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Exploration of Additively manufactured Microcellular PLA

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Abstract

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This thesis investigates the 3D printing of Polylactic Acid (PLA) using CO₂-saturated filament, comparing it with the solid-state microcellular foaming process. The study examines the impact of various 3D printer nozzle temperatures (180°C to 210°C) and CO₂ saturation pressures (1 MPa to 4 MPa) on the mechanical properties of PLA. The study reveals that when PLA sheets are 3D printed and undergoes the solid-state foaming process, we see porous structure with decent reduction in relative density and tensile strength but with a very high strain to failure performance. Whereas, when saturated PLA filament is used to 3D print specimens, all the gas escapes when the PLA melts and only a fraction of gas is present at atmospheric pressure which results in a very low porosity (void structure of ~10%). Additionally, higher saturation pressures enhance gas uptake but result in crystallization. Tensile tests show a 10-15MPa reduction in tensile strength when compared to untreated 3D printed dogbone samples of tensile strength ~50MPa. These findings contribute to understanding the limitations and potential improvements in the mechanical properties of 3D printed PLA for industrial applications.

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Chapter 1.0 Introduction:

The innovation of infusing plastics with bubbles to create microcellular structures originated in the 1980s. This technology, initially applied to polystyrene using nitrogen gas to instigate the nucleation of bubbles, marked a significant progression in the field of material science. The foundational work of Professor Nam P. Suh in examining this technology through the lens of process design and manufacturing heralded a new chapter in polymer processing. Subsequent research has explored this technology across various polymers, primarily thermoplastics, for diverse practical applications.

In the realm of Polycarbonate (PC), profound insights into the influence of process parameters on microcellular foams were contributed by Professor Vipin Kumar along with John Weller. The fabrication of microcellular foams encompasses a two-step methodology. Initially, a polymer sample is placed within a pressurized environment and permeated with a high-pressure gas. Upon reaching a state of gas saturation, the specimen is then subjected to a thermal process. It is heated to a critical threshold, proximate to the polymer's glass transition temperature, initiating the formation of a multitude of bubbles that result in a microcellular structure. This phenomenon is driven by the instability caused by a sudden decrease in gas solubility upon heating the gas-saturated polymer, compelling bubble nucleation. As this transformation transpires while the polymer is in a solid state, this method is referred to as the "solid-state process."

The solid-state process has been effectively applied to an array of amorphous and semi-crystalline thermoplastics, including PVC, ABS, PET, PETG, and CPET. The burgeoning interest in this technology is largely attributed to its capacity to diminish the requisite amount of plastic, primarily in thin-walled packaging, by decreasing the polymer density. Recent advancements have facilitated the reduction of cell sizes significantly, achieving dimensions near 100 nanometers and the creation of nanofoams in various polymer types utilizing the solid-state process at sub-room temperatures.

Building on the existing framework of microcellular foams, this investigation pivots towards a novel application of this technology in the realm of additive manufacturing. Specifically, the focus is directed at the polymer Polylactic Acid (PLA), which is processed through a 3D printer. In this unique approach, the 3D printer acts as a conduit for melting the PLA filament across a spectrum of temperatures, ranging from 210°C to 180°C. This study meticulously examines how variations in the 3D printing parameters influence the ductility and toughness of the printed type 4 dogbone specimens. The research aims to discern the implications of the 3D printing environment on the material properties of PLA, thereby expanding the potential of microcellular foams in advanced manufacturing techniques.

1.1 Goals and Motivation:

The primary objective of this project was to explore and evaluate the feasibility of a novel method for foaming Polylactic Acid (PLA) through 3D printing. This innovative approach offers a significant advantage over traditional solid-state foaming processes, such as those using water baths, by allowing precise control over the geometry of the foamed specimen. This capability to tailor the specimen's shape and structure is essential for advancing applications in additive manufacturing where complex and customized designs are increasingly demanded.

A critical aspect of this study was the detailed examination of how varying 3D printing parameters, particularly the extrusion temperatures, influence the ductility and toughness of PLA. The experimental range spanned from 220°C to 180°C, carefully chosen to observe the material behavior under different thermal conditions. It was observed during the experiments that temperatures below 180°C are impractical for this process. Specifically, at temperatures approaching the melting point of PLA at 175°C, the polymer fails to maintain a molten state necessary for printing and does not adhere to the print bed, thus impeding the printing process.

To comprehensively investigate these parameters, four distinct extrusion temperatures—220°C, 200°C, 190°C, and 180°C—were meticulously tested. Additionally, CO₂ gas pressures of 1 MPa, 3 MPa, and 4 MPa were applied to study their effects on the foaming process. The pressures of 1 MPa and 4 MPa were evaluated using traditional solid-state methods, while a unique study was conducted at 3 MPa to understand the prolonged desorption characteristics of PLA over a month-long period.

This prolonged desorption study involved initially 3D printing PLA samples immediately after saturation and subsequently printing additional samples weekly for four weeks. This approach enabled the observation of changes in the material's mechanical properties and microstructure over time. Type 4 dogbone specimens were printed at each stage, and their tensile strengths were rigorously tested. Additionally, Scanning Electron Microscopy (SEM) was employed to analyze the microstructural changes in the PLA samples from each desorption phase, providing detailed insights into the effects of gas saturation and the 3D printing process on the material's properties.

The goal of this project extends beyond simply testing a new method; it aims to contribute significant advancements in the understanding of PLA's behavior under various manufacturing conditions. By exploring these detailed parameters and their impacts, this research seeks to enhance the utility and performance of PLA in diverse applications, pushing the boundaries of what can be achieved with 3D printing technology in polymer engineering.

Chapter 2.0 Process Space Exploration:

2.0 Introduction

This chapter delves into the process space exploration for foaming Poly(lactic acid) (PLA) using both 3D printing and traditional solid-state processes. The goal is to understand the impact of various parameters, such as pressure, temperature, and process techniques, on the material properties, particularly the ductility and toughness of PLA. The experiments were conducted at the University of Washington, with detailed observations and results presented below.

2.1 University of Washington PLA Samples

2.1.1 Experimental Setup

The PLA samples were 3D printed using a PRUSA Mark 3 FDM 3D printer, with PLA filament provided by PRUSA. Samples for density measurement and SEM micrographs were prepared with dimensions of 25.4 mm x 25.4 mm and a thickness of 1 mm. These samples were then placed inside a pressure vessel designed for a maximum pressure of 6 MPa.

The process parameters for the 3D printer were as follows:

- **Layer Thickness:** 0.2 mm
- **Filament Diameter:** 1.75 mm
- **Nozzle Temperature:** 210-180°C
- **Bed Temperature:** 65°C

The solid-state foaming process parameters included:

- **Pressures Explored:** 1, 1.5, 2, 2.5, 3, and 4 MPa
- Switched from Synthetic Oil Bath to Water for Solid-State Foaming due to PLA's Porous Nature
- **Water Bath Foaming Temperature:** 50-110°C

2.1.2 Gas Sorption Experiments

The gas sorption behavior was studied at different pressures to understand the saturation kinetics and ultimate gas uptake by the PLA samples.

1 MPa:

- The gas concentration reached a plateau at around 1.5% at about 24 hours, then increased to 2% by the end of 48-50 hours.

1.5 MPa:

- The gas concentration plateaued at around 2.75% at 24 hours and rose to 3.75% by 48-50 hours.

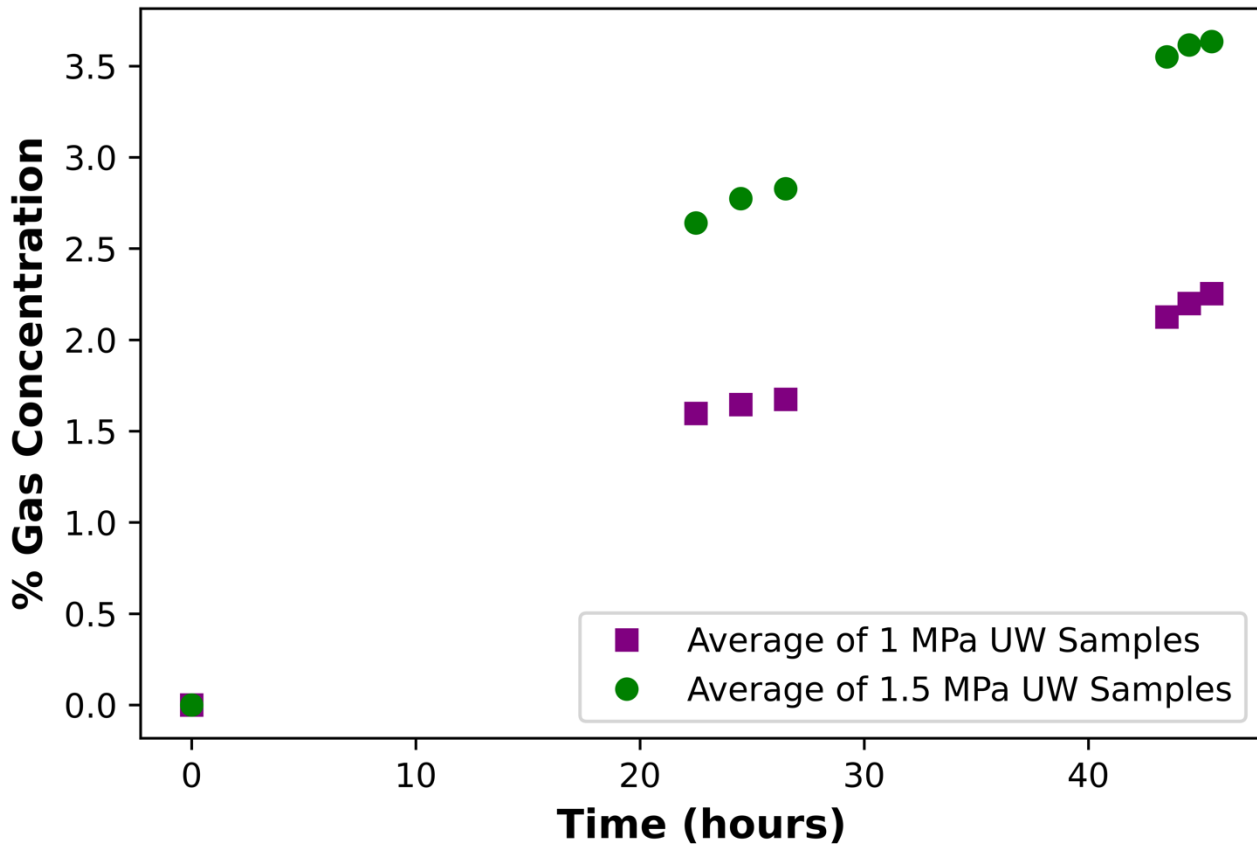


Figure 1: Gas Sorption Plot for 1 and 1.5MPa

3 MPa:

- In 2023, the gas concentration reached 8% at about 10 hours, peaked at 10% around 15 hours, and plateaued at 9% by 24 hours.
- In 2024, the concentration reached 12% in under 5 hours and plateaued at the same level by 24 hours.

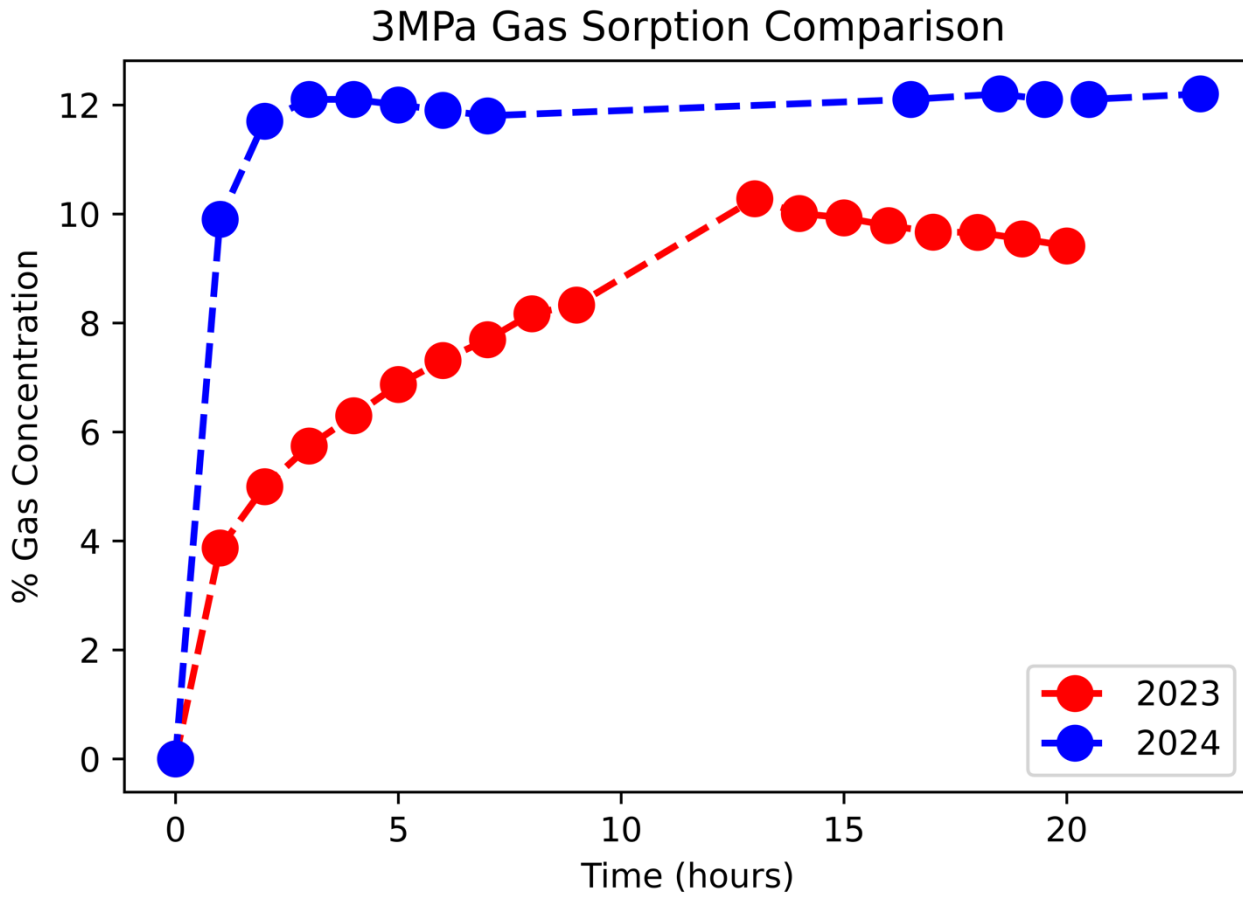


Figure 2: Gas Sorption Plot for 3MPa

4 MPa:

- The gas concentration reached 16% within 6 hours and rose to 17.5% by 24 hours, again corroborating with the anomalous behavior of PLA not following Henry's Law.

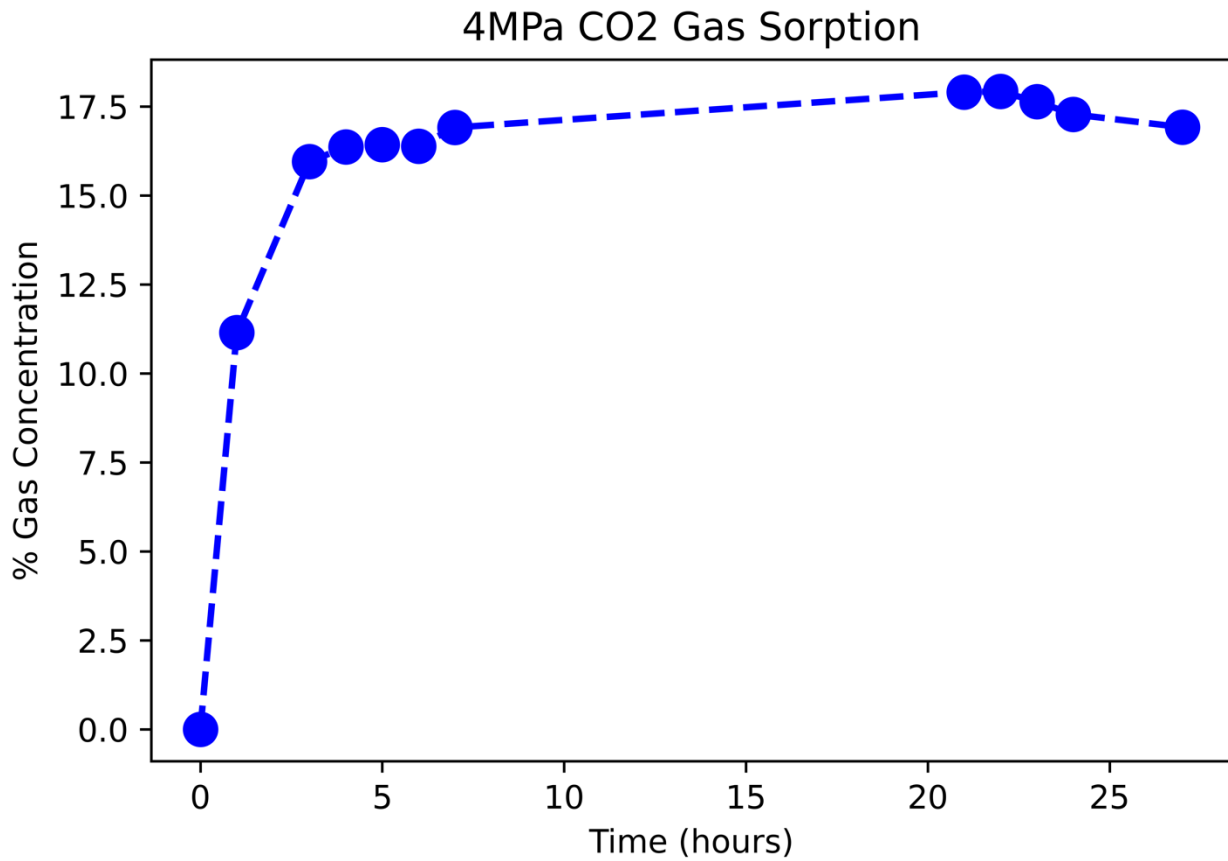


Figure 3: Gas Sorption Plot for 4MPa

2.2 Boston University PLA Experiments

Motivation and Background:

As a collaboration between Professor Vipin Kumar (University of Washington) and Professor Keith Brown (Boston University) a few preliminary experiments were performed on additively manufactured PLA (Polylactic Acid) to understand its behavior and properties after the Solid-State Process.

Sample Shape and Dimensions:

1. 25.4 x 25.4 x 1.14 mm (1" x 1" Square)
2. Flower

Process Space Experiments:

A. Solubility and Diffusivity Measurements:

Specimens of dimensions of 25.4 x 25.4 x 1.14 mm (1" x 1" Square) were cut out from a 100 x 100 mm sheet sent from Prof. Brown's lab (Boston University). These specimens were saturated at a specified saturation temperature and pressure respectively.

B. Foam sample preparation and characterization:

The 1" x 1" samples were saturated in a pressure vessel maintained at room temperature 25 °C for at least 48 hours. The specimens were saturated at each of the following saturation pressures: 1 MPa (145 psi), 1.5 MPa (218 psi), 2 MPa (290 psi) and 2.5 MPa (363 psi). After saturation at a given pressure, the samples were removed from the pressure vessel and allowed to desorb gas in a laboratory freezer to reduce the amount of gas loss. At the end of the desorption period, the samples were foamed in a synthetic oil bath for 30 seconds to create steady-state structure (i.e., all cell growth has stopped). The foaming temperatures and saturation pressures used in this experiment (conducted on January 4th, 2023) are shown in the table 1.

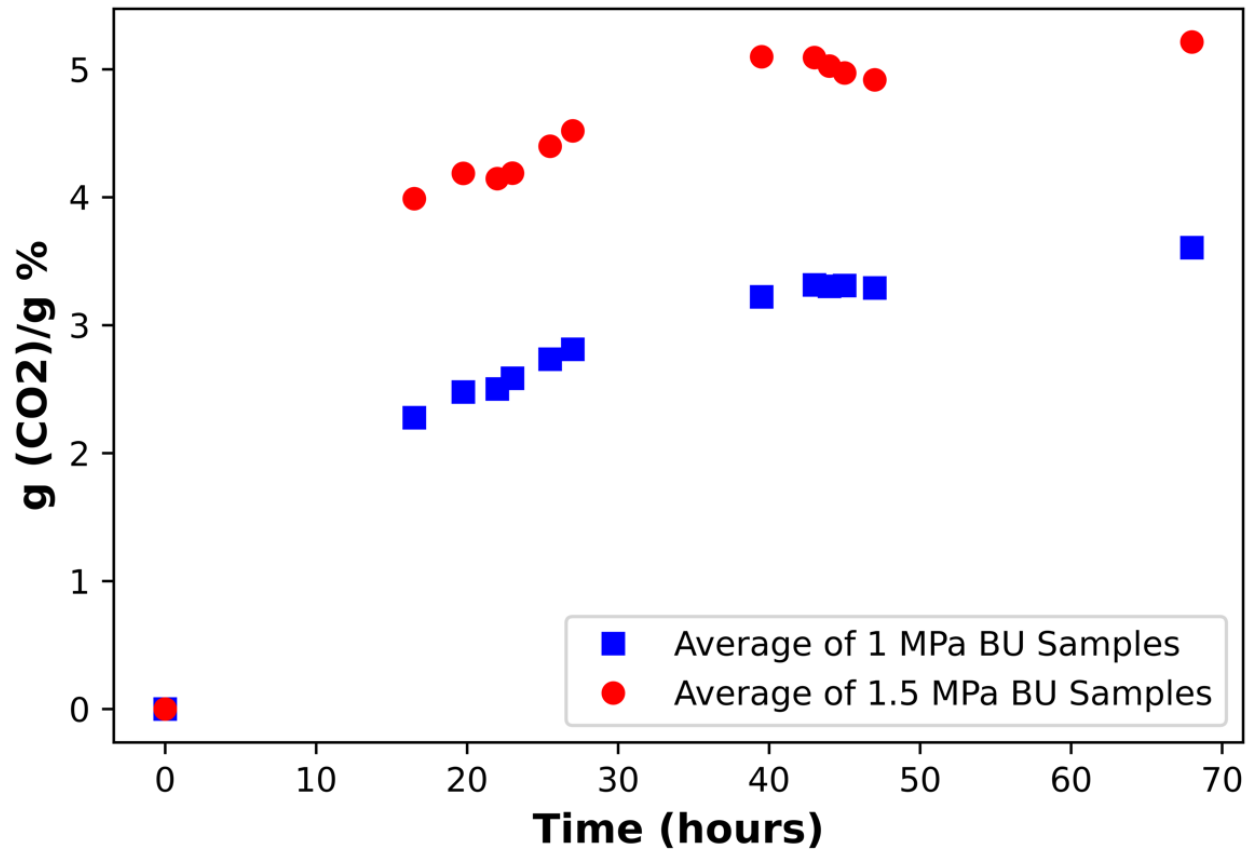


Figure 4: Sorption Plot for 1 And 1.5 MPa Boston University Samples

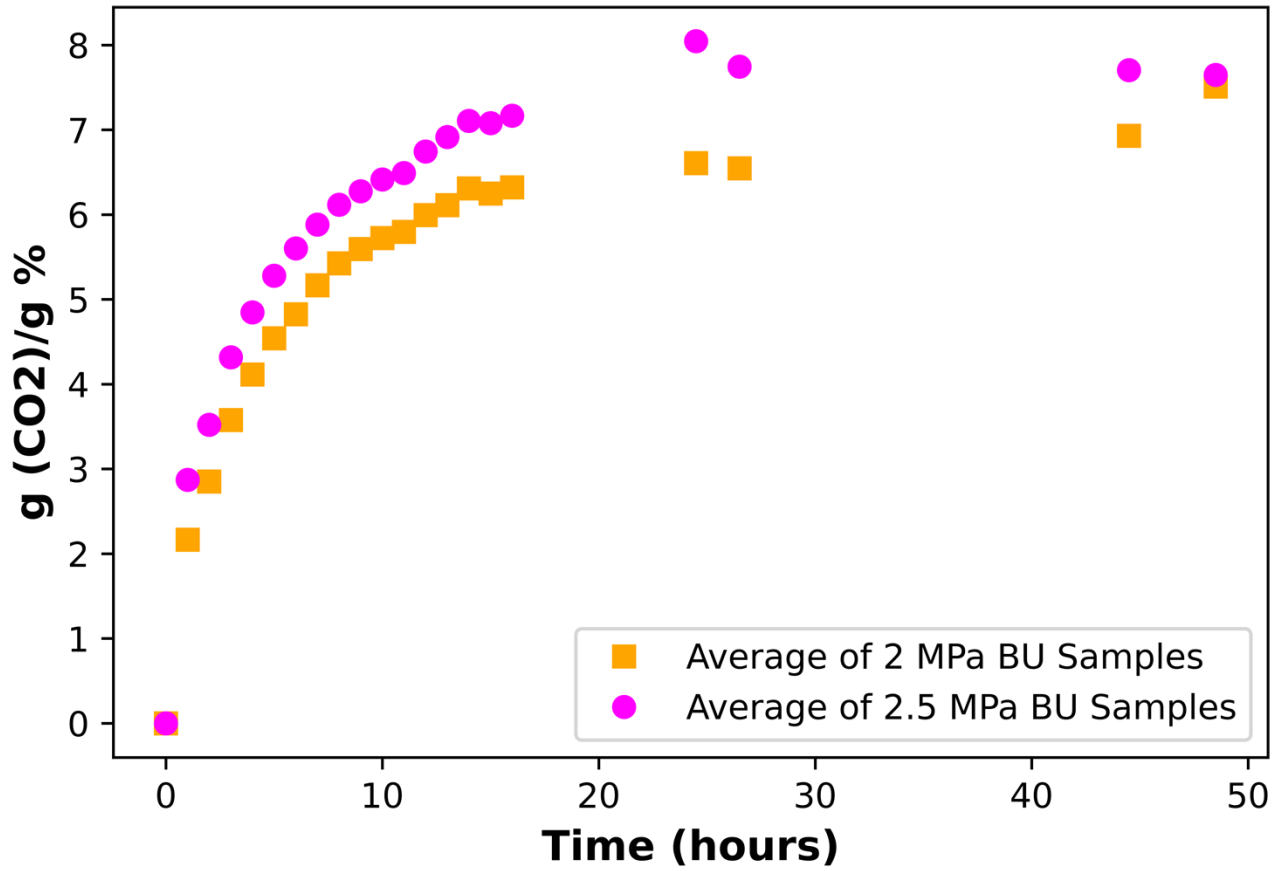


Figure 5: Sorption Plot for 2 And 2.5 MPa Boston University Samples

2.3 Results and Discussion

The results from the experiments conducted at various pressures provide insight into the gas sorption behavior of PLA and the relative density that was achieved by the solid-state foaming process influence of different processing parameters on the material's properties.

