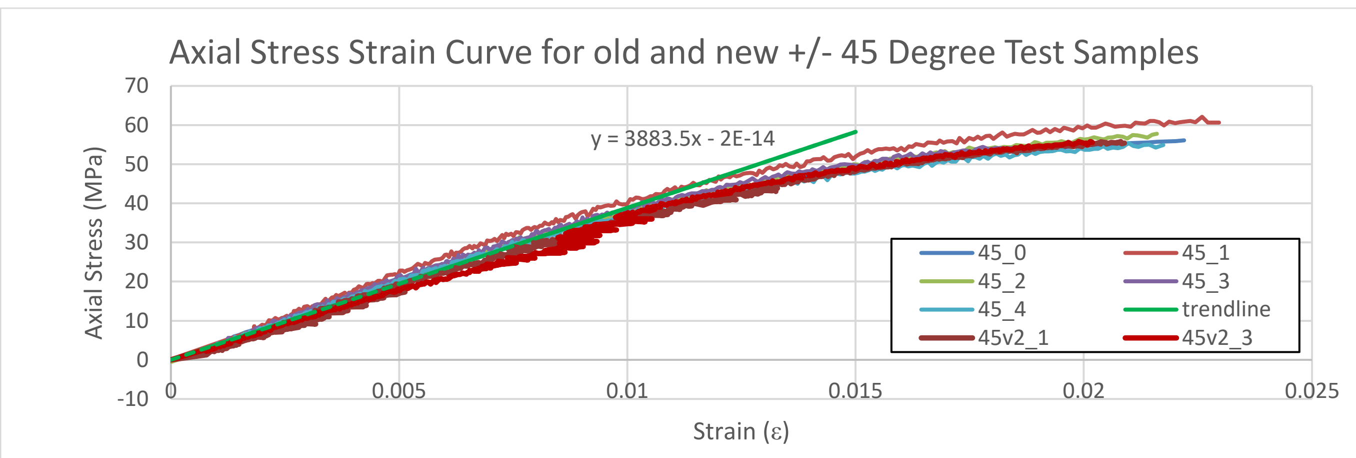

Figure 7: Axial Stress vs Strain Curve for +/-45 degree specimens for old and new coupons (labelled as "45v2")

As can be seen in Figure 7, the new specimens follow the same curve with the key difference being a slightly lower elongation at failure. Also, the modulus of elasticity for the elastic region reduced slightly (from 4.0 GPa to 3.9 GPa) although the change is too small to be significant.

3.2.2 Microstructure

CT scans were done to study the microstructure of the new specimens and attempt to discover what caused the lack of improvement in tensile strength and rigidity. Tomography scan showed a significant improvement in the uniformity of the microstructure, as can be seen in Figure 8.

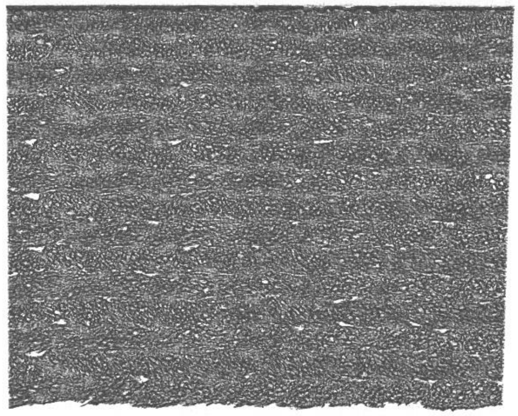

Figure 8: CT scan of the second fabrication attempt of the +/- 45 degree specimen

Gaps between filament passes that were very dominant in the first attempt have been eliminated. It appears that the increased nozzle temperature as well as the contribution from the heat plate improved the bonding of filament passes. However, there still appears to be some porosity evenly distributed within the structure (white dots on the CT scan). To assess the amount of mass loss, three different masses of the specimens were compared. First was the theoretical mass of the specimen if it was cast and had a completely monolithic structure (calculated as a product between density of the reinforced PEEK and volume of the 5 dogbones). Second mass was taken from the g-code generator, Simplify3D, which calculated the predicted mass of plastic consumption for the print. The third mass was the actual mass of the specimens after fabrication. The three masses are presented in Table 4.