2.3.1 Relative Density and influence of Solid-State Foaming temperature on University of Washington PLA samples

The gas sorption and foaming temperature behavior was analyzed for various pressures, and the resultant relative densities were plotted to compare the gas uptake characteristics at different saturation conditions and how crystallinity effects the polymer's cell nucleation capabilities.

1 MPa:

- The 1MPa samples showed a relative density of 0.7968 at around 80°C and dropped to 0.656 at a foaming temperature of 90°C and the. Further dropped to 0.364 at 100°C. The lowest relative density achieved at 1MPa was reported to be 0.2504 at 110°C. Furthermore, at 120°C the relative density was 0.3456. After which the high temperature resulted in collapse of the microstructure which resulted in the increase of the relative density of the polymer back to 0.4248.

1.5 MPa:

- The gas concentration reached a stable plateau after approximately 24 hours for both 1 MPa and 1.5 MPa samples. This suggests a relatively predictable saturation behavior at these lower pressures resulting in a very linear drop in relative density from 0.794 at 80°C, 0.4104 at 90°C all the way to 0.1096 at 100°C. It was observed that going from 100°C to 130°C results in thermal degradation of the nucleated pores inside the polymer which results in raising the relative density of PLA from 0.1096 to 0.132 at 110°C, and 0.1824 at 120°C and 0.2408 at 130°C.

2 MPa:

- For samples saturated at 2MPa, the relative density observed were, 0.5472 at 80°C, to 0.2792 at 90°C, 0.1192 at 100°C. Now, instead of relative density to rise again because of pores collapse due to high temperature it was observed that the relative density dropped further to 0.1208 at 110°C, and 0.1160 at 120°C to the lowest at 130°C which was 0.0936.

2.5 MPa:

- At 2.5 MPa, it was observed that the samples have crystallized with randomly distributed crystal structures throughout the sample which resulted in a consistent high relative density of 0.7984 at all six temperatures that were tested ranging from 80°C to 130°C.

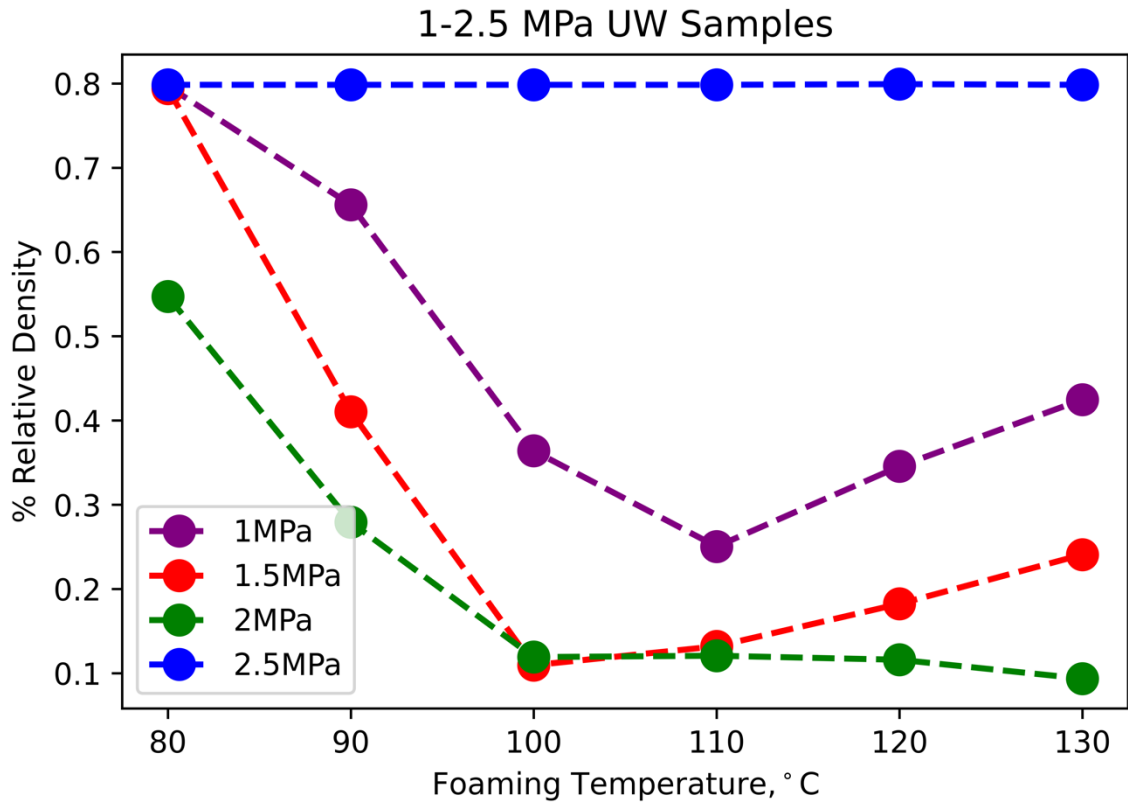


Figure 6: Relative densities of samples saturated from 1-2.5MPa

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
1.0	80	0.7968
1.0	90	0.6560
1.0	100	0.3640
1.0	110	0.2504
1.0	120	0.3456
1.0	130	0.4248

Table 1: 1 MPa process parameters

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
1.5	80	0.7940
1.5	90	0.4104
1.5	100	0.1096
1.5	110	0.1320
1.5	120	0.1824
1.5	130	0.2408

Table 2: 1.5 MPa process parameters

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
2.0	80	0.5472
2.0	90	0.2792
2.0	100	0.1192
2.0	110	0.1208
2.0	120	0.1160
2.0	130	0.0936

Table 3: 2 MPa process parameters

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
2.5	80	0.7984
2.5	90	0.7984
2.5	100	0.7984
2.5	110	0.7984
2.5	120	0.7992
2.5	130	0.7984

Table 4: 2.5 MPa process parameters

2.3.2 Relative Density and influence of Solid-State Foaming temperature on Boston University PLA samples

Similarly, gas sorption and foaming temperature behavior was analyzed at various pressures, and the resultant relative densities were plotted for PLA samples sent from Professor Keith Brown's lab from Boston University.

1 MPa:

- The 1MPa, two specimens were tested at 60°C and 70°C which resulted in consistent relative density of 0.81 which could be an indication that PLA sourced from different suppliers could impact the chemical, mechanical and thermal properties of PLA.

1.5 MPa:

- For samples saturated with carbon dioxide at 1.5 MPa, we saw that the first sample foamed at a slightly higher temperature of 80°C with a relative density of 0.81 while the second sample reached a relative density of 0.54 when it was foamed at 90°C. Apart from regular 1mm thick PLA sheets, Professor Brown also sent intricately 3D printed flower shaped structures. After saturating 1 of the flowers at 1.5 MPa it was observed that water bath foaming process didn't distort the geometry of the sample instead the sample grew by 138.4% in diameter and 77.2% in height and resulted in a relative density of 0.81.

2 MPa:

- At 2MPa, a slightly different behavior was observed at 80°C, first sample reached a drop in relative density of 0.39 while the second sample reached a very low relative density of 0.14 at 100°C which is a significant drop from 0.39.

2.5 MPa:

- At 2.5 MPa, it was observed that the first sample crystallized and resulted in a relative density of 0.81 when foamed at 100°C while the second sample was foamed at 110°C which resulted in a slight drop in the relative density of 0.69.

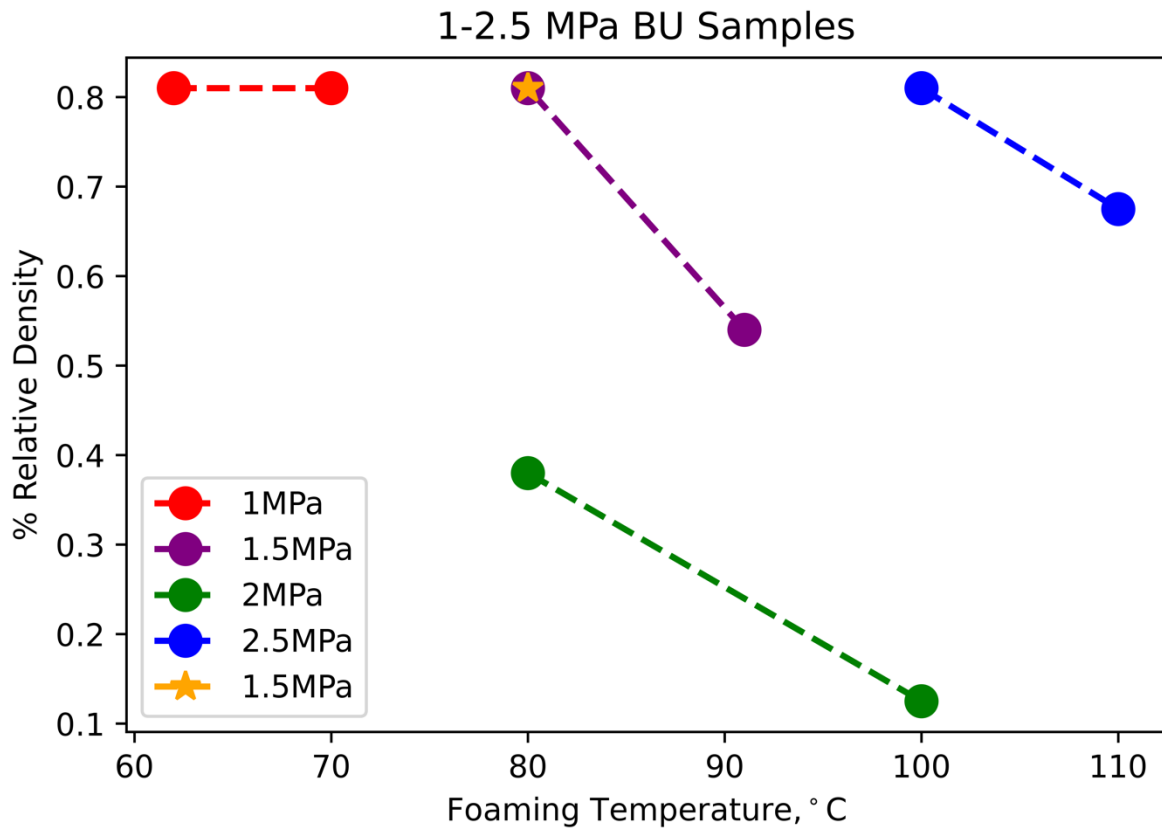


Figure 7: Relative densities of Boston University samples saturated from 1-2.5MPa

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
1.0	60	0.81
1.0	70	0.81
1.5	80	0.81
1.5	90	0.54
2.0	80	0.39
2.0	100	0.14
2.5	100	0.81
2.5	110	0.69

Table 5: Boston University samples process parameters

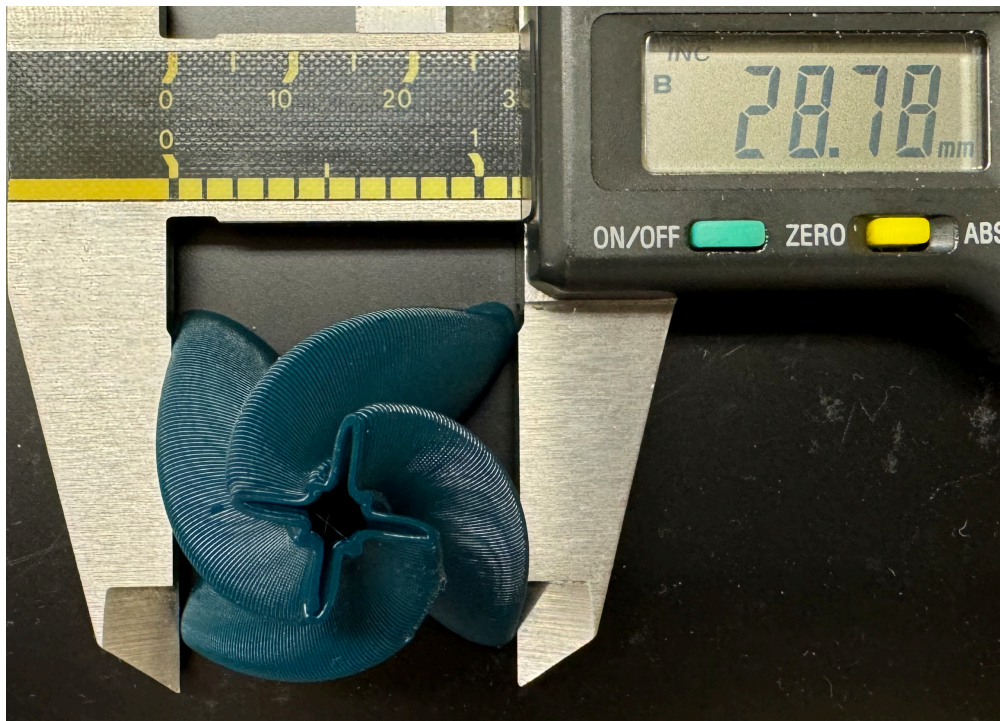


Figure 8: Unfoamed flower shaped specimen diameter

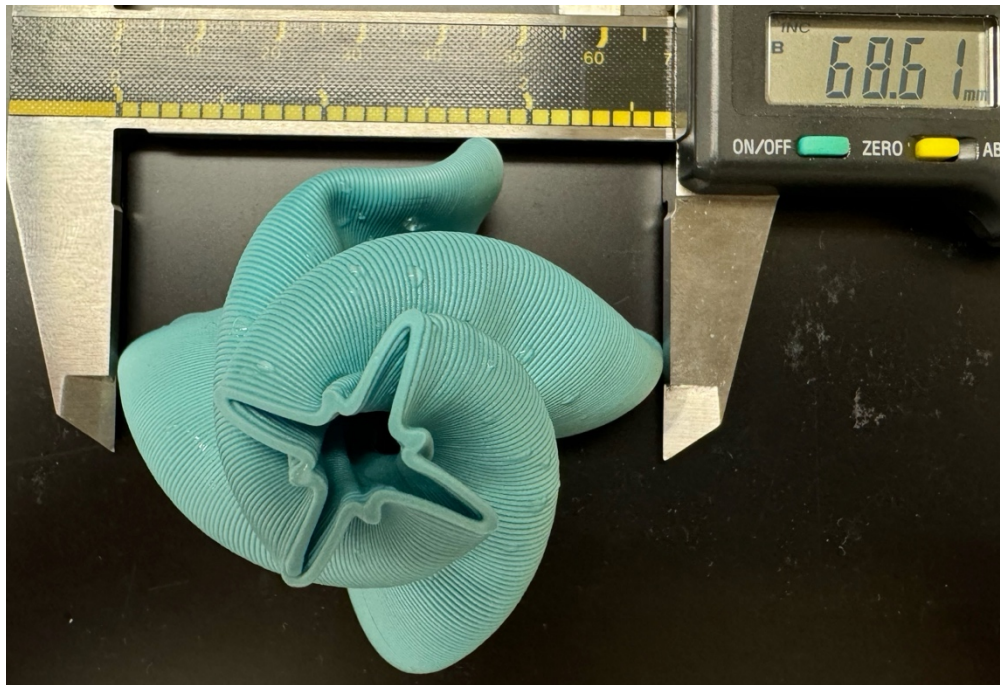


Figure 9: Foamed flower shaped specimen diameter

2.3.3 Relative Density and influence of Foaming temperature on University of Washington PLA samples via 3D Printing

In this experiment the saturated 3D printing PLA filament is taken out from the pressure vessel and the installed on to the Prusa Mark 3 3D printer to print specimens of 24.5mm x 24.5mm x 1mm thick square shaped dimensions along with ASTM Type-4 dogbone tensile coupons. For PLA filament saturated at 4MPa, the filament was allowed to desorb for 3 hours because such high pressure caused the filament to lose rigidity and become very “soft and ductile”. After the desorption, the filament regained its firmness and was feasible to install back on to the 3D printer. Again, the filament was printed at four different temperatures, 180°C, 190°C, 200°C and 210°C. We were not able to go below 180°C because PLA melts at around 170°C and the 3D printer won't be able to melt and extrude the PLA filament.

1 MPa:

- Under 1 MPa saturation, the relative density of the PLA filament showed a consistent increase with rising extrusion temperatures. At 180°C, the relative density was measured at 0.8909. As the temperature increased to 190°C, the relative density slightly rose to 0.8929. This trend continued at 200°C, where the relative density reached 0.8936. At the highest tested temperature of 210°C, the relative density peaked at 0.8982. The increase in relative density with temperature suggests that at these high temperatures, most of the pores were destroyed, resulting in random voids spread throughout the specimens.

3 MPa:

- Under 3 MPa saturation, the relative density of the PLA filament was examined over a four-week period to assess the impact of prolonged desorption. All samples were consistently printed at 210°C. In the first week, the relative density was measured at 0.9015. By the second week, it increased slightly to 0.9067, indicating some structural changes due to gas desorption over time. In the third week, the relative density rose to 0.9106, reflecting further desorption effects. By the fourth week, the relative density reached 0.9132, suggesting a continual but gradual increase in density as desorption progressed. These observations indicate that prolonged desorption impacts the foaming characteristics of PLA, leading to a gradual increase in relative density over time.

4 MPa:

- Under 4 MPa saturation, the relative density of the PLA filament was analyzed at different extrusion temperatures. At 180°C, the relative density was recorded at 0.8771. When the temperature was increased to 190°C, the relative density showed a slight increase to 0.8776. At 200°C, the relative density decreased slightly to 0.8710. However, at 210°C, the relative density increased again to 0.8848. These variations in relative density with temperature indicate that the high temperatures led to the destruction of most pores, leaving only random voids spread throughout the specimens.

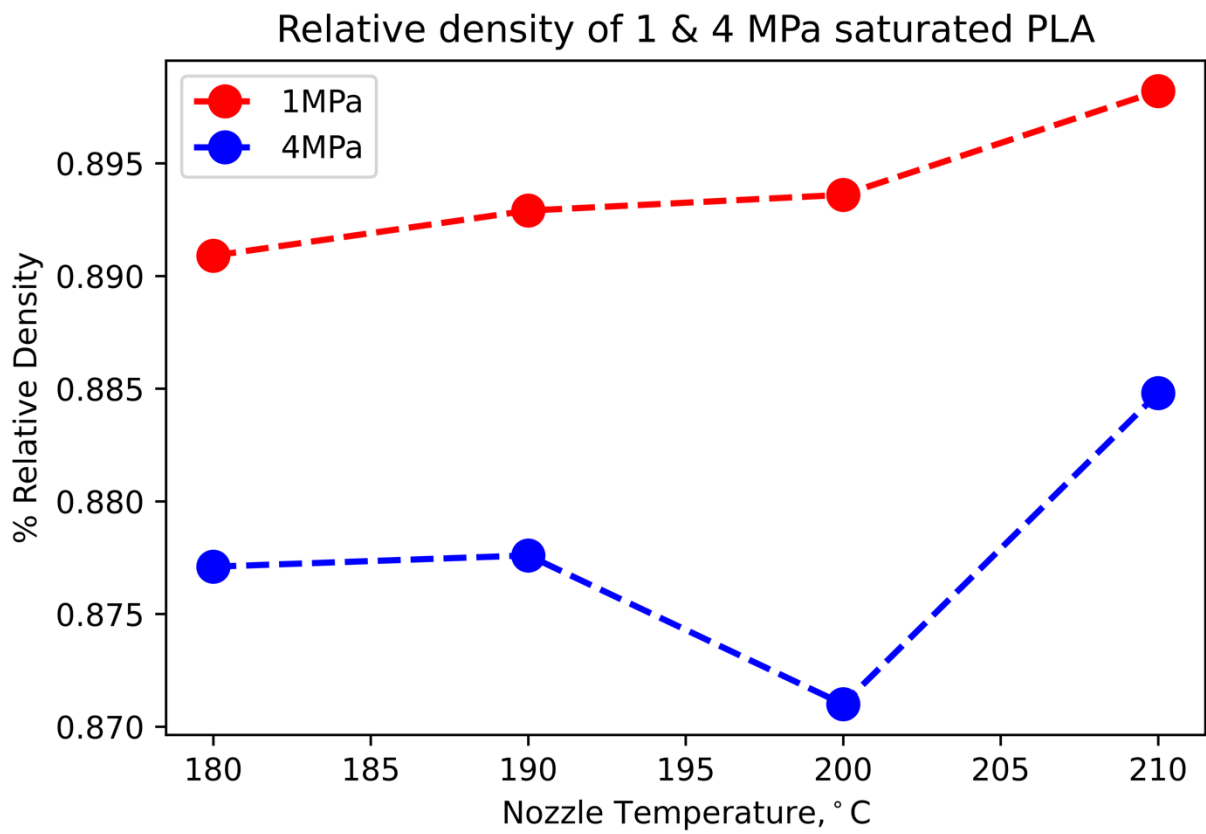


Figure 10: Relative densities of samples saturated at 1 and 4 MPa

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
1.0	180	0.8909
1.0	190	0.8929
1.0	200	0.8936
1.0	210	0.8982

Table 6: 1 MPa saturated PLA filament process parameters

Saturation Pressure (MPa)	Foaming Temperature (°C)	Relative Density
4.0	180	0.8771
4.0	190	0.8776
4.0	200	0.8710
4.0	210	0.8848

Table 7: 4 MPa saturated PLA filament process parameters

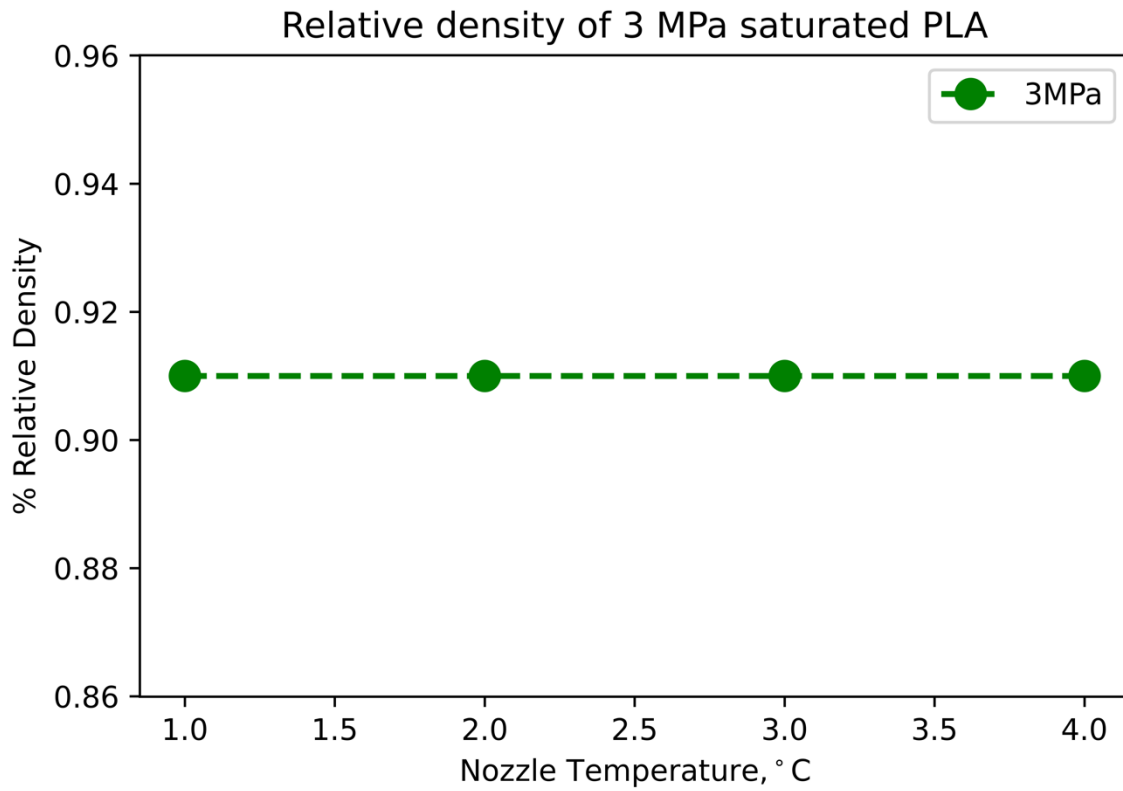


Figure 11: Relative densities of samples saturated at 3 MPa

Saturation Pressure (MPa)	Days	Foaming Temperature (°C)	Relative Density
3.0	1	210	0.9015
3.0	7	210	0.9067
3.0	14	210	0.9106
3.0	21	210	0.9132

Table 8: 3 MPa process parameters via 3D printer over four weeks

2.3.4 Impact of Pressure and Foaming Temperature on Relative Density

The gas sorption experiments revealed a clear correlation between saturation pressure and the rate of gas absorption in PLA. Higher pressures resulted in quicker saturation times and higher gas concentrations, indicating that pressure is a critical factor in the foaming process.

2.3.4.1 Solid-State Foaming Process

Analysis of 1 MPa Experiments

At 1 MPa, the relative density of the PLA samples decreased significantly with increasing foaming temperatures. The samples showed a relative density of 0.7968 at 80°C, which dropped to 0.2504 at 110°C, indicating a significant increase in foaming efficiency at higher temperatures. However, beyond 110°C, the relative density began to rise again, reaching 0.4248 at 130°C, due to thermal degradation of the polymer matrix and collapse of the microcellular structure. The increased temperatures led to the destruction of most pores, resulting in random voids spread throughout the specimens. This highlights the delicate balance required in optimizing foaming temperatures to maximize efficiency without compromising the structural integrity of the foam.

Analysis of 1.5 MPa Experiments

The 1.5 MPa experiments demonstrated a similar trend, with the relative density decreasing from 0.7940 at 80°C to 0.1096 at 100°C. This significant reduction in density underscores the effectiveness of higher pressures in promoting gas absorption. However, as the temperature increased further to 130°C, the relative density increased to 0.2408, indicating thermal degradation and collapse of the foam structure. This behavior suggests that while higher pressures facilitate better foaming, the optimal temperature range remains critical to prevent structural collapse.

Analysis of 2 MPa Experiments

For samples saturated at 2 MPa, the relative density exhibited a steady decline with increasing temperature, reaching the lowest value of 0.0936 at 130°C. This consistent reduction in density highlights the enhanced foaming efficiency at higher pressures, likely due to the increased gas solubility and diffusion within the polymer matrix. The minimal increase in relative density at higher temperatures indicates that the polymer matrix maintained its integrity better at this pressure, suggesting a potential advantage of using 2 MPa for achieving low-density foams without significant thermal degradation.

Analysis of 2.5 MPa Experiments

At 2.5 MPa, the samples displayed a relatively constant high relative density of around 0.7984 across all tested temperatures. This behavior is indicative of crystallization within the polymer matrix, resulting in a more rigid and less foamed structure. The formation of randomly distributed crystal structures throughout the sample likely impeded the creation of voids, leading to consistently higher densities. This observation suggests that while higher pressures can enhance

gas absorption, they may also promote crystallization, thereby reducing the effectiveness of the foaming process.

2.3.4.2 3D Printing Process

Analysis of 1 MPa Experiments

Under 1 MPa saturation, the relative density of the PLA filament showed a consistent increase with rising extrusion temperatures. At 180°C, the relative density was measured at 0.8909. As the temperature increased to 190°C, the relative density slightly rose to 0.8929. This trend continued at 200°C, where the relative density reached 0.8936. At the highest tested temperature of 210°C, the relative density peaked at 0.8982. The increase in relative density with temperature suggests that at these high temperatures, most of the pores were destroyed, resulting in random voids spread throughout the specimens.

Analysis of 3 MPa Experiments

Under 3 MPa saturation, the relative density of the PLA filament was examined over a four-week period to assess the impact of prolonged desorption. All samples were consistently printed at 210°C. In the first week, the relative density was measured at 0.9015. By the second week, it increased slightly to 0.9067, indicating some structural changes due to gas desorption over time. In the third week, the relative density rose to 0.9106, reflecting further desorption effects. By the fourth week, the relative density reached 0.9132, suggesting a continual but gradual increase in density as desorption progressed. These observations indicate that prolonged desorption impacts the foaming characteristics of PLA, leading to a gradual increase in relative density over time.

Analysis of 4 MPa Experiments

Under 4 MPa saturation, the relative density of the PLA filament was analyzed at different extrusion temperatures. At 180°C, the relative density was recorded at 0.8771. When the temperature was increased to 190°C, the relative density showed a slight increase to 0.8776. At 200°C, the relative density decreased slightly to 0.8710. However, at 210°C, the relative density increased again to 0.8848. These variations in relative density with temperature indicate that the high temperatures led to the destruction of most pores, leaving only random voids spread throughout the specimens.

2.3.5 Comparative Analysis and Critical Observations

The comparative analysis across different pressures reveals several critical insights:

Pressure-Temperature Interaction

The interaction between pressure and temperature is crucial in determining the foaming efficiency of PLA. Higher pressures generally enhance gas absorption, leading to lower relative densities. However, the optimal foaming temperature range is essential to prevent thermal degradation and collapse of the foam structure.

Structural Integrity

While higher pressures promote better foaming, they also increase the risk of crystallization, as observed in the 2.5 MPa experiments. This crystallization can lead to a more rigid structure with higher relative densities, reducing the overall effectiveness of the foaming process.

Optimal Conditions

The optimal conditions for foaming PLA were identified at 2 MPa and 110°C, where the lowest relative density of 0.0936 was achieved without significant thermal degradation. This suggests that a balance between pressure and temperature is critical for achieving high-quality foamed structures.

Thermal Degradation

The rise in relative density beyond optimal temperatures highlights the impact of thermal degradation on the foam structure. This underscores the importance of precise temperature control during the foaming process to maintain the integrity of the microcellular structure.

Crystallization Effects

The high relative densities observed at 2.5 MPa across all temperatures indicate that crystallization significantly affects the foaming efficiency. This suggests that while higher pressures can enhance gas absorption, they may also promote crystallization, which could be detrimental to the foaming process.

Chapter 3.0 Microstructure

3.1 SEM Analysis of 1.5 MPa Saturated PLA Foamed at 80°C

Procedure:

1. 3D Printing:

- PLA samples were 3D-printed into 1 mm thick sheets using a PRUSA Mark 3 FDM 3D printer. The printing parameters included a layer thickness of 0.2 mm and a nozzle temperature of 210°C. The samples were designed to have dimensions suitable for subsequent saturation and foaming experiments.

2. Saturation with CO₂:

- The printed PLA sheets were placed in a pressure vessel capable of withstanding pressures up to 6 MPa. The vessel was filled with CO₂ gas and pressurized to 1.5 MPa.
- The samples were left to saturate for 48 hours, allowing the CO₂ to diffuse uniformly throughout the PLA matrix.

3. Foaming Process:

- After saturation, the samples were carefully removed from the pressure vessel.
- The foaming process was conducted by immersing the saturated PLA sheets in a hot water bath maintained at 80°C. This temperature was selected based on preliminary experiments to achieve optimal pore formation.
- The samples were held in the hot water bath for a specified duration to ensure complete foaming.

4. Sample Preparation for SEM:

- To prepare the samples for SEM analysis, they were first cooled to liquid nitrogen temperature. A small notch was made on the specimen to guide the fracture.
- The samples were then rapidly frozen in liquid nitrogen for approximately one minute.
- Using pliers, the frozen samples were fractured along the notch to create a clean, exposed surface.
- The exposed fracture surfaces were marked to distinguish the edge and center regions for subsequent SEM imaging.

5. SEM Imaging:

- The fractured samples were mounted on SEM stubs using conductive carbon tape. The samples were then sputter-coated with a thin layer of gold and palladium to enhance conductivity and improve image quality.
- SEM imaging was performed at magnifications suitable for observing the microstructure and pore distribution. Two specific regions were imaged: the edge (500 μm scale) and the center (400 μm scale) of the sample.

6. Image Analysis:

- The SEM images were analyzed using ImageJ software. The software was used to measure the pore size and diameter accurately.
- Multiple measurements were taken across different regions of the sample to ensure a representative analysis of the pore size distribution.

SEM Images:

1. Edge (500 μm scale):

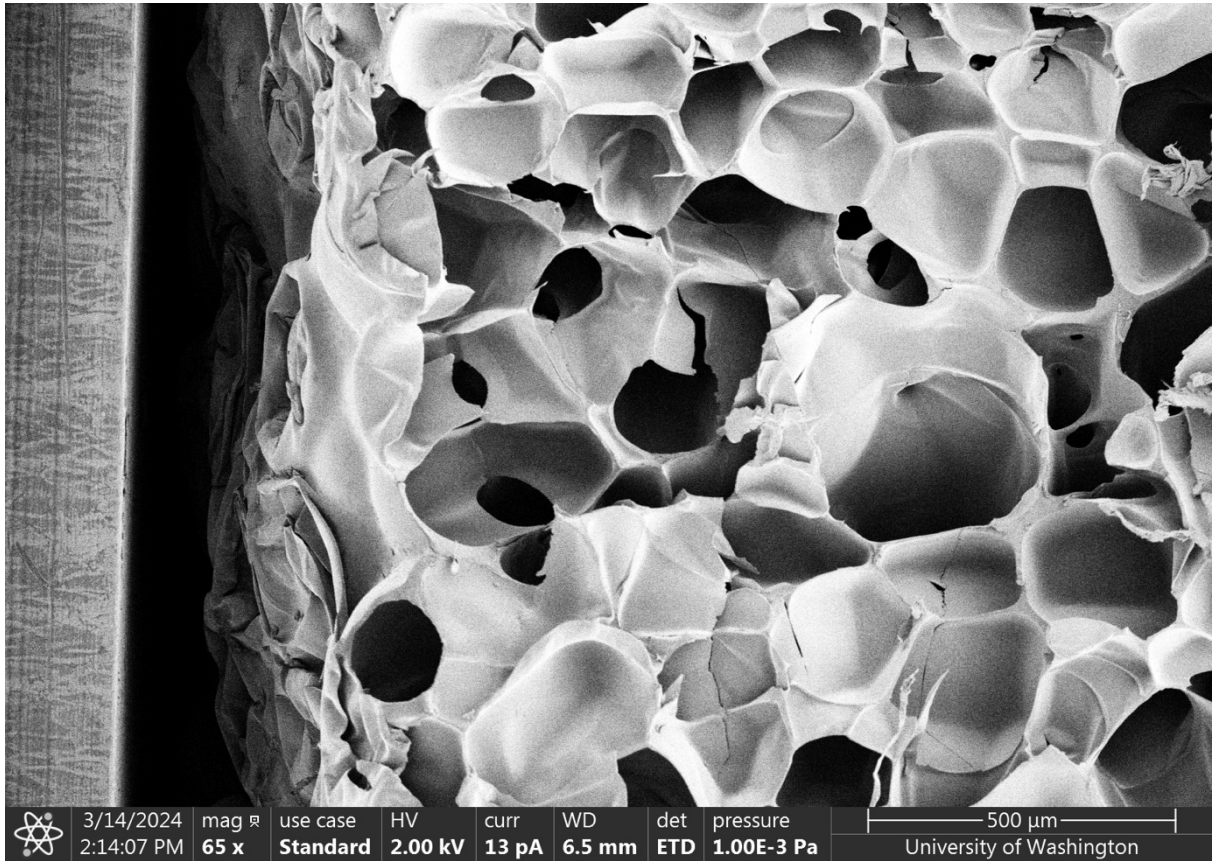


Figure 12: Edge of 3D printed PLA and solid-state foamed at 80°C

- The SEM image of the edge shows a relatively uniform distribution of pores. The pores are well-defined, with an average size of approximately 0.80 μm .
- The structure indicates effective foaming at the edges, with distinct pores uniformly distributed along the edge.

2. Center (400 μm scale):

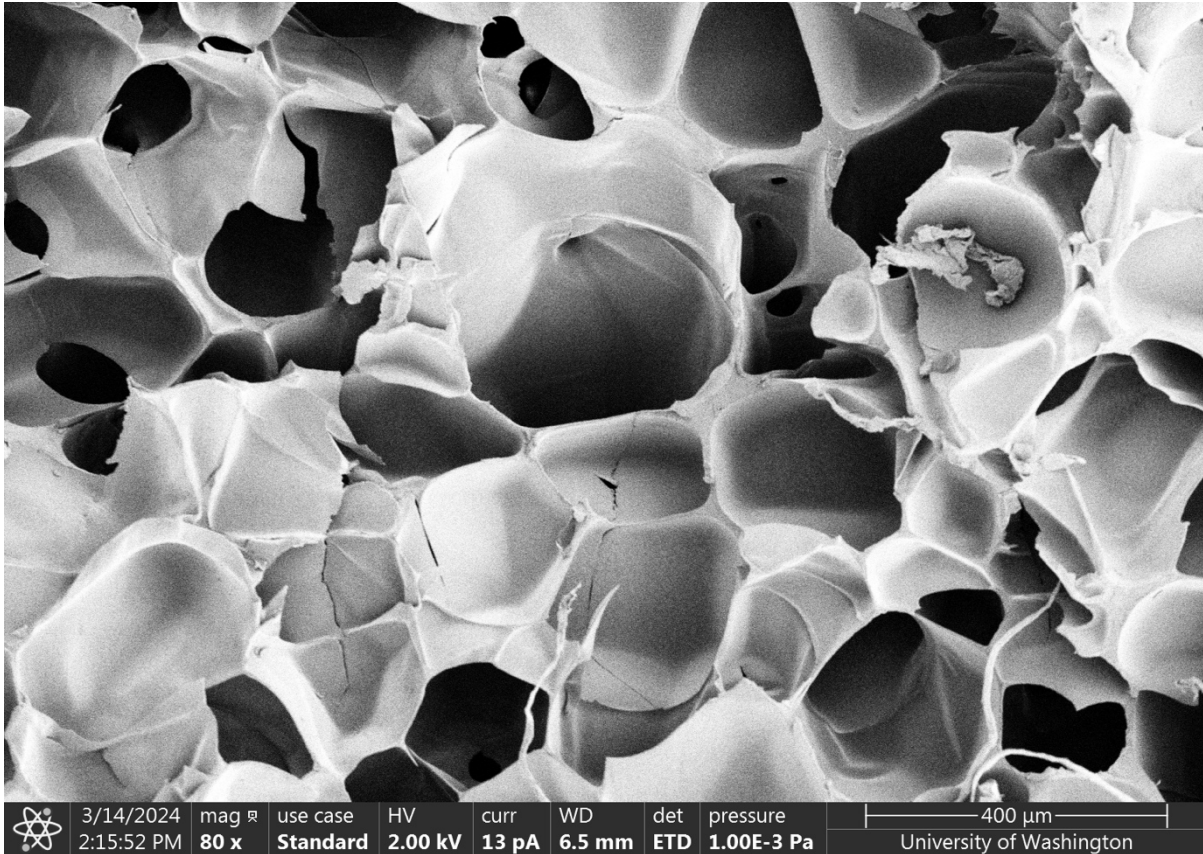


Figure 13: Center of 3D printed PLA and solid-state foamed at 80°C

- The SEM image of the center section reveals a similar distribution pattern of pores, with an average size consistent with the edge, around 0.80 μm .
- The uniformity of pores suggests that the foaming process effectively penetrated through the sample, maintaining consistent pore sizes from edge to center.

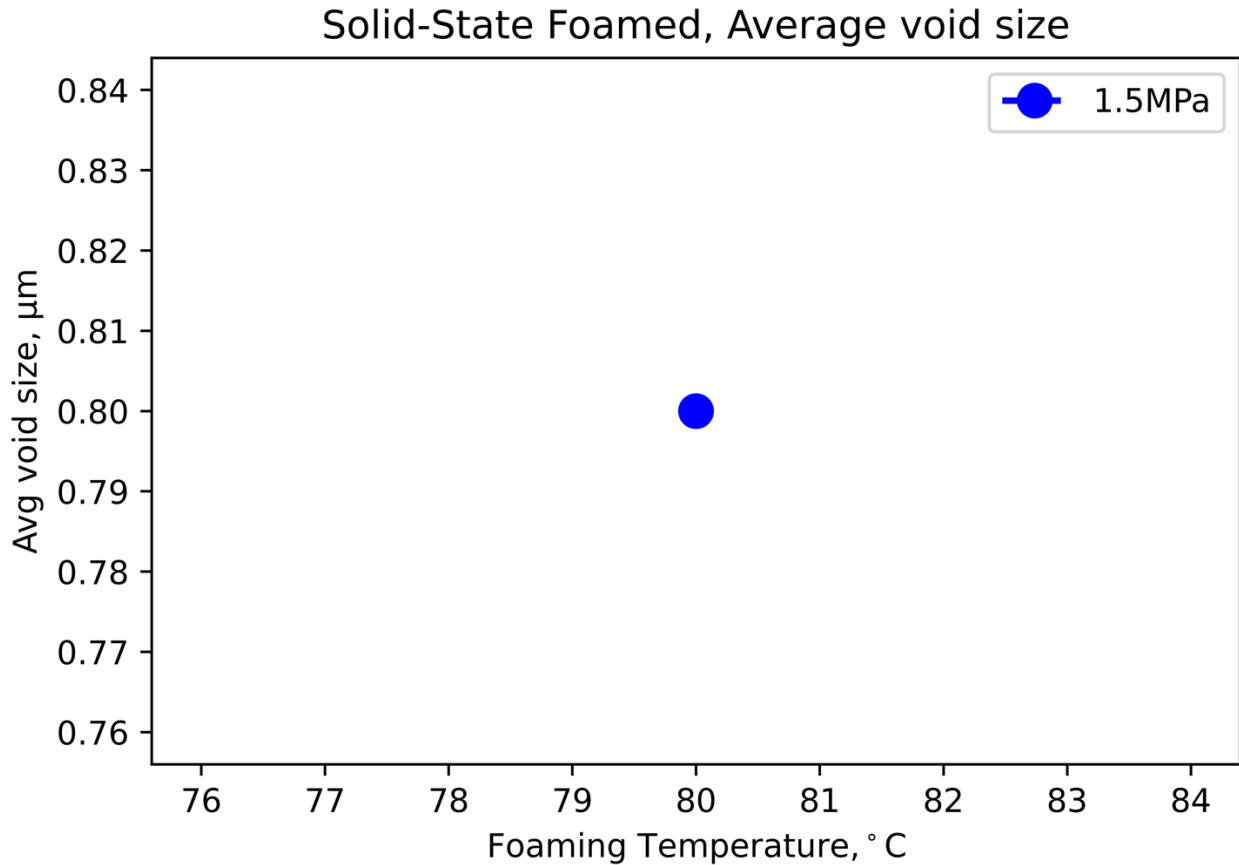


Figure 14: Average Pore Size for Solid-State Foamed 3D Printed PLA

Observations:

- The average pore size of approximately 0.80 μm is consistent across both the edge and the center of the sample.
- The foaming process at 80°C resulted in a homogeneous distribution of pores, indicating a successful saturation and foaming protocol.
- The structural integrity appears maintained, with well-defined pores indicating minimal coalescence or collapse, which is crucial for mechanical performance.

Pore Size Distribution vs. Foaming Temperature:

- The plot of average pore size against the foaming temperature confirms the observed SEM images. At 80°C, the average pore size is around 0.80 μm, indicating a stable foaming process at this temperature for 1.5 MPa saturation.
- This consistency in pore size distribution is critical for predicting the mechanical behavior and potential applications of the foamed PLA.

3.2 Microstructure Analysis of 1 MPa Saturated PLA at Various 3D printing extrusion temperatures

Detailed Procedure for SEM Sample Preparation

1. **Saturation:** The PLA filament were saturated with carbon dioxide at 1 MPa for 48 hours.
2. **Extrusion:** The saturated filament was reinstalled into the 3D printer and extruded at varying temperatures of 180°C, 190°C, 200°C, and 210°C.
3. **3D Printing:** 24.5mm x 24.5mm x 1mm square samples for SEM imaging and Type-4 tensile test coupons also of 1mm thickness were printed with the saturated PLA filament.
4. **Freeze Fracturing:** The extruded 1mm thick square samples were frozen using liquid nitrogen. A notch was made on each specimen to facilitate controlled fracturing. After freezing for one minute, the samples were fractured using pliers to expose the internal structure.
5. **SEM Imaging:** The fractured surfaces were coated with a thin layer of gold and palladium to enhance conductivity and then observed under a Scanning Electron Microscope (SEM) at various magnifications.
6. **Image Analysis:** The SEM images were analyzed using ImageJ software to measure the size of the voids.