Table 4. Mass analysis of the reinforced PEEK specimens

Mass Type	Source	Mass of 5 dogbones
Theoretical, 100% density	Density Calculation	67.62g
Theoretical, expected print mass	Simplify3D	64.70g
Actual coupon mass	Measurement	49.07g

Based on the masses listed in Table 4, the actual mass was only 72.5% of what it should have been at perfect density, and 75.8% of the mass predicted by the 3D printing software. Therefore, despite the improvement of the fabrication process, the prints have between 24.2% - 27.5% air. Future effort will be focused understanding and eliminating the causes that contribute to these air pockets.

3.2.3 Discussion

A study conducted by Sommacal et al. [8] studied porosity that occurred when printing with PEEK that has 30% of carbon fiber reinforcement. The study looked at how parameters like nozzle size and layer height impacted the generation of porosities. Although some parameters marginally reduced the amount of porosity, all specimens had between 15.8% and 22% of voids. The changes in parameters that seemed to aid in reduction of porosity were: increasing nozzle size, reducing layer height and increasing the amount extrusion per travel distance. However, the study discovered that even the original filament that was supplied to them by the manufacturer had 19.9% percent porosity.

Porosity seems to be caused specifically by the presence of carbon fibers. A study by Hu et al. [9] examined properties of pure PEEK, PEEK with 2% CF content, and PEEK with 5% CF content. It was discovered that increasing the amount of carbon fiber in the filament created more porosity. Additionally, the study established that excessive carbon fiber content diminished mechanical properties. The results of the study showed that the specimens with 5% content had a smaller ultimate tensile strength than both pure PEEK and PEEK reinforced by 2% CF.

Initially it was assumed that maybe the excessive temperature of 485 ^{o}C contributed to the porosity. However, many studies show that PEEK does not begin to degrade at this temperature. One of these studies, conducted by Kumar et al. [10] shows that PEEK with 20% CF content does not begin to degrade until 515 ^{o}C and at 519 ^{o}C it will only lose 5% of its mass. For pure PEEK these temperatures are even higher.

Increased printing temperature, reduced printing speed, and contribution of the heating plate above the printing surface is expected to help removing the porosities between filament passes. The printing parameters for the second attempt is summarized in Table 3.

4 FUTURE WORK

Considering the results obtained during testing and findings of research studies referenced in this report, the following steps will be taken in the future. First, a tomography scan will be done of the initial filament to determine the level of porosity in the stock material. Second, specimens will be printed using pure PEEK to confirm that these defects occur as a result of carbon fiber content. Third, if it is confirmed that the fibers are causing the porosity, fabrication will be attempted again using a wider nozzle, smaller layer height and higher extrusion scaling factor (as suggested by Sommacal et al. [8] in their study.

5 CONCLUSION

In conclusion, the initial tests showed that mechanical properties for composite polymers fabricated using FFF greatly depend on the printing parameters. This resulted in difficulties when attempting to reproduce specimens of satisfactory quality even when all manufacturer requirements are followed. Tensile tests, SEM, and CT scanning showed that it is difficult to avoid porosity and defects in the microstructure which adversely affect the mechanical properties of the material. Further research revealed some parameters that might improve the quality of the microstructure and these clues will guide future work. It is of paramount importance to establish what parameters decrease the quality of the microstructure in order to produce specimens of consistent quality. After this issue is resolved, characterization will continue in pursuit of the initial goal of characterizing and simulating the behavior of honeycomb panels made from PEEK reinforced with short carbon fibers using additive manufacturing.

6 ACKNOWLEDGMENTS

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