3.2.1 SEM Observations and Analysis for 1 MPa Saturated PLA at 180°C Extrusion Temperature

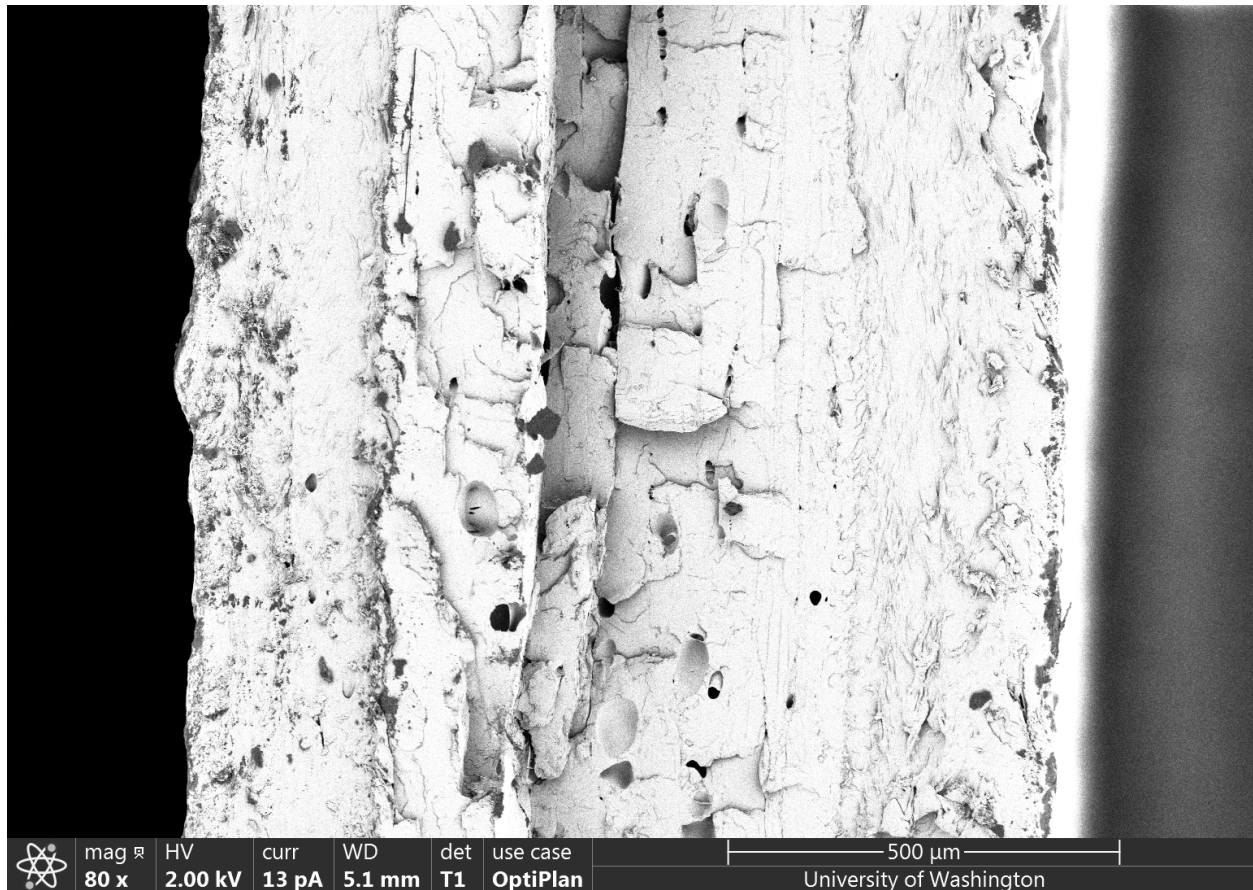


Figure 15: 3D printed 1MPa saturated PLA at extrusion temperature of 180°C

General Observations:

- **Void Distribution:** The voids are non-uniformly distributed with varied sizes.
- **Void Shape:** The voids exhibit irregular shapes, indicating the initial stages of void formation where the gas has begun to nucleate but not fully expanded.
- **Average Void Size:** Approximately 36.8 μm.

3.2.2 SEM Observations and Analysis for 1 MPa Saturated PLA at 190°C Extrusion Temperature

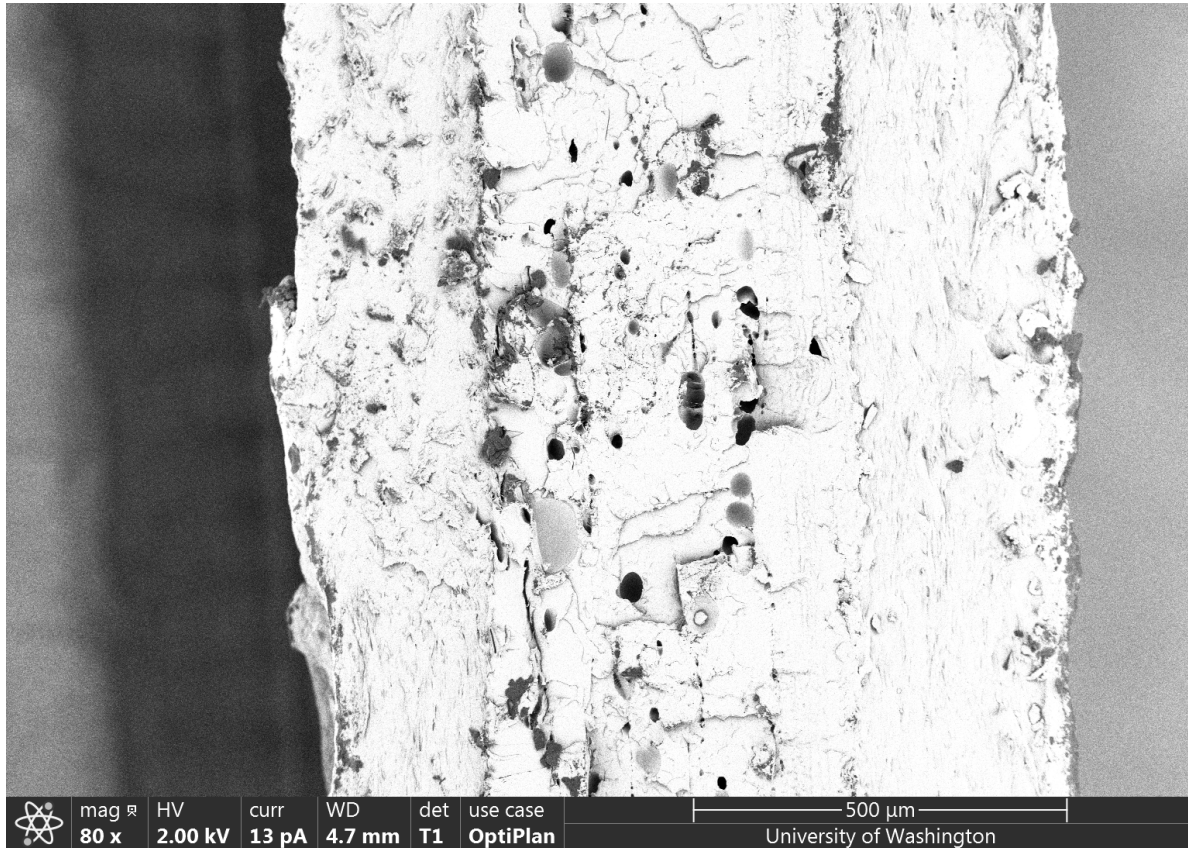


Figure 16: 3D printed 1MPa saturated PLA at extrusion temperature of 190°C

General Observations:

- **Void Distribution:** The voids have significantly reduced with a 10°C jump in extrusion temperature.
- **Void Shape:** The voids exhibit more regular shapes, indicating further gas expansion.
- **Average Void Size:** Approximately 22.1 μm

3.2.3 SEM Observations and Analysis for 1 MPa Saturated PLA at 200°C Extrusion Temperature

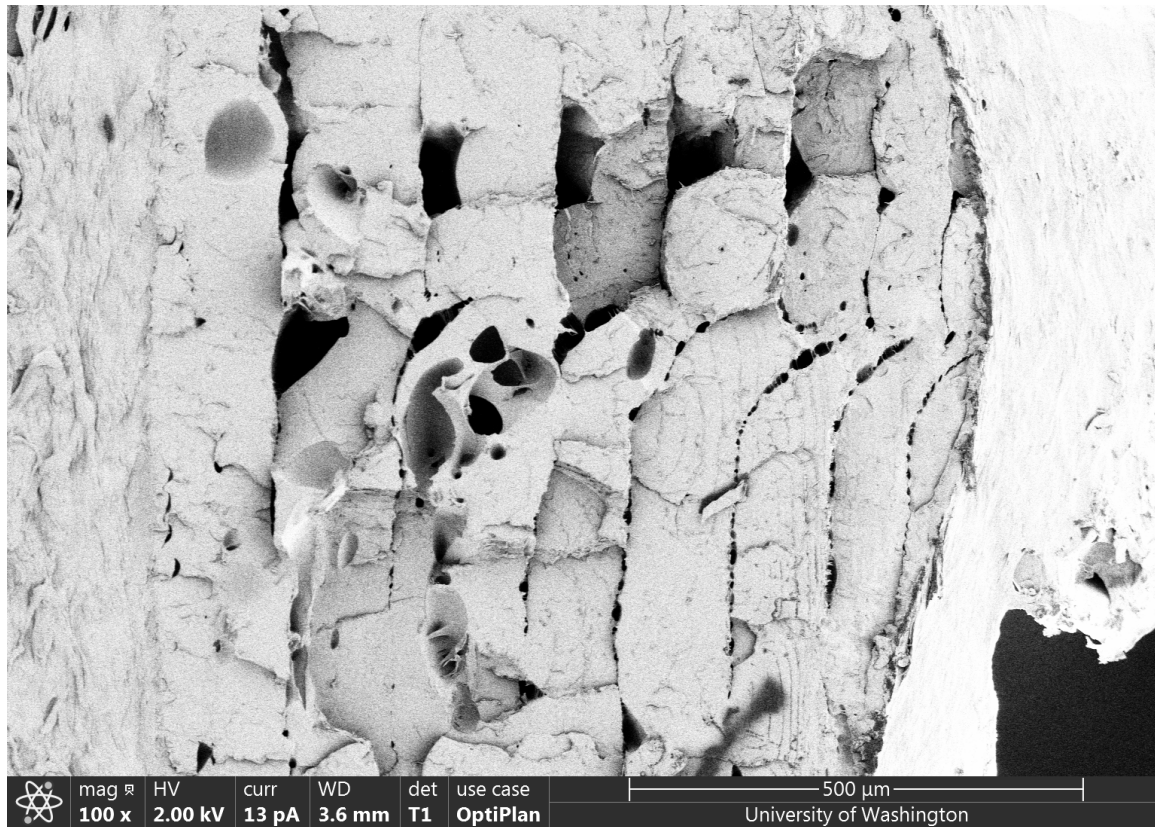


Figure 17: 3D printed 1MPa saturated PLA at extrusion temperature of 200°C

General Observations:

- **Void Distribution:** The voids are significantly reduced in size and number.
- **Void Shape:** The voids are mostly spherical, but many have collapsed due to the high temperature, and we also see gaps in the 3D printing process as the individual layers and voids among them are clearly visible.
- **Average Void Size:** Approximately 0.23 μm.

3.2.4 SEM Observations and Analysis for 1 MPa Saturated PLA at 210°C Extrusion Temperature

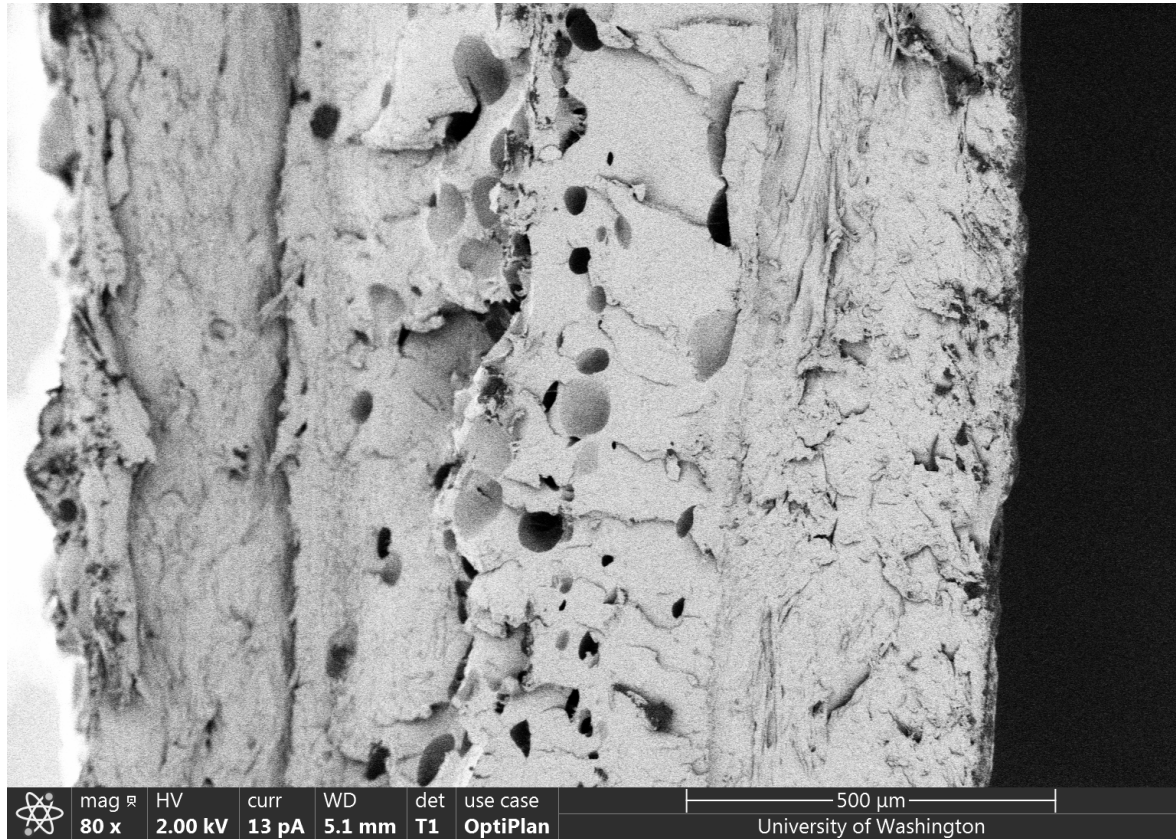


Figure 18: 3D printed 1MPa saturated PLA at extrusion temperature of 210°C

General Observations:

- **Void Distribution:** There are a lot of much smaller voids visible.
- **Void Shape:** The voids have a more spherical shape and some larger voids have closed appearance.
- **Average Void Size:** In the range of 0.1 µm.

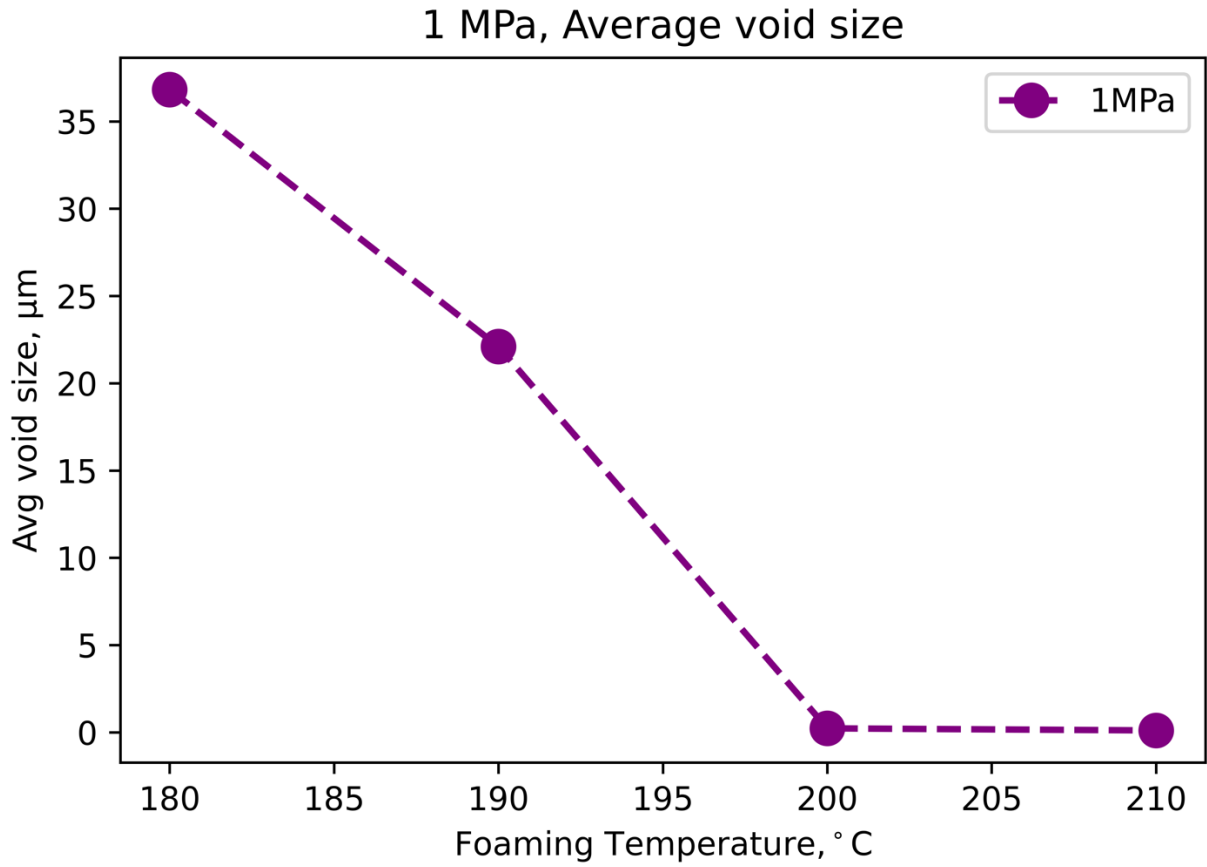


Figure 19: Average Pore Size for 1MPa saturated 3D Printed PLA at various extrusion temperatures

3.3 Microstructure Analysis of 3 MPa Saturated PLA desorbed over a span of 4 weeks at a constant extrusion temperature for 210°C

For this experiment the saturated PLA filament at 3MPa was allowed to desorb for three hours on the day it was de-pressurized and taken out of the pressure vessel. The saturated filament was then installed into the 3D printer and a batch of six Type-4 tensile test coupons were printed. After that, a 24.5mm x 24.5mm x 1mm square shaped specimen was also printed to be used for SEM analysis.

To the SEM sample a notch was made to facilitate controlled fracturing by liquid nitrogen, the submersion time under liquid nitrogen was 1 minute. After which the sample was fractured using pliers to expose the imaging surface for SEM. It was carefully tagged and bagged for SEM.

3.3.1 SEM Observations and Analysis for 3 MPa Saturated PLA for week 1

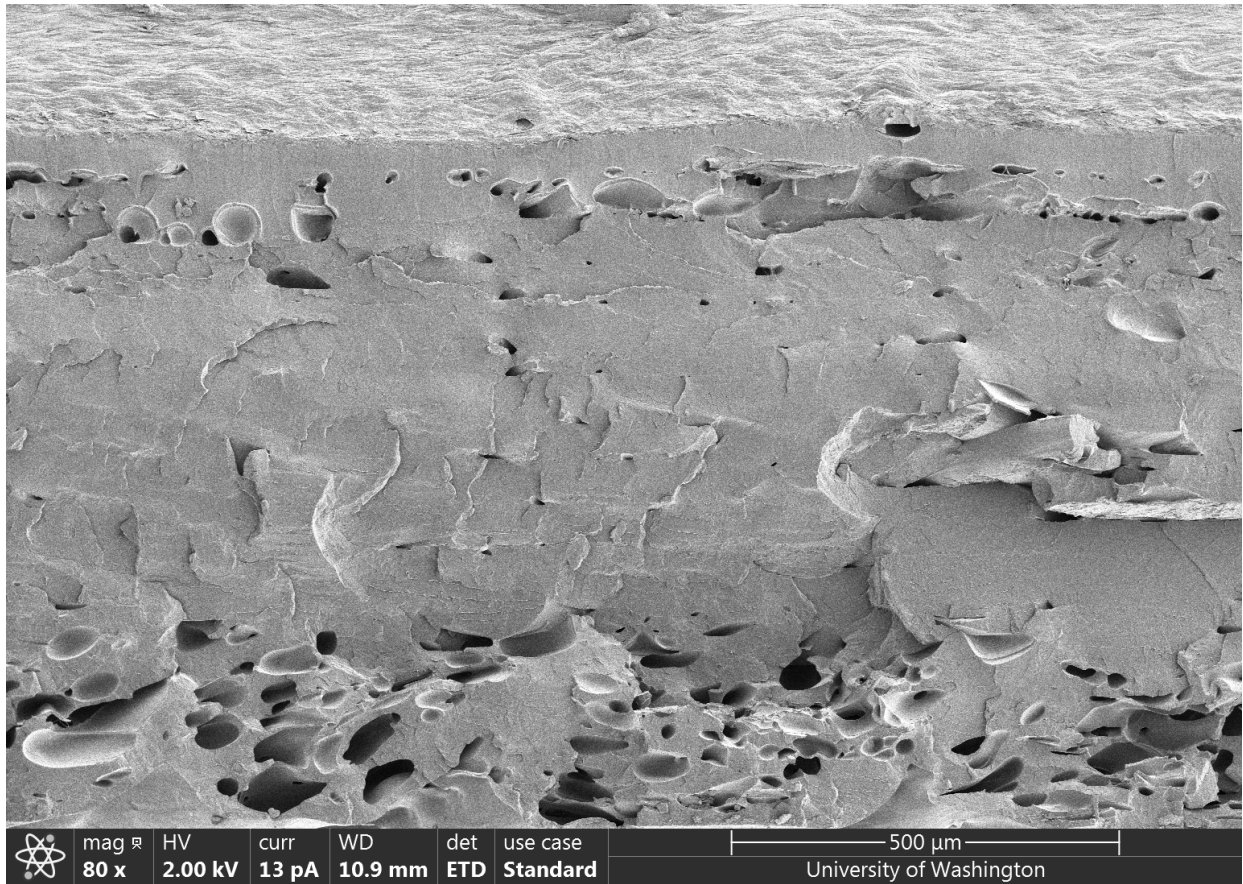


Figure 20a: 3D printed 3MPa saturated PLA at 1 week at 500μm

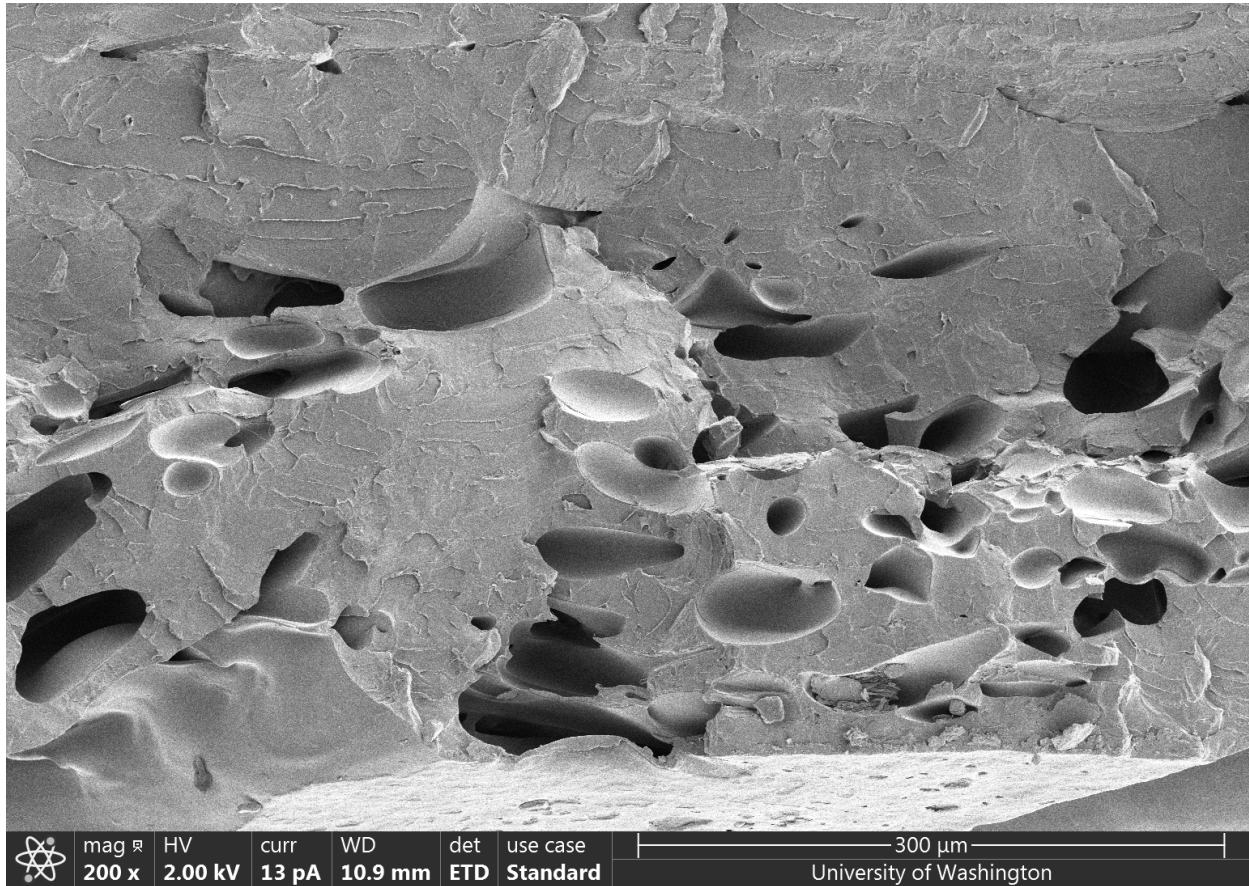


Figure 20b: 3D printed 3MPa saturated PLA at 1 week at 300µm

General Observations:

- **Void Distribution:** There are a lot of consistent voids visible at the bottom of the specimen.
- **Void Shape:** The voids have a more oval shape and some larger voids have closed appearance.
- **Average Void Size:** In the range of 0.18 µm.

3.3.2 SEM Observations and Analysis for 3 MPa Saturated PLA for week 2

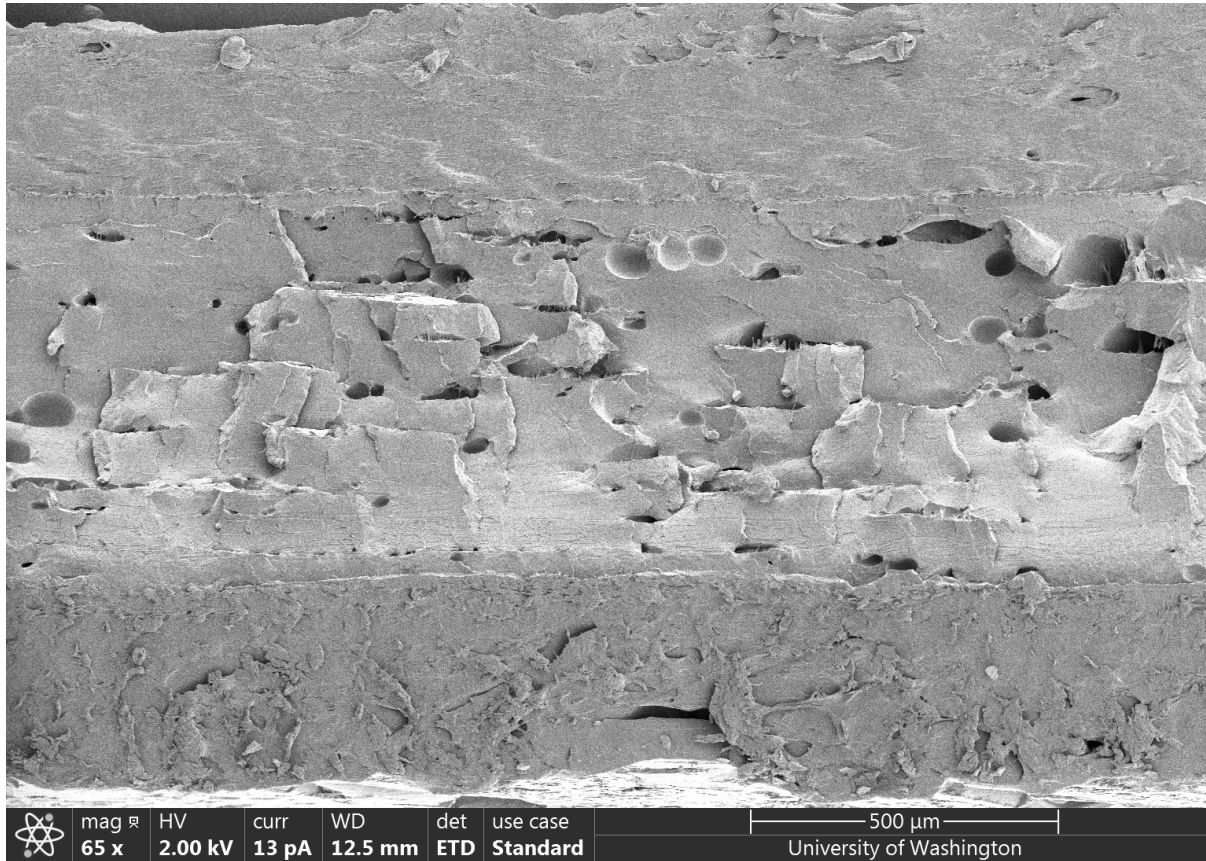


Figure 21: 3D printed 3MPa saturated PLA at 2 weeks at 500μm

General Observations:

- **Void Distribution:** There are a lot of smaller closed voids that can also be characterized as circular indents
- **Void Shape:** The voids have a circular shape, and some larger voids can be seen to the left of the micrograph.
- **Average Void Size:** In the range of 0.29 μm.

3.3.3 SEM Observations and Analysis for 3 MPa Saturated PLA for week 3

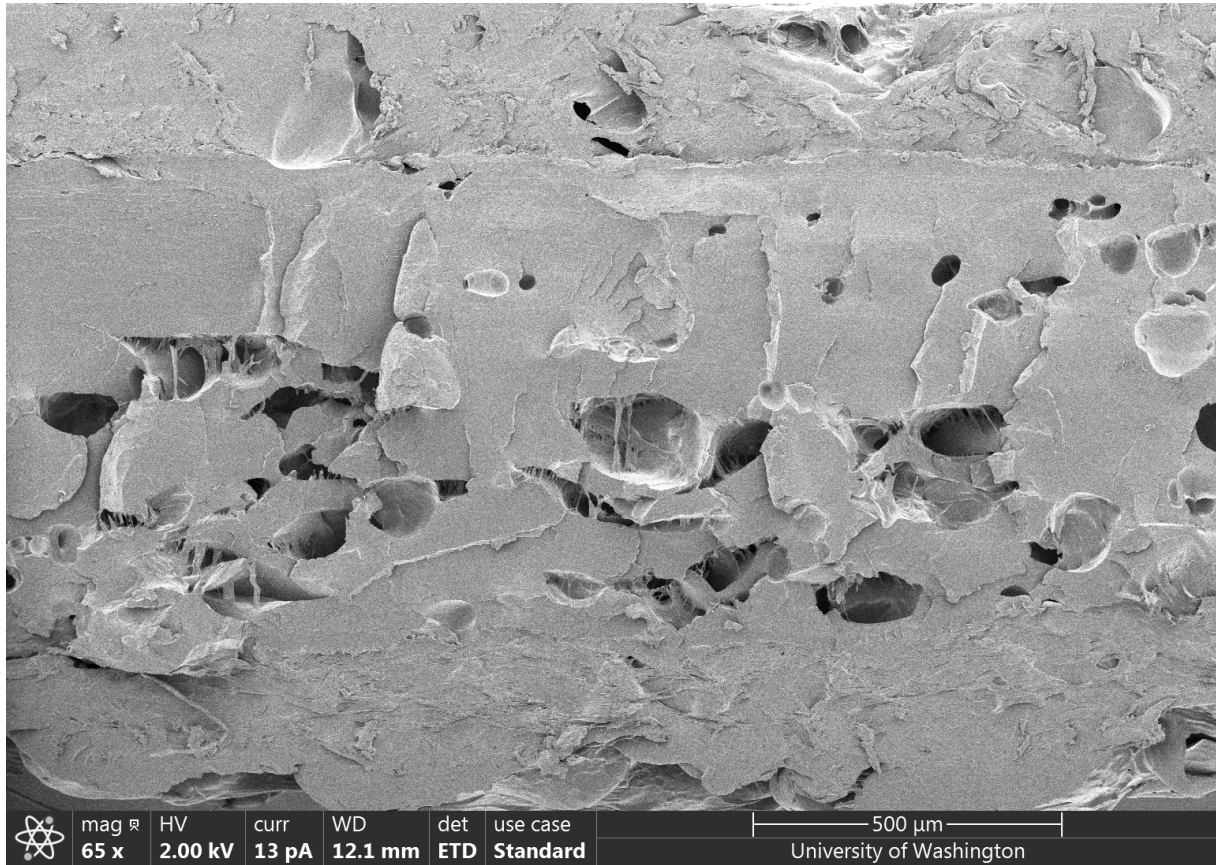


Figure 22a: 3D printed 3MPa saturated PLA at 3 weeks at 500μm

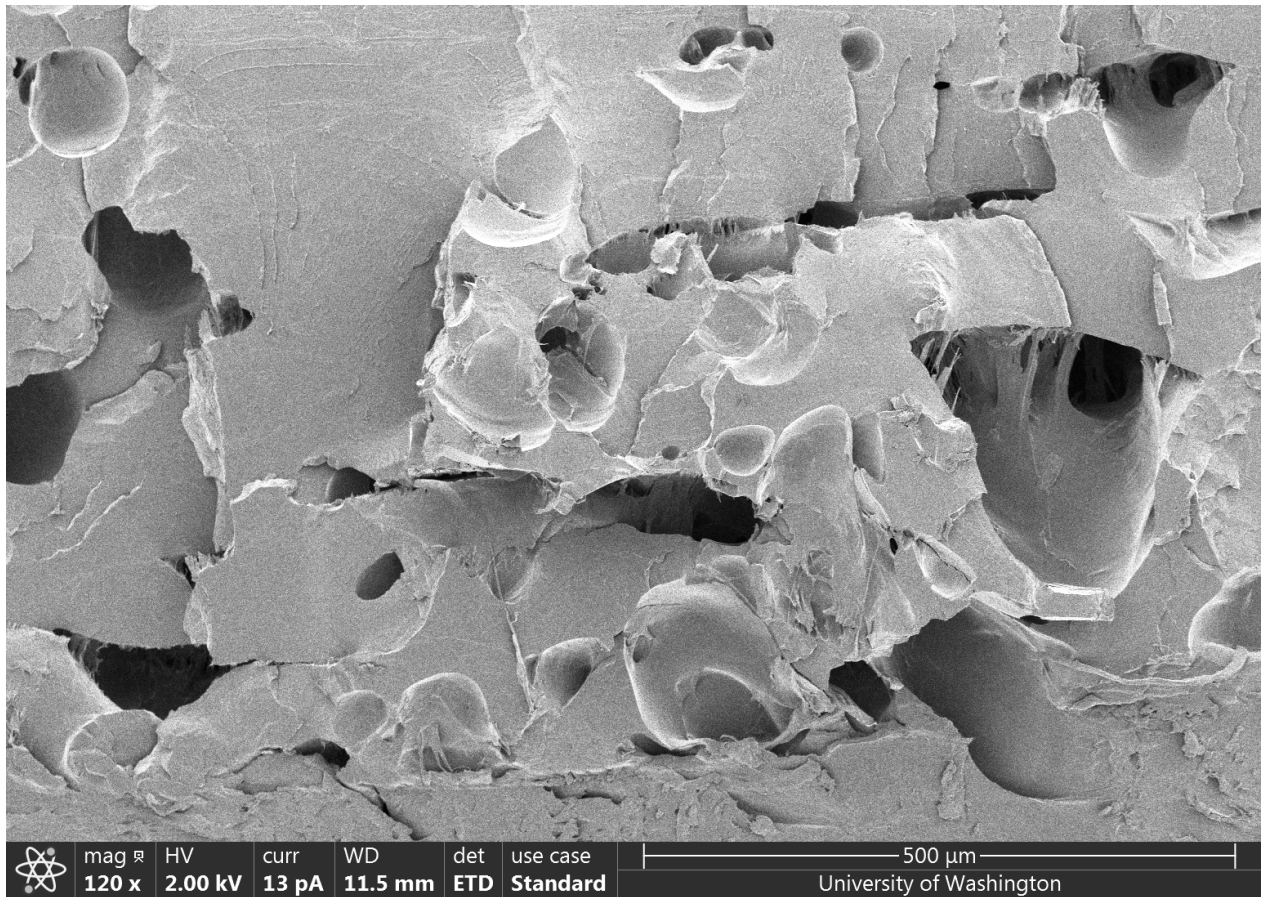


Figure 22b: 3D printed 3MPa saturated PLA at 3 weeks at 500µm

General Observations:

- **Void Distribution:** There voids are irregular in distribution.
- **Void Shape:** The voids have a dissimilar shapes and sizes with a lot of fibrous structures observed within these voids. On macro scale, after the 3D printing process the top surface was a lot rougher than week 1 and week 2.
- **Average Void Size:** In the range of 0.37 µm.

3.3.4 SEM Observations and Analysis for 3 MPa Saturated PLA for week 4

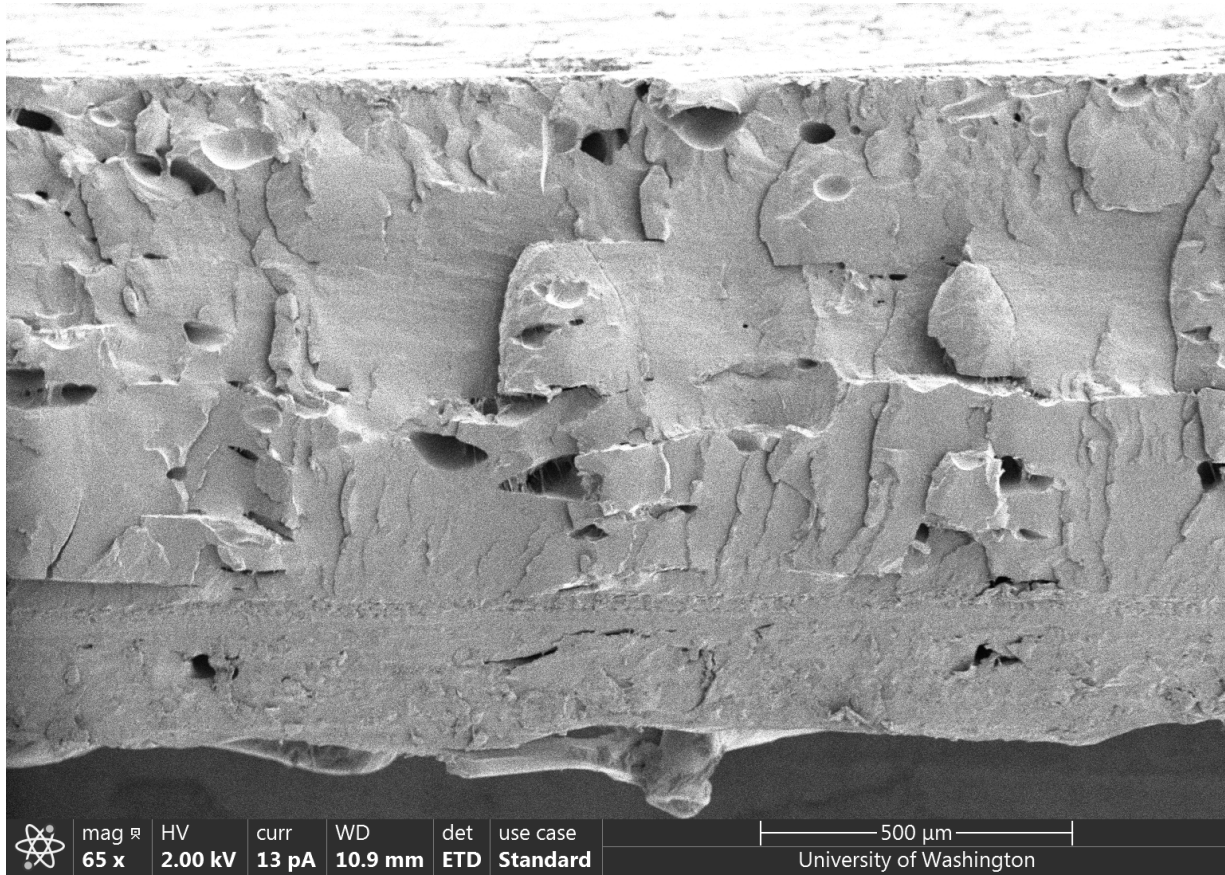


Figure 23a: 3D printed 3MPa saturated PLA at 4 weeks at 500μm

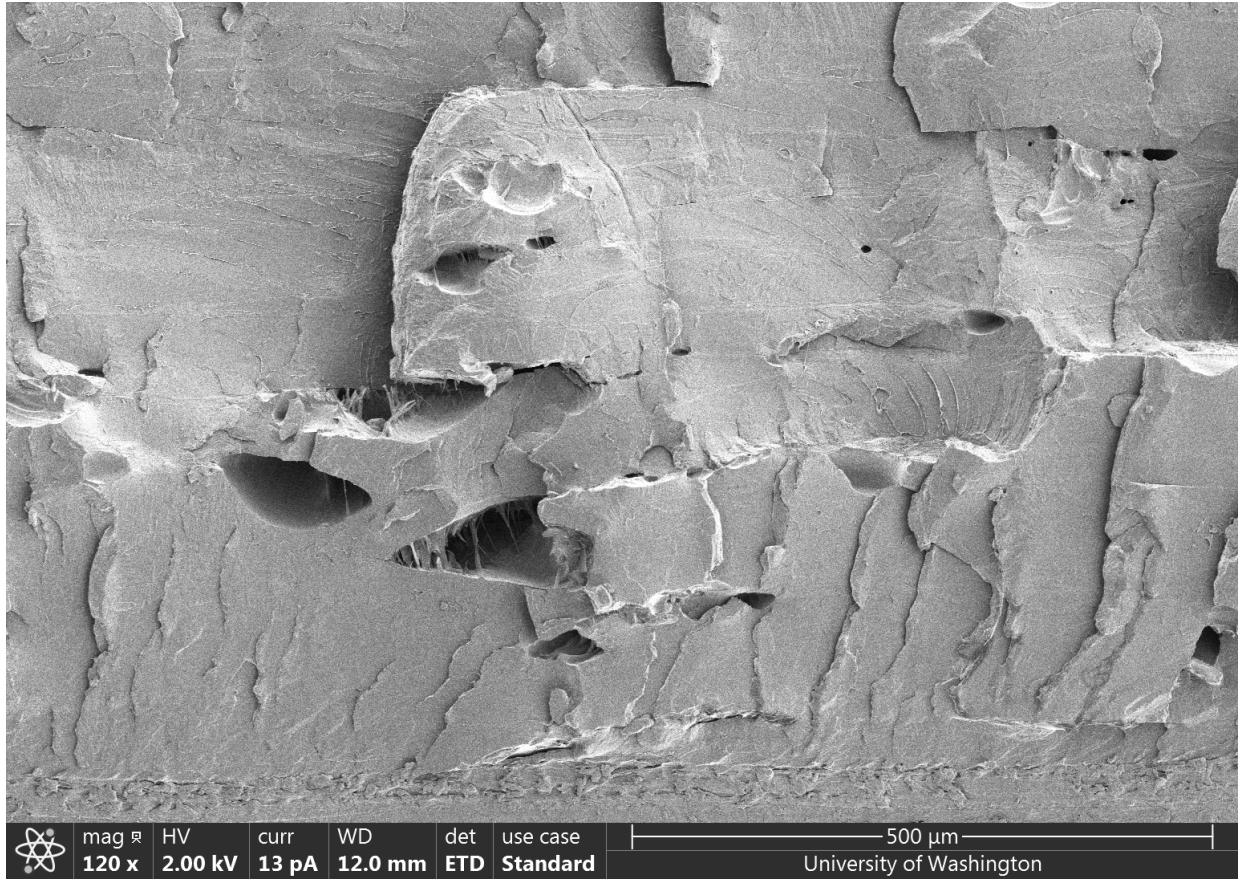


Figure 23b: 3D printed 3MPa saturated PLA at 4 weeks at 500µm

General Observations:

- **Void Distribution:** There voids are irregular in distribution and are more sparsely scattered.
- **Void Shape:** The voids still have those fibrous looking structures inside some larger voids and the specimens still had a rough surface after 3D printing.
- **Average Void Size:** In the range of 0.33 µm.

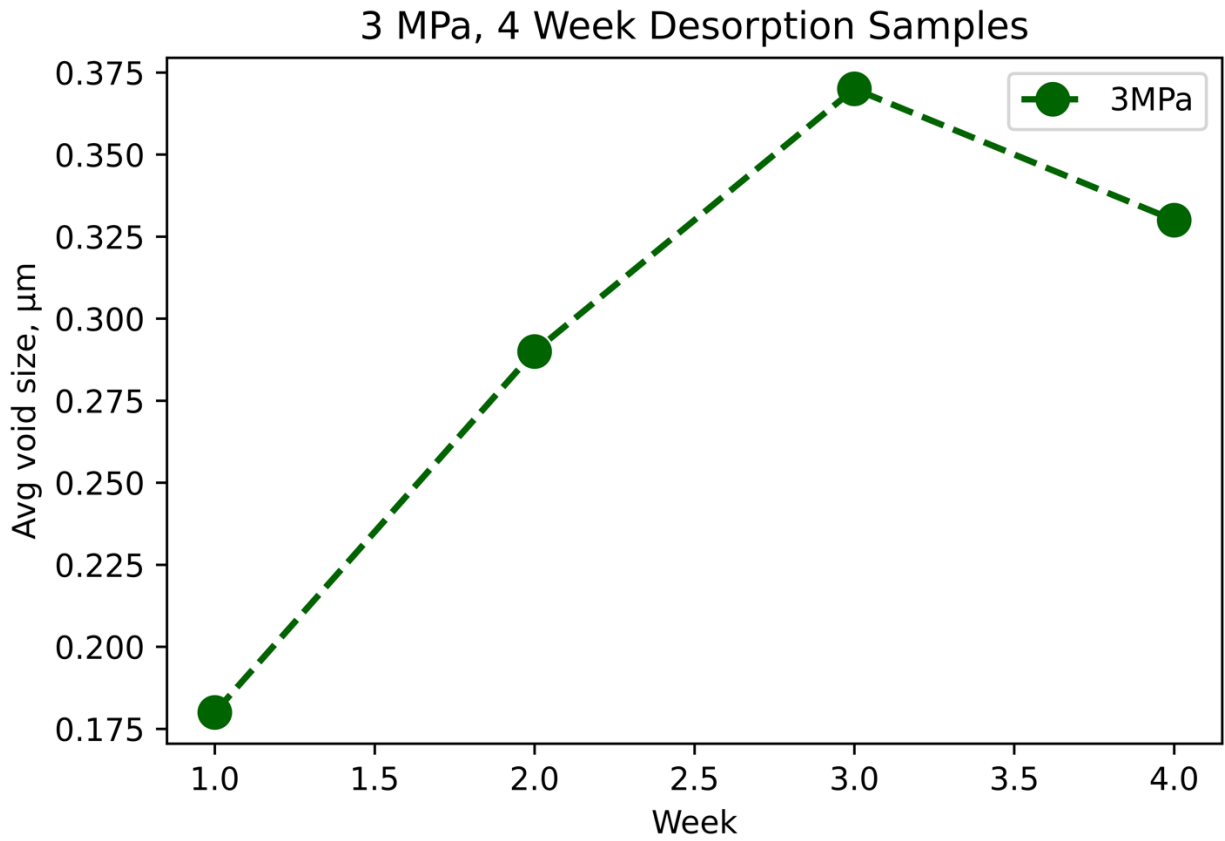


Figure 24: Average Pore Size for 3MPa saturated 3D Printed PLA over a span of 4 weeks

3.4 Microstructure Analysis of 4 MPa Saturated PLA at Various 3D printing extrusion temperatures

These experiments were like the 1MPa saturated PLA filament that were installed into the 3D printer and the tensile and SEM specimens were printed. One variation in these experiments was the PLA filament was allowed to desorb for three hours for the filament to regain some of its structural firmness as the filament was quite soft when it was taken out from the pressure vessel.

3.4.1 SEM Observations and Analysis for 4 MPa Saturated PLA at 180°C Extrusion Temperature



Figure 25: 3D printed 4MPa saturated PLA at extrusion temperature of 180°C

General Observations:

- **Void Distribution:** There voids are irregular in distribution and are more sparsely scattered.
- **Void Shape:** The voids are more rectangular in shape and the printed layer have a lot of cracks.
- **Average Void Size:** In the range of 0.16 μm.

3.4.2 SEM Observations and Analysis for 4 MPa Saturated PLA at 190°C Extrusion Temperature

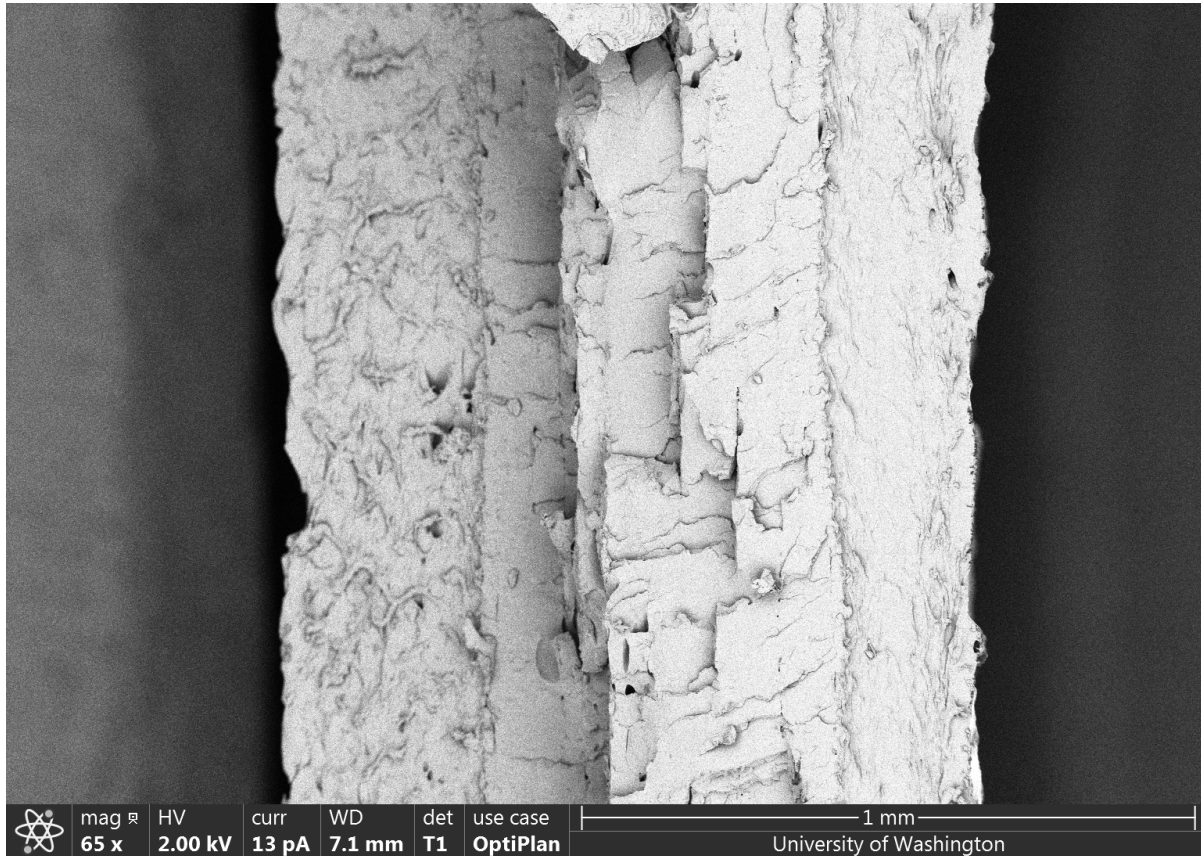


Figure 26: 3D printed 4MPa saturated PLA at extrusion temperature of 190°C

General Observations:

- **Void Distribution:** This specimen hardly had any voids present, and the ones we did observe were very small.
- **Void Shape:** The voids are circular in shape.
- **Average Void Size:** In the range of 0.05 μm .

3.4.3 SEM Observations and Analysis for 4 MPa Saturated PLA at 200°C Extrusion Temperature

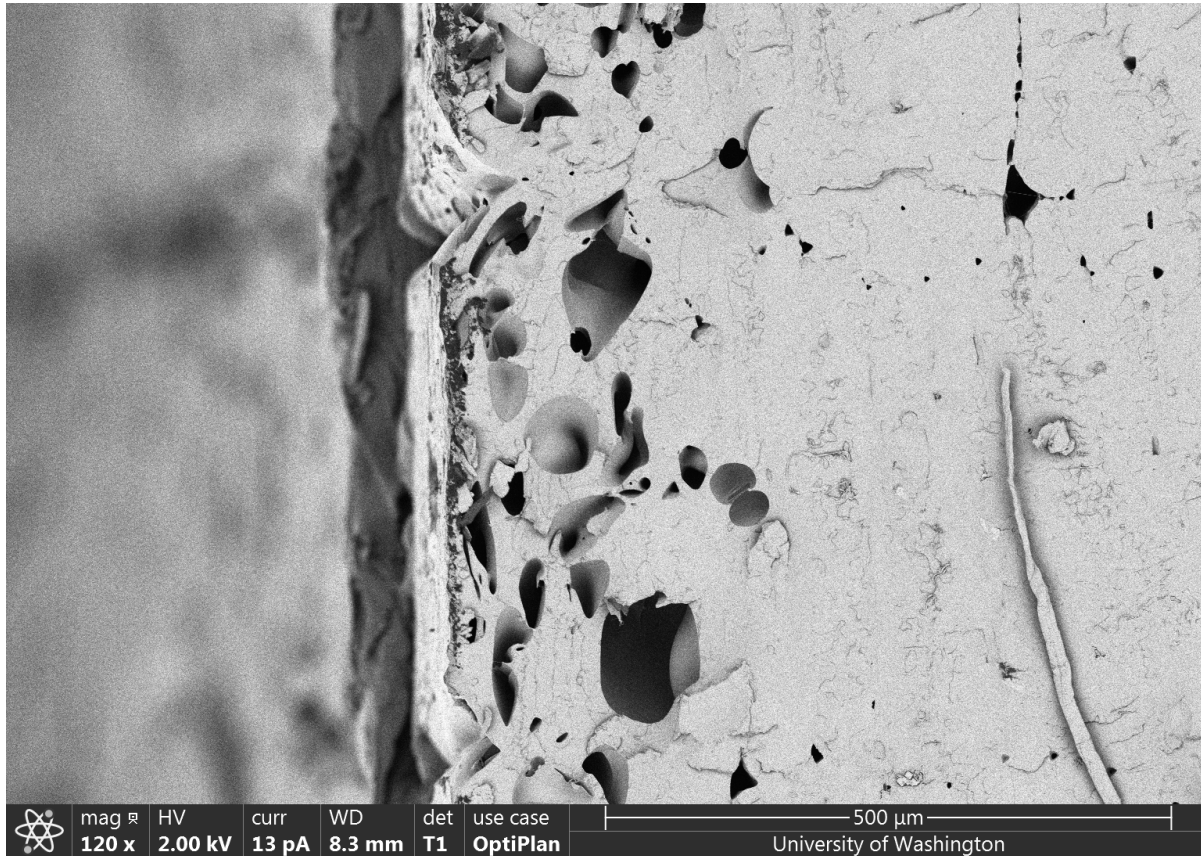


Figure 27: 3D printed 4MPa saturated PLA at extrusion temperature of 200°C

General Observations:

- **Void Distribution:** The voids were observed on the top side of the specimen with a healthy distribution of voids tightly packed near the top surface.
- **Void Shape:** The majority of the voids have a shape close to a circle.
- **Average Void Size:** In the range of 0.27 μm.

3.4.4 SEM Observations and Analysis for 4 MPa Saturated PLA at 210°C Extrusion Temperature

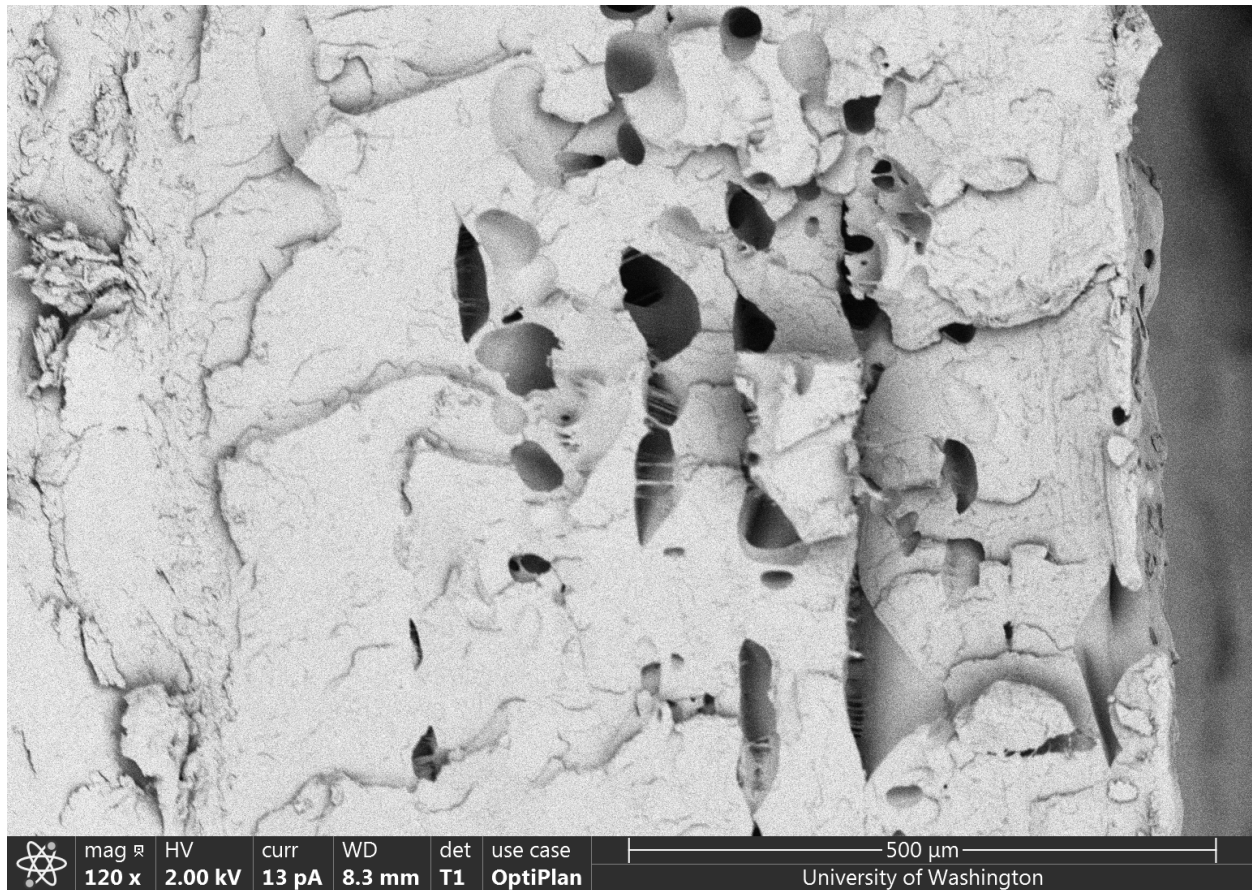


Figure 28: 3D printed 4MPa saturated PLA at extrusion temperature of 210°C

General Observations:

- **Void Distribution:** The voids were again observed on the top side of the specimen with a most of the voids clumped together, distribution of voids was tightly packed near the top surface.
- **Void Shape:** The majority of the voids had an oval shape and we also observed some of the fibrous structure inside some of the larger voids.
- **Average Void Size:** In the range of 0.23 μm.

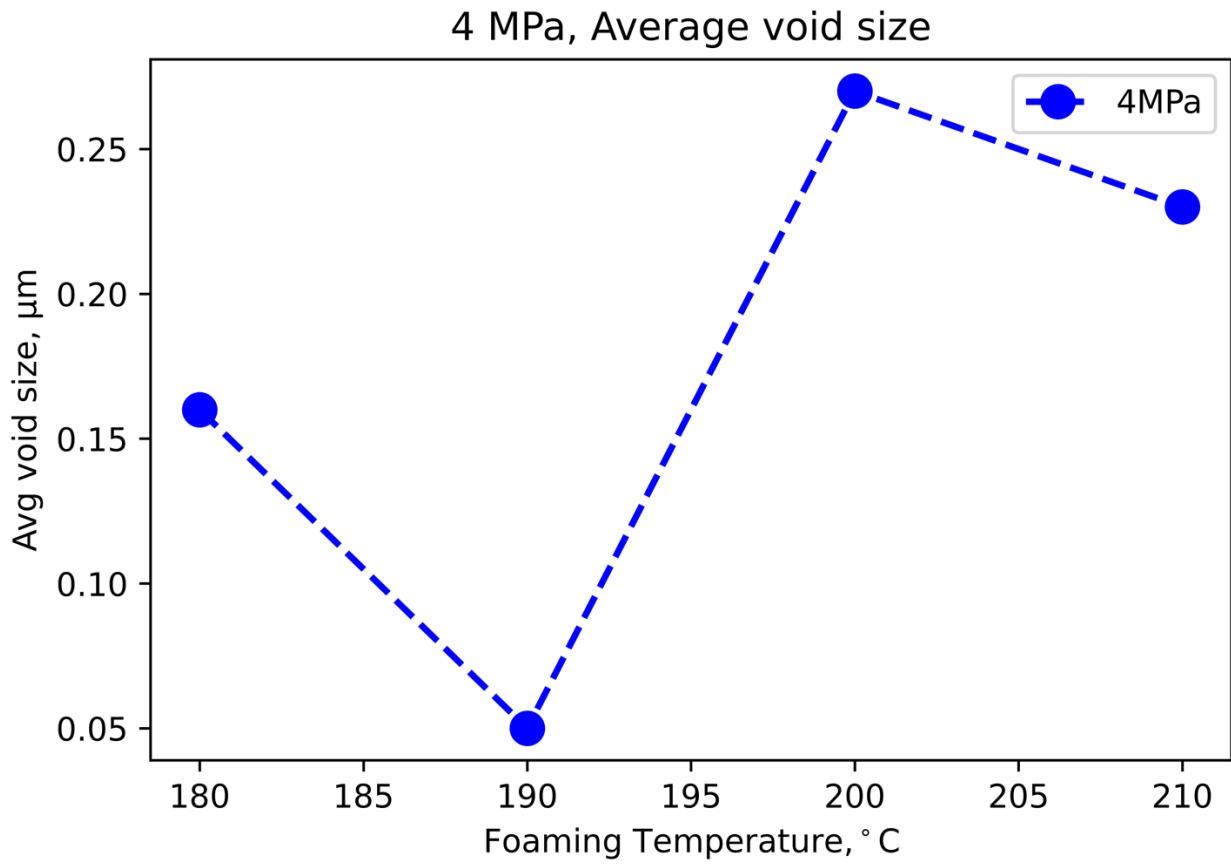


Figure 29: Average Pore Size for 4MPa saturated 3D Printed PLA at various extrusion temperatures

Chapter 4.0 Tensile Behavior

4.1 Tensile Behavior of Solid-State Foamed and Unfoamed PLA

The tensile strength plot for solid-state PLA, foamed after 3D printing and saturating the PLA in 1.5 MPa CO₂, followed by foaming in water at 80°C, reveals several key observations:

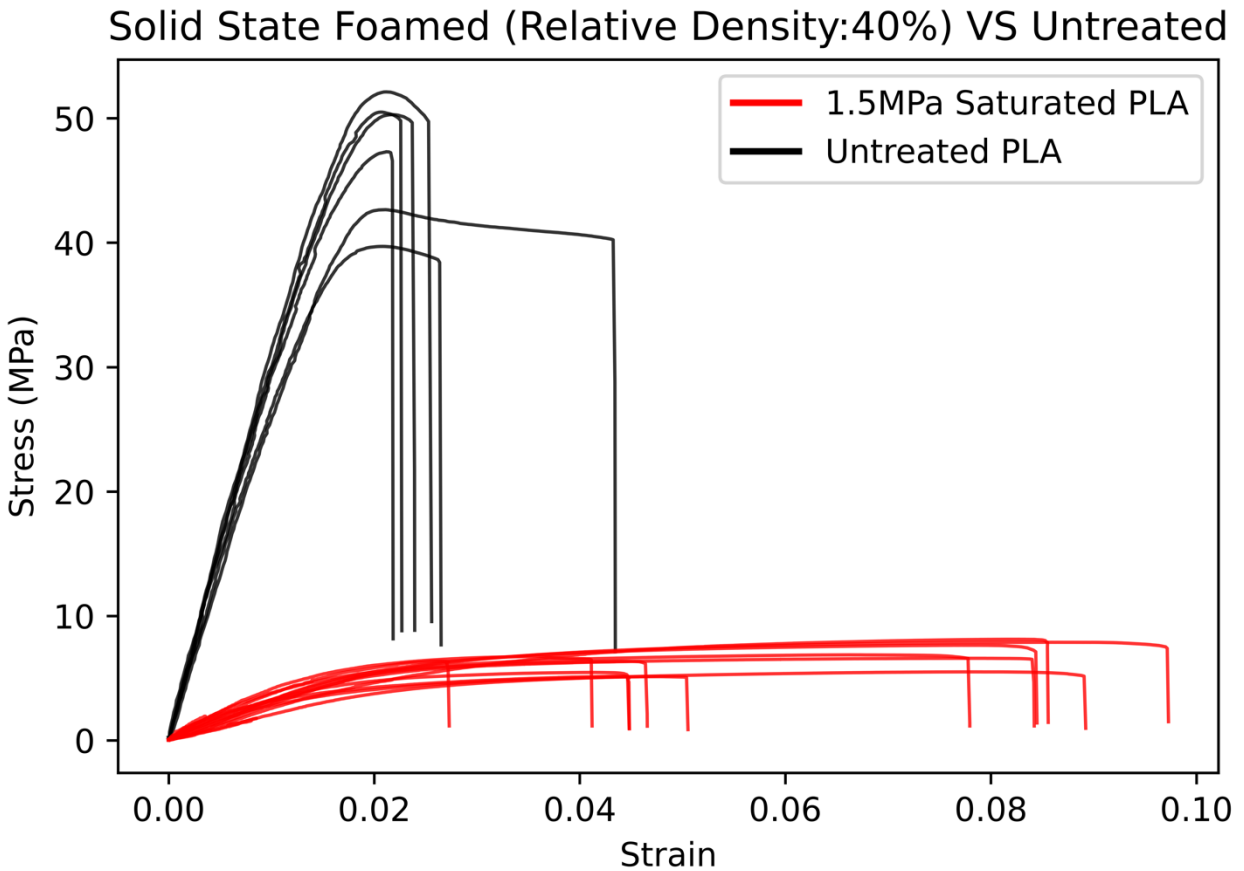


Figure 30: Tensile Test Plot for Solid-State Foamed vs non-foamed 3D Printed Type-4 Dogbone specimens

1. Tensile Strength:

The unfoamed PLA samples exhibit significantly higher tensile strength of about 50MPa compared to the foamed samples of about 7MPa. The foamed samples show a noticeable reduction of 86% in tensile strength, indicating that the foaming process has compromised the material's ability to withstand tensile loads.

2. Higher strain to failure:

The plot clearly shows that the 1.5MPa saturated PLA filament exhibits significantly higher strain to failure compared to the untreated PLA filament. The saturated filament not only withstands higher initial stress but also deforms more before breaking, indicating its ability to endure greater deformation. This higher strain to failure means the saturated PLA filament can absorb more energy and handle more extensive deformation before failure, demonstrating its improved toughness and performance. The CO₂ saturation process at 1.5MPa effectively enhances the mechanical properties of PLA, making it a more robust and resilient material.

3. Impact of Foaming:

The introduction of foaming at 80°C in water has significantly altered the mechanical properties of PLA. The presence of voids and possible structural irregularities within the foamed samples likely contributes to the reduced tensile strength but increased ductility. The foaming process appears to create a more compliant material that can deform more extensively before failing, although at the cost of tensile strength.

4. Variability in Results:

Both sets of samples (foamed and unfoamed) exhibit some variability in their tensile responses, as indicated by the spread of the curves. This suggests that the foaming process might introduce inconsistencies in the material structure, potentially due to variations in bubble size, distribution, and overall uniformity within the samples.

4.2 Tensile Behavior of 1 MPa Saturated PLA Filament with Varying Extrusion Temperatures

The following section details the tensile behavior of PLA filaments saturated at 1 MPa CO₂ and subsequently 3D printed at varying extrusion temperatures. The tensile tests were conducted to analyze the impact of these extrusion temperatures on the mechanical properties of the PLA samples.

4.2.1 Tensile Test Results at 180°C

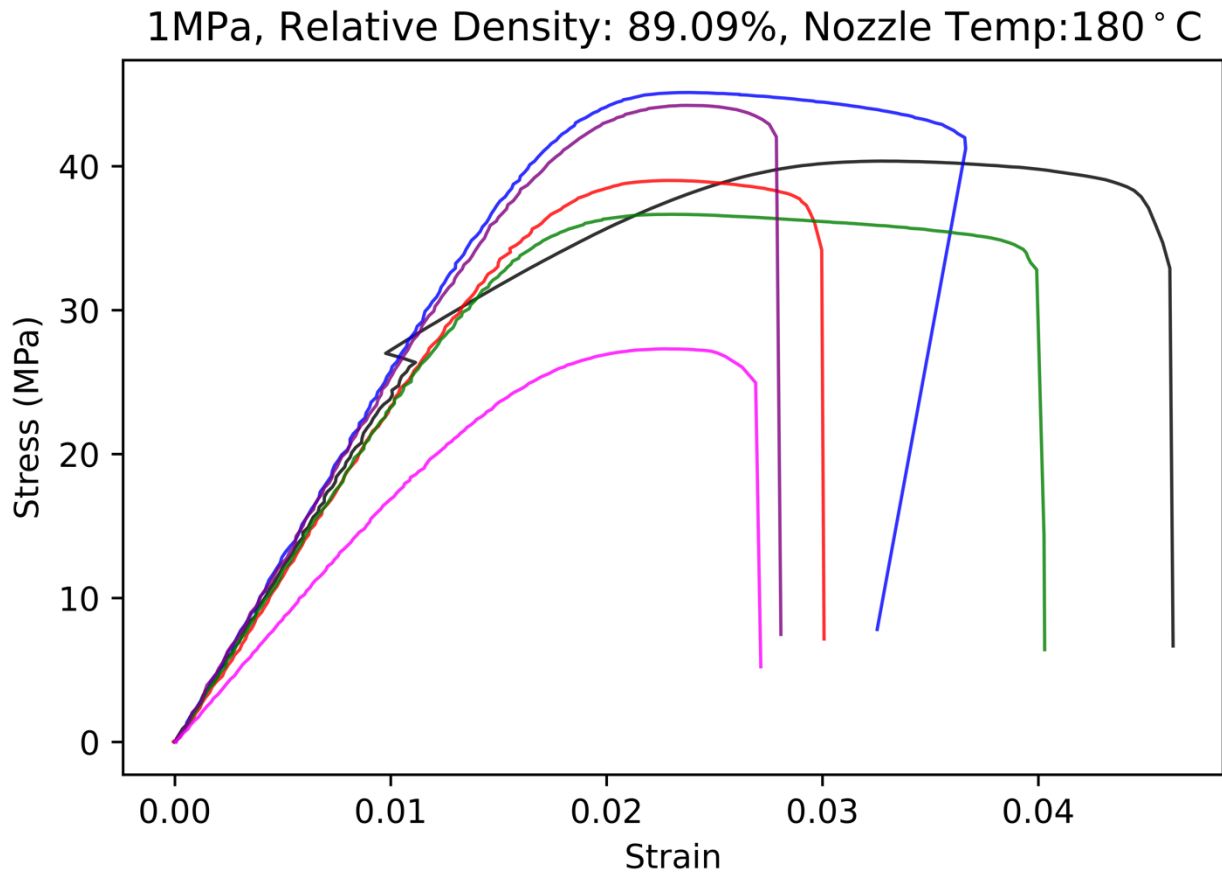


Figure 31: Tensile Test Plot for 1MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 180°C

Observations:

The stress-strain curves for the samples extruded at 180°C show relatively high tensile strength, reaching peak stresses around 40 MPa. The curves exhibit a sudden drop after reaching peak stress, indicating a brittle nature with minimal plastic deformation before failure. There is variability in the strain at failure, suggesting that while some samples can undergo some degree of deformation, others fail earlier. The relative density of 89.09% suggests that the material retained a significant portion of its structural integrity post-foaming.

4.2.2 Tensile Test Results at 190°C

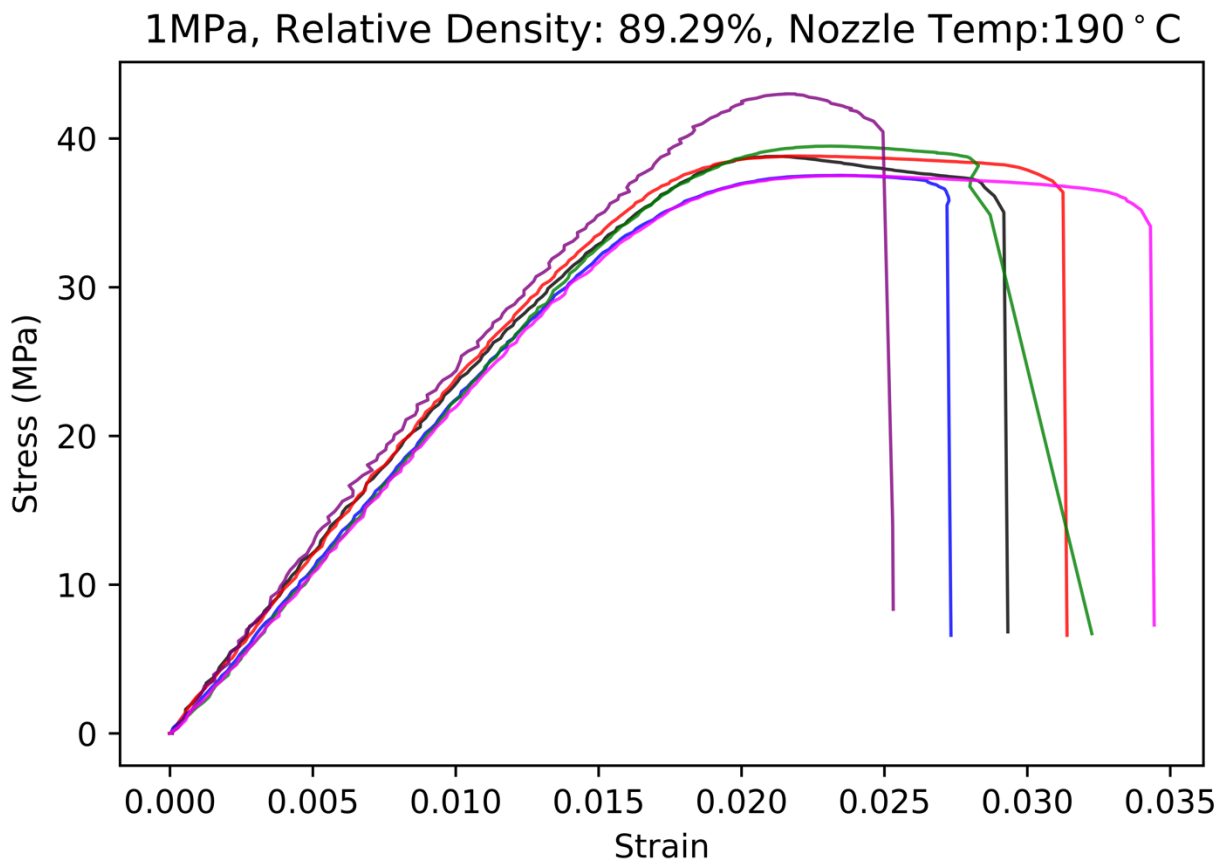


Figure 32: Tensile Test Plot for 1MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 190°C

Observations:

The stress-strain curves for the samples extruded at 190°C also show high tensile strength, with peak stresses comparable to those observed at 180°C. The samples demonstrate a brittle failure mode, with minimal plastic deformation before failure. The strain at failure is slightly higher than the 180°C samples, indicating a marginal improvement in ductility at this temperature. The relative density of 89.29% remains high, like the 180°C samples, suggesting that the extrusion temperature does not significantly affect the structural integrity at this level.

4.2.3 Tensile Test Results at 200°C

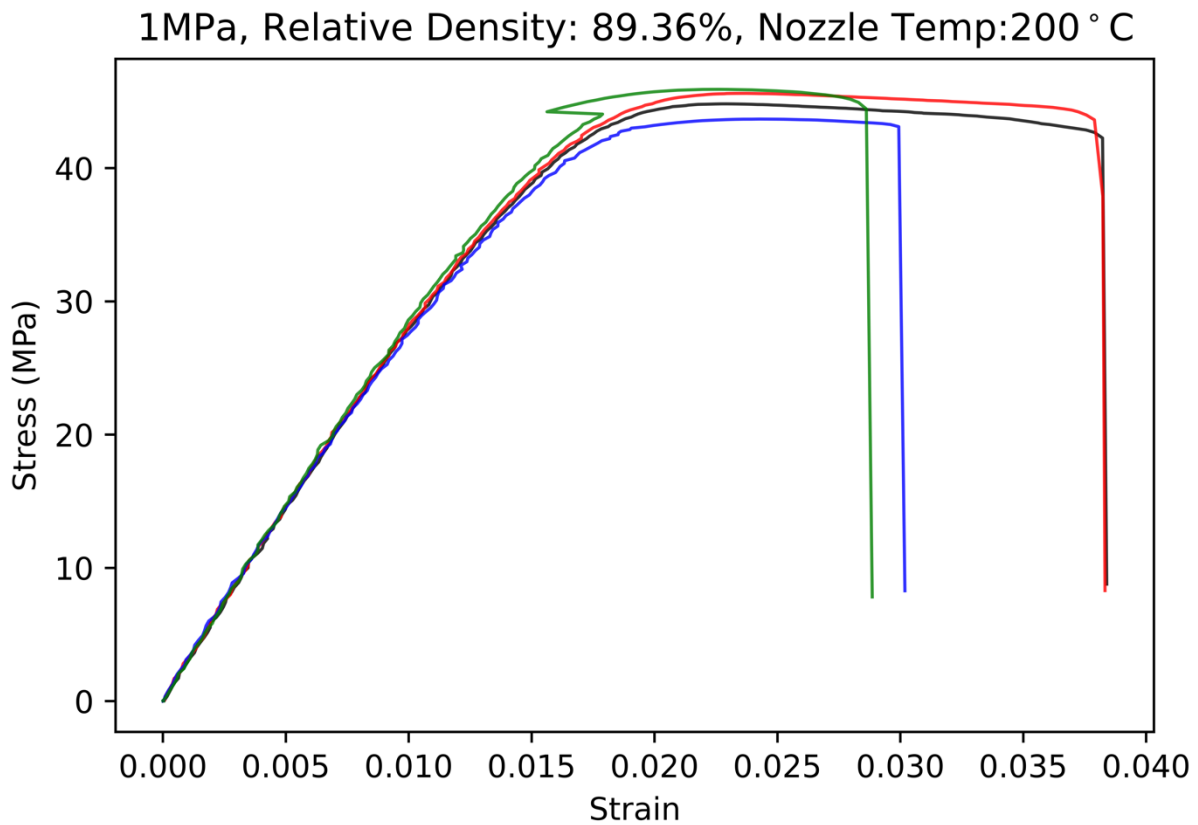


Figure 33: Tensile Test Plot for 1MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 200°C

Observations:

The stress-strain curves for the samples extruded at 200°C remained in the 40MPa tensile strength range. The failure mode remains brittle, with minimal plastic deformation observed before failure. The relative density of 89.36% indicates that the material maintains its structural integrity, with minimal impact from the higher extrusion temperature.

4.2.4 Tensile Test Results at 210°C

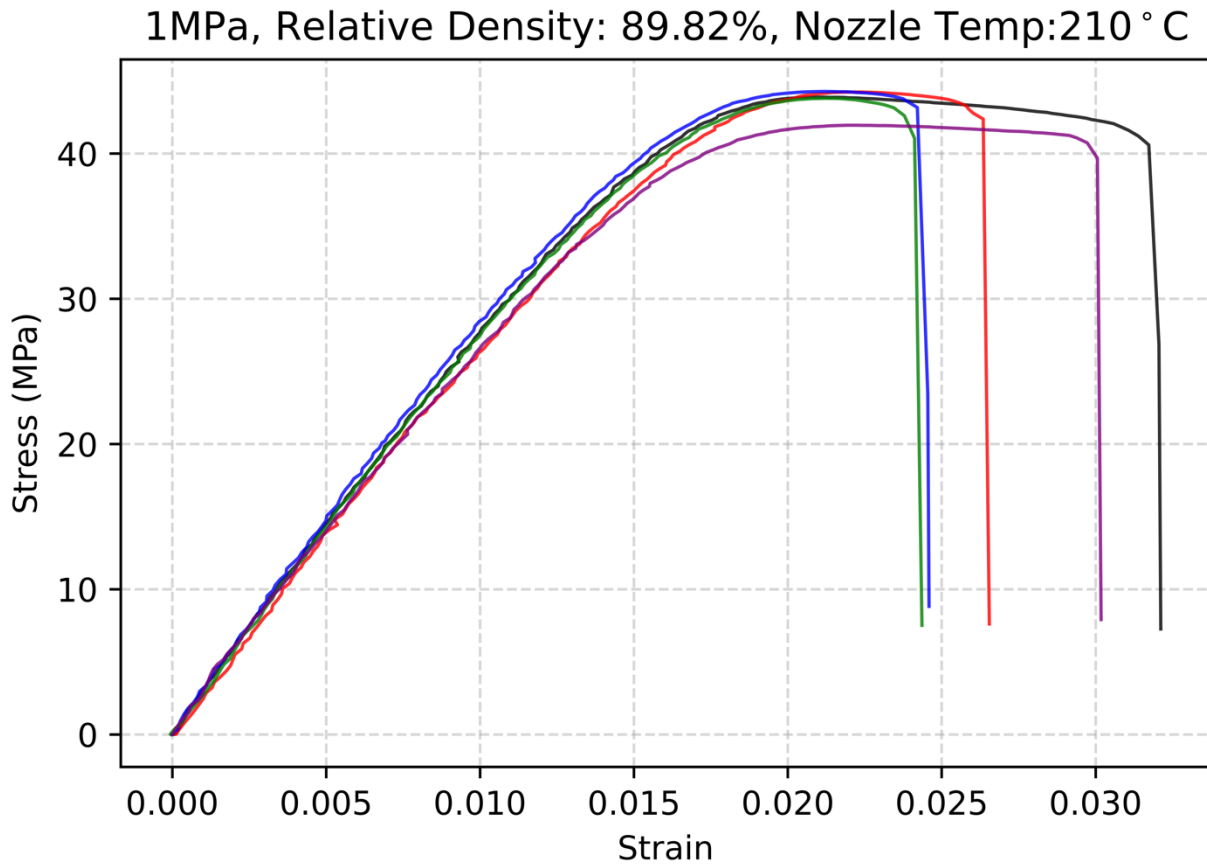


Figure 34: Tensile Test Plot for 1MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C

Observations:

The stress-strain curves for the samples extruded at 210°C show consistent high tensile strength, with peak stresses around 40 MPa. The samples exhibit a brittle failure mode, similar to those extruded at lower temperatures. The strain at failure is comparable to the 190°C samples, indicating stable ductility at higher temperatures. The relative density of 89.82% suggests that the structural integrity of the material remains largely unaffected by the extrusion temperature.

4.3 Tensile Behavior of 3 MPa Saturated PLA Filament with Weekly Printing over Four Weeks

The following section details the tensile behavior of PLA filaments saturated at 3 MPa CO₂ and subsequently 3D printed at a constant extrusion temperature of 210°C. The samples were printed weekly over a span of four weeks to observe the effects of prolonged desorption on the mechanical properties of the PLA samples. It is important to note that for week 1, the samples were first allowed to desorb for 3 hours before printing due to the soft and pliable nature of the PLA filament at pressures higher than 2.5 MPa.

4.3.1 Tensile Test Results for Week 1

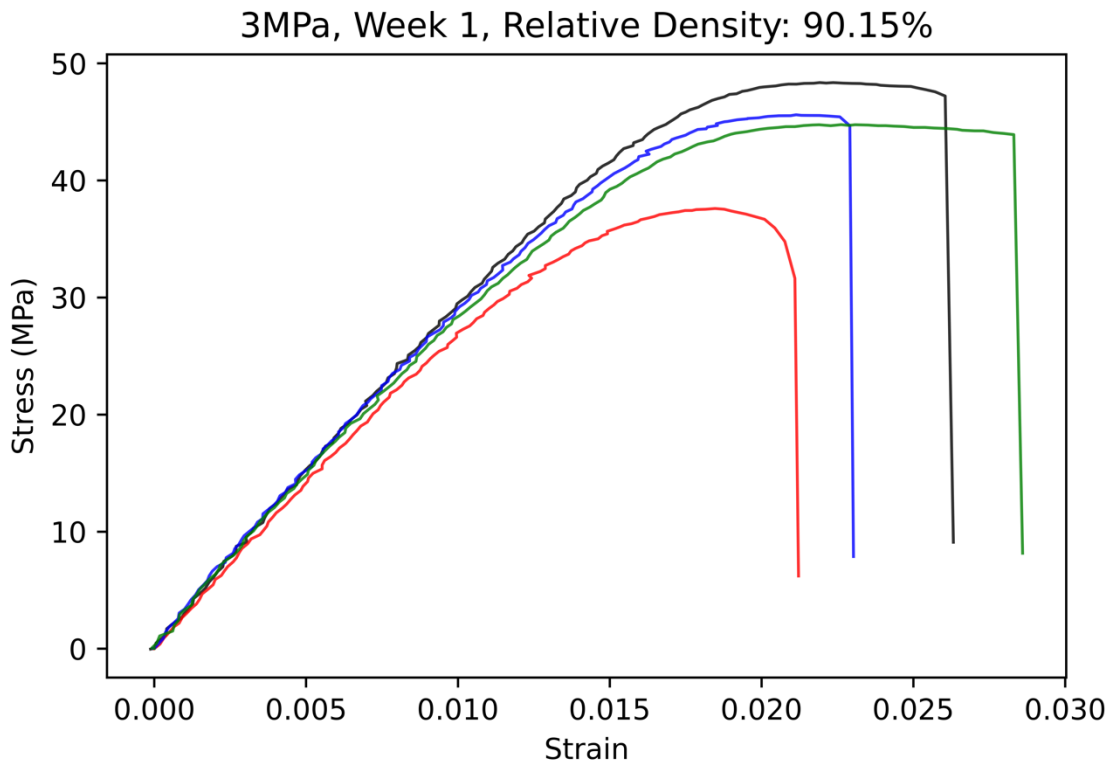


Figure 35: Tensile Test Plot for 3MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C for week 1

Observations:

The stress-strain curves for the samples printed in week 1 show relatively high tensile strength, reaching peak stresses around 45 MPa. The curves exhibit a brittle failure mode with minimal plastic deformation before failure. The strain at failure is relatively consistent across the samples, indicating a uniform response to tensile loading. The relative density of 90.15% suggests that the material retained a significant portion of its structural integrity post-desorption.

4.3.2 Tensile Test Results for Week 2

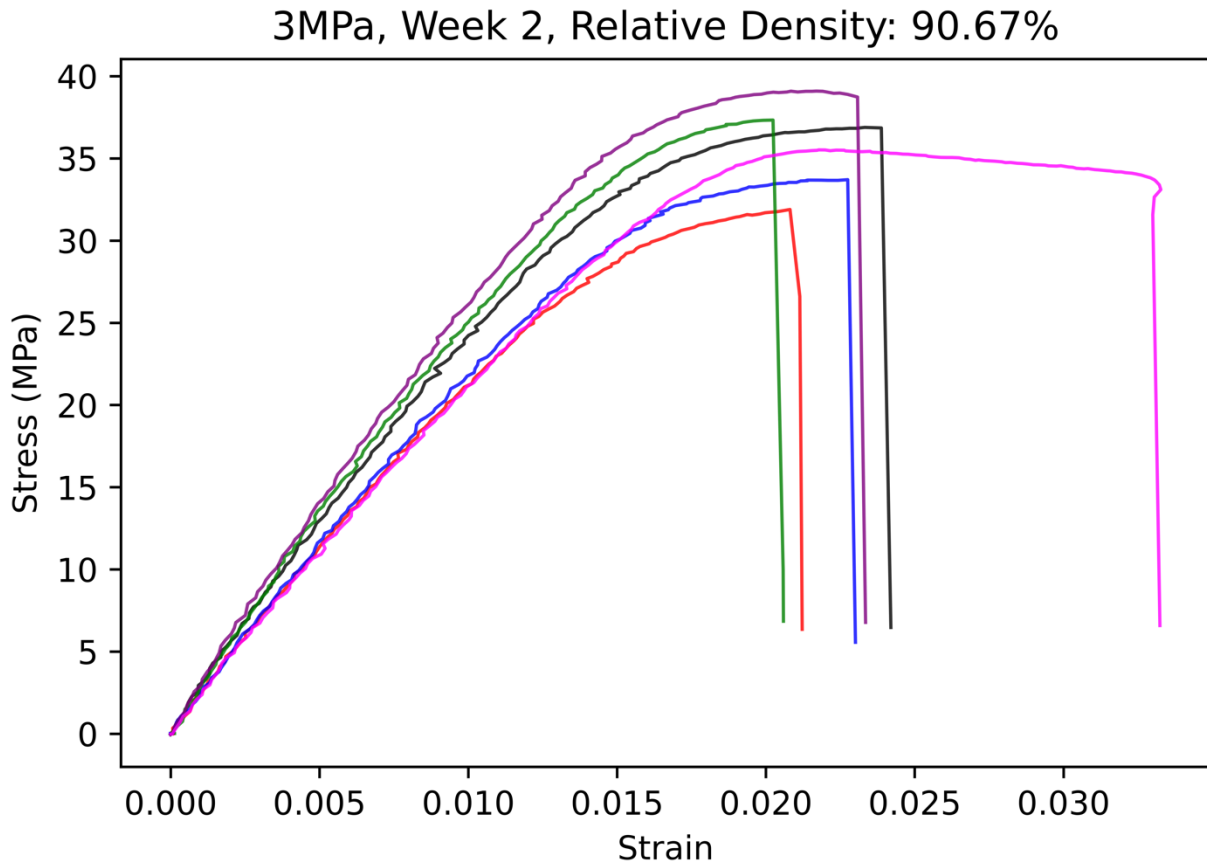


Figure 36: Tensile Test Plot for 3MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C for week 2

Observations:

The stress-strain curves for the samples printed in week 2 also show high tensile strength, with peak stresses comparable to those observed in week 1. The samples demonstrate a brittle failure mode, with minimal plastic deformation before failure. The strain at failure shows a slight increase compared to week 1, indicating a marginal improvement in ductility. The relative density of 90.67% remains high, suggesting that the material's structural integrity improved slightly post-desorption.

4.3.3 Tensile Test Results for Week 3

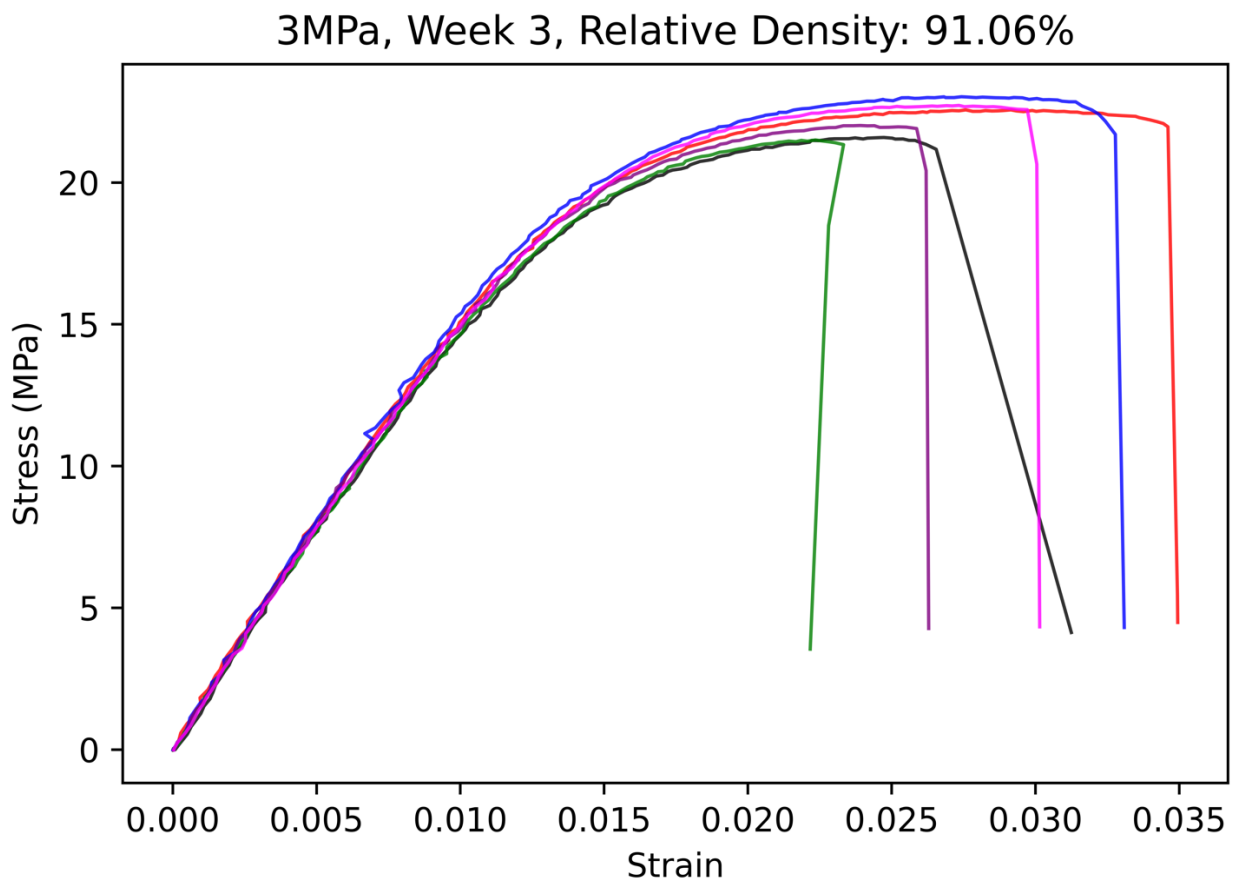


Figure 37: Tensile Test Plot for 3MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C for week 3

Observations:

The stress-strain curves for the samples printed in week 3 exhibit a further increase in peak stress, with values reaching around 50 MPa. The failure mode remains brittle, with minimal plastic deformation observed before failure. The strain at failure is higher compared to weeks 1 and 2, indicating improved ductility with prolonged desorption. The relative density of 91.06% suggests continued improvement in the material's structural integrity over time.

4.3.4 Tensile Test Results for Week 4

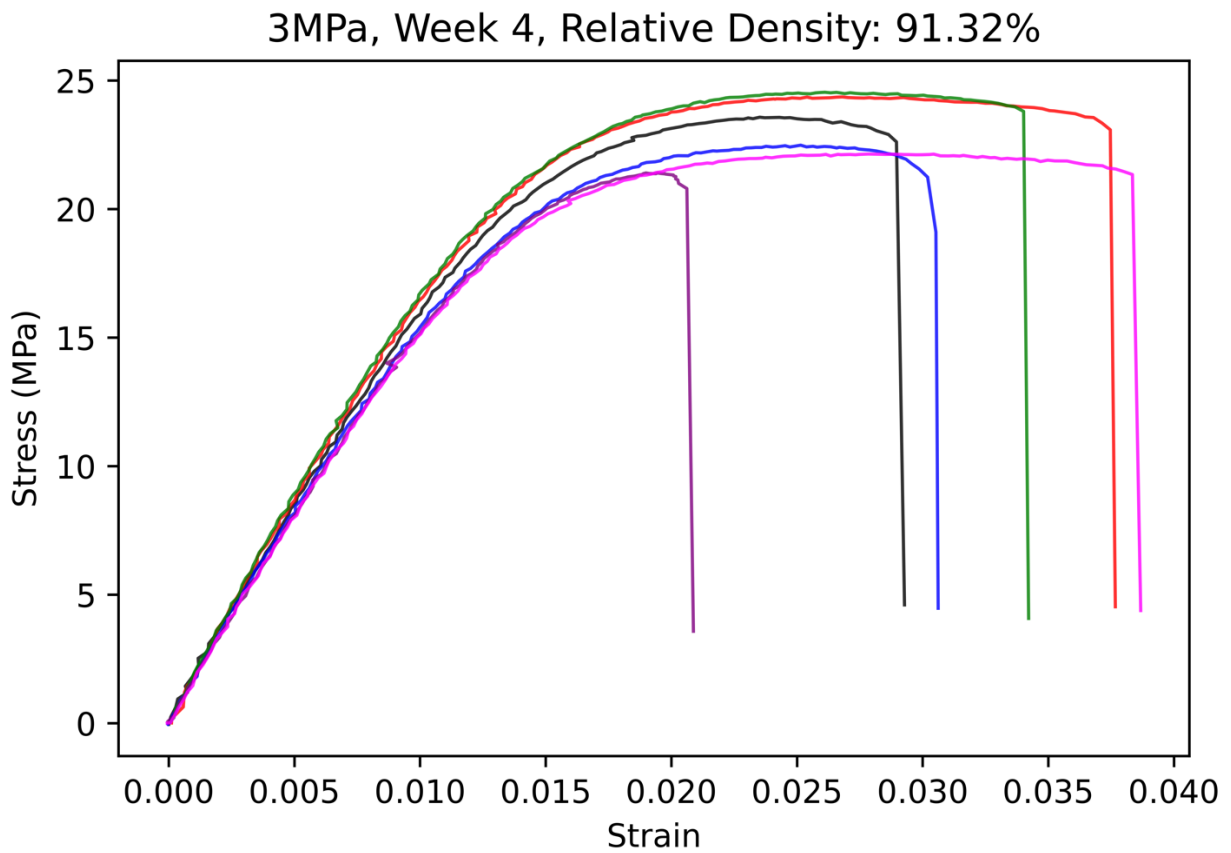


Figure 38: Tensile Test Plot for 3MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C for week 4

Observations:

The stress-strain curves for the samples printed in week 4 show consistent high tensile strength, with peak stresses around 25 MPa. The samples exhibit a brittle failure mode, similar to those printed in earlier weeks. The strain at failure is comparable to week 3, indicating stable ductility with prolonged desorption. The relative density of 91.32% indicates that the material maintained its structural integrity, with minimal impact from the extended desorption period.

4.4 Tensile Behavior of 4 MPa Saturated PLA Filament with Varying Extrusion Temperatures

The following section details the tensile behavior of PLA filaments saturated at 4 MPa CO₂ and subsequently 3D printed at varying extrusion temperatures. The tensile tests were conducted to analyze the impact of these extrusion temperatures on the mechanical properties of the PLA samples.

4.4.1 Tensile Test Results at 180°C

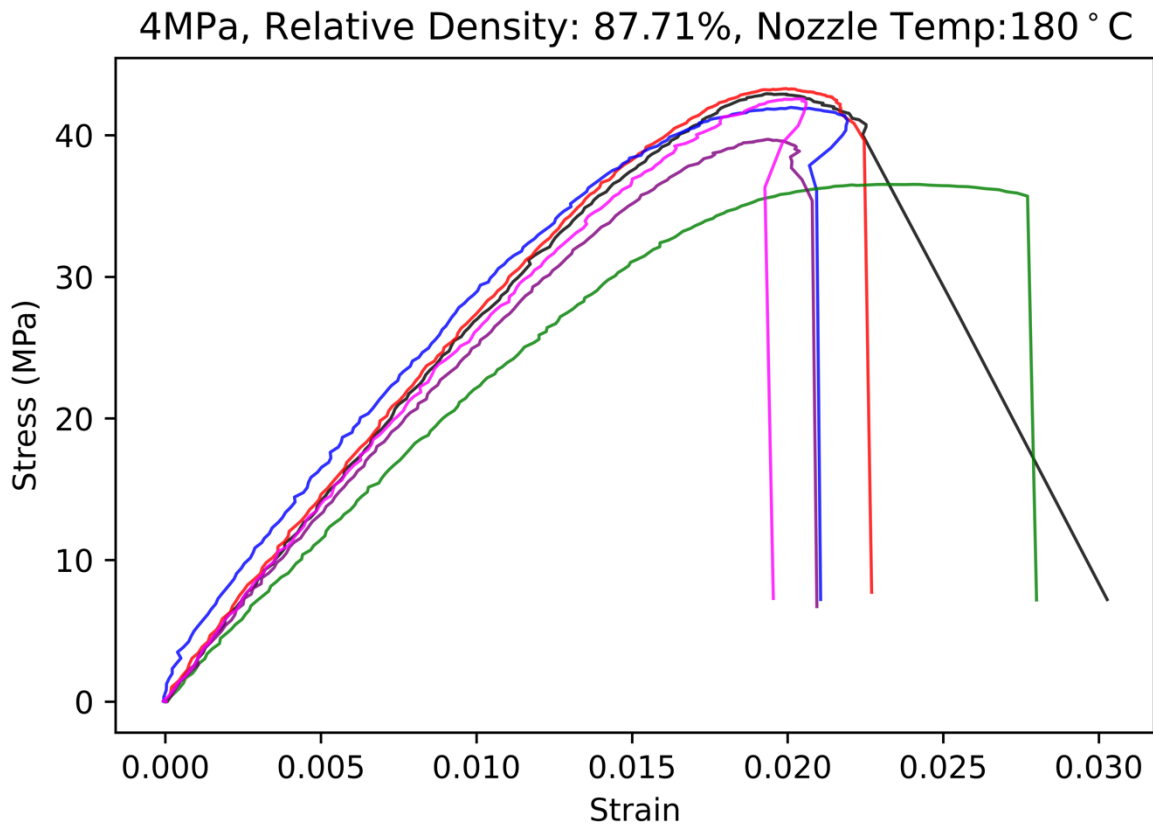


Figure 39: Tensile Test Plot for 4MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 180°C

Observations:

The stress-strain curves for the samples extruded at 180°C show relatively high tensile strength, reaching peak stresses around 40 MPa. The samples exhibit a brittle failure mode with minimal plastic deformation before failure. There is some variability in the strain at failure, suggesting a degree of inconsistency in the material's response to tensile loading. The relative density of 87.71% indicates that the material retains most of its structural integrity post-saturation and foaming, despite some loss in density.

4.4.2 Tensile Test Results at 190°C

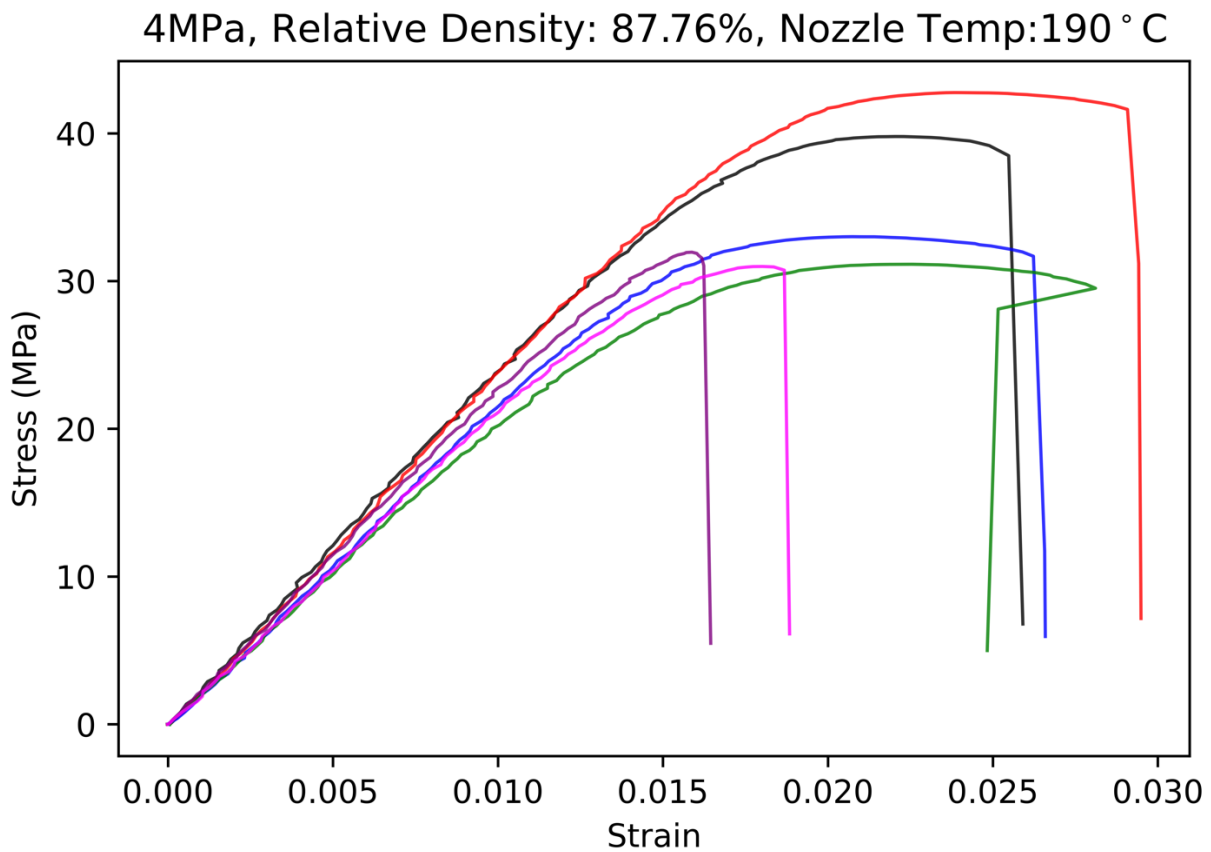


Figure 40: Tensile Test Plot for 4MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 190°C

Observations:

The stress-strain curves for the samples extruded at 190°C also show high tensile strength, with peak stresses comparable to those observed at 180°C. The samples demonstrate a brittle failure mode, with minimal plastic deformation before failure. The strain at failure is slightly higher than the 180°C samples, indicating a marginal improvement in ductility at this temperature. The relative density of 87.76% remains high, similar to the 180°C samples, suggesting that the extrusion temperature does not significantly affect the structural integrity at this level.

4.4.3 Tensile Test Results at 200°C

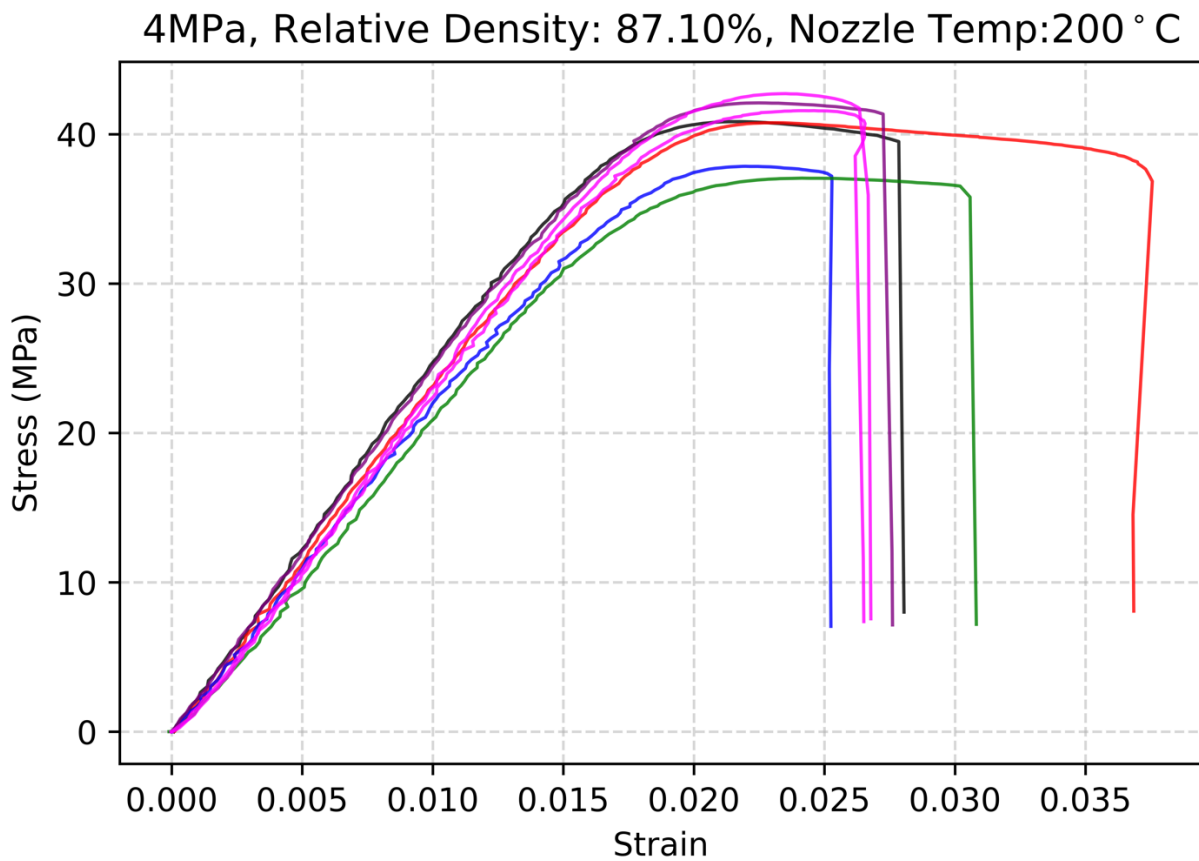


Figure 41: Tensile Test Plot for 4MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 200°C

Observations:

The stress-strain curves for the samples extruded at 200°C exhibit consistent high tensile strength, reaching around 40 MPa. The failure mode remains brittle, with minimal plastic deformation observed before failure. The strain at failure shows a further increase compared to 190°C, indicating an improvement in ductility. The relative density of 87.10% suggests that the material maintains its structural integrity, with minimal impact from the higher extrusion temperature.

4.4.4 Tensile Test Results at 210°C

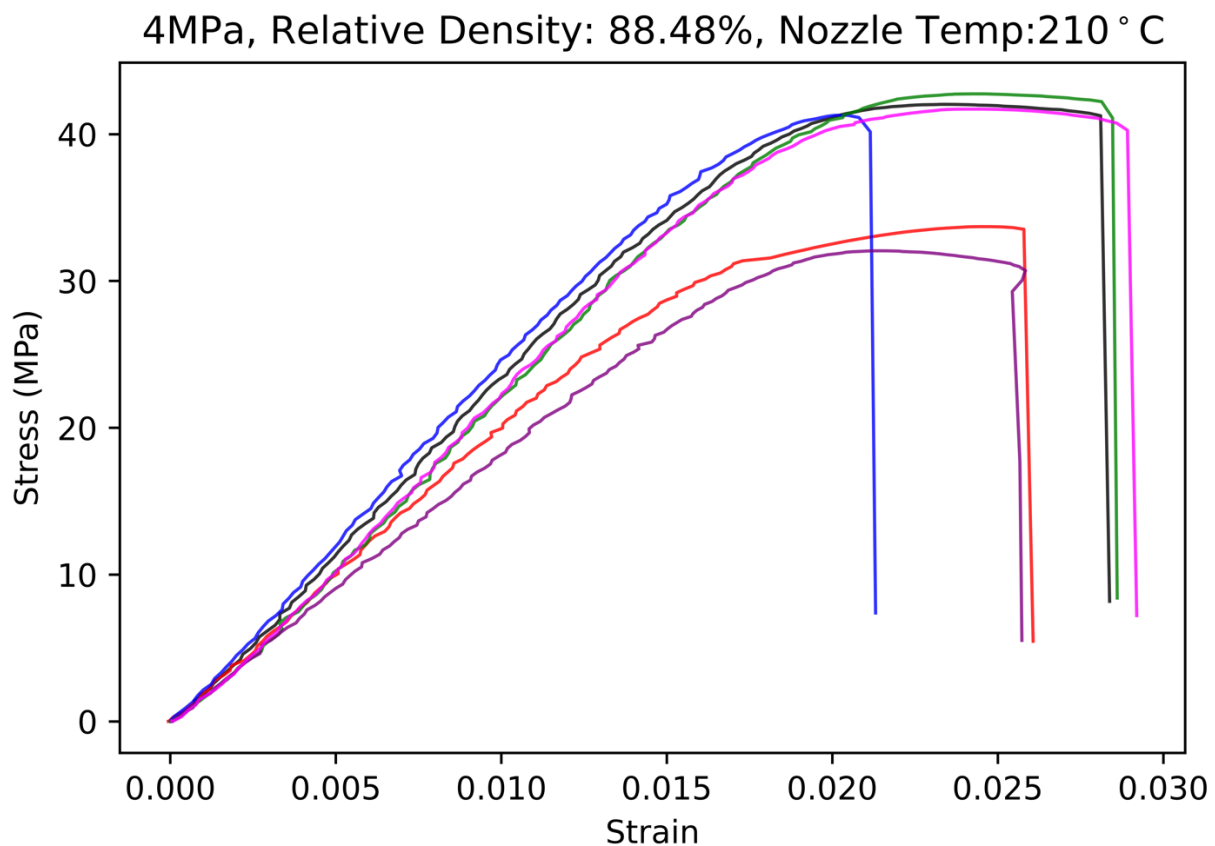


Figure 42: Tensile Test Plot for 4MPa CO₂ saturated PLA filament 3D Printed Type-4 Dogbone specimens at Nozzle temperature 210°C

Observations:

The stress-strain curves for the samples extruded at 210°C show consistent high tensile strength, with peak stresses around 40 MPa. The samples exhibit a brittle failure mode, similar to those extruded at lower temperatures. The strain at failure is comparable to the 200°C samples, indicating stable ductility at higher temperatures. The relative density of 88.48% indicates that the structural integrity of the material remains largely unaffected by the extrusion temperature.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

This study explored the mechanical properties and microstructure of Polylactic Acid (PLA) processed through 3D printing with CO₂ saturation. We explored the possibility of 3D printing microcellular porous structures across a printed geometry but after observing the results and facing several parametric challenges of using a 3D printer to mimic similar results we had with the solid-state foaming process, it's evident that creating microcellular pores in PLA through 3D printing is not feasible. From our experiments we have a clear picture that 3D printing process behaves very similar to extrusion process where the polymer is completely melted before it's been given a shape. Thus, in doing so we lose almost all the gas trapped in the polymer which results in a very low porous/void density of about 10%. The primary conclusions are as follows:

1. **Tensile Behavior:**

- **Brittleness:** The tensile tests revealed a very brittle nature of the specimens after 3D printing with saturated filament. The brittle fracture patterns indicate that it compromises tensile strength significantly.
- **Gas Removal:** The 3D printing process significantly removed the gas from the saturated filament, resulting in a relative density ranging between 80-90%. This shows that the gas sorption and subsequent desorption phases are critical in defining the final material properties.
- **Collapse of Porous Structures:** Melting of the PLA polymer during the 3D printing process results in a lack of porous structure, due to the fact that PLA loses gas at the nozzle.

When comparing solid-state foamed and unfoamed PLA, the unfoamed samples had significantly higher tensile strength (~50 MPa) compared to the foamed samples (~7 MPa), showing an 86% reduction due to the foaming process. However, the foamed samples exhibited greater resistance before failing, with higher strain to failure. For PLA filaments saturated at 1 MPa and printed at nozzle temperatures of 180°C, 190°C, 200°C, and 210°C, the tensile strength remained consistently 10MPa below (~40 MPa) controlled specimens, displaying a brittle failure mode with minimal plastic deformation. The relative densities ranged between 89.09% and 89.82%, indicating that the printing process removed most of the gas from the filament, leading to a denser structure.

PLA filaments saturated at 3 MPa and printed weekly over four weeks showed consistent tensile strength within the range of (~40-35 MPa) in the first two weeks and dropped to 25-20 MPa from week three to four, and an average relative density of ~90.5%. Similarly, PLA filaments saturated at 4 MPa and printed at different temperatures maintained similar tensile strength (~40 MPa), and relative densities between 87.5%. The study reveals that 3D printed PLA tends to be brittle due to the removal of gas during printing, resulting in low porosity and higher density. The melting of the polymer during printing hinders the formation of a porous structure. Higher saturation pressures enhance gas uptake but increase the risk of crystallization, affecting the pore forming process.

2. **Optical Properties:**

- **Refraction of Light:** The presence of voids within the polymer caused light refraction, giving the PLA its distinct white color. This optical characteristic could have potential applications in fields where specific visual properties of materials are required.

3. **Process Parameters:**

- **Saturation Pressure:** The experiments demonstrated that higher saturation pressures (up to 4 MPa) lead to more significant gas uptake but also increase the risk of crystallization, which can hinder the pore forming process.
- **Nozzle Temperature:** The available nozzle temperature range was identified as 180°C to 210°C. Below 180°C, the polymer does not maintain a molten state necessary for printing because the melting point of PLA is 170°C.

5.2 Recommendations for Future Work

One way we can achieve cellular structure is by 3D printing PLA samples and saturating them CO₂ at different pressures and then using the solid-state foaming process to introduce a consistent cellular structure inside the polymer. As we saw from this study taking route results in the formation of cellular structure inside the PLA microstructure and further improvements can be made by optimizing the process parameters like saturation pressure and solid-state foaming temperature. A vital observation made during this study was these cellular structures are very porous in nature and they absorbed a lot of synthetic oil when they were foamed in a synthetic oil bath which makes it completely unsuitable for SEM observations. So, we switched to distilled water bath as an alternative to synthetic oil for the solid-state foaming process. The resulting samples when completely dried had no issues during the sputter coating process and were safe to observe under the scanning electron microscope.

- **High-Pressure Saturation:** Further exploration of pressures between 5-10 MPa to understand their impact on the mechanical properties and microstructure of PLA. These higher pressures could enhance gas absorption and potentially result in porous microstructure through the solid-state microcellular foaming process.
- **Layer Thickness:** Investigate the effects of reducing layer thickness during 3D printing. Thinner layers could lead to more uniform void distribution and potentially enhance the mechanical properties of the printed specimens.
- **Biodegradable Fillers:** Introduce biodegradable fillers, such as cellulose or natural fibers, to improve mechanical properties. These fillers could help reinforce the PLA matrix, reducing brittleness and enhancing toughness.
- **Crystallization Kinetics:** Conduct detailed studies on the crystallization kinetics of PLA under different saturation and foaming conditions. Understanding these kinetics could help optimize the balance between gas absorption and mechanical stability.

Chapter 6: References

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