Additive manufacturing of lightweight structures: Microfibrillated cellulose - PLA biofoams

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ABSTRACT

Extrusion-based polymer additive manufacturing (AM) technology is growing rapidly. The introduction of fiber reinforced feedstock materials and recent developments in the manufacturing systems have promulgated large scale AM of composites to create new industries and applications. Synthetic fibers such as carbon and glass fibers are commonly used to reinforce polymer composites. However, increasing environmental and long-term sustainability concerns are leading to new materials using cellulose fiber reinforcement in bio-derived polymers. These materials offer new property sets, new supply chains and have the potential to provide economical solutions leading to new applications. Large scale AM can be attractive for many different applications because of its ability to freeform manufacture complex geometries; each application may require different material properties. One of the novel application areas for large scale AM is 3D printing of lightweight materials via foaming. Although achieving low density is the key in light weighting via foaming, mechanical performance is also important for many applications. In this study the impact of micro-cellulose fibers (MFC) on foaming behavior and the mechanical properties of additively manufactured parts is investigated. MFC-polylactic acid (PLA) feedstock pellets were prepared at varying MFC content (5, 10, 15 and 20 wt.%) to understand the impact of cellulose fiber content on density and mechanical properties of the AM biocomposites. Also, the impact of extrusion speed and foaming agent content on the AM biocomposites is investigated. Although achieving uniform printed foam structure is challenging with the presence of cellulose fibers, promising results were accomplished with density values below 0.5g/cm^3.

Keywords: Additive manufacturing, biocomposites, microcellulose, cellulose fiber, foam, lightweight

INTRODUCTION

Extrusion-based polymer additive manufacturing (AM) is rapidly becoming a viable technology for advanced manufacturing. Recent developments in large scale AM have introduced the need for fibrillar reinforcing materials. While carbon and glass fibers are traditional reinforcing materials for AM composites, long-term sustainability concerns call for the use of renewable alternatives such as bio-derived polymer systems with cellulosic fibers. AM's ability to freeform production parts of complex geometries opens the method up to various applications, including the printing of lightweight materials via extrusion foaming. Extrusion foaming has been widely used to produce lightweight materials [1, 2]. Composite systems benefit from extrusion foaming methods attributable to light weighting while retaining rigidity and mechanical performance from fibrillar reinforcement. Carter et al developed rigid rod polyphenylenes through single-screw foam extrusion using butane as a blowing agent [3]. Vaikhanski and Nutt developed a composite foam sandwich structure from expandable PVC microspheres and continuous aramid fibers using vibration infiltration and heated molds [4]. Extrusion foaming can also be used to produce lightweight biocomposites. Hoffman et al utilized the Celuka technique along with chemical blowing agents to manipulate the densities of polypropylene-based wood plastic composites. The density of their wood plastic composite boards was reduced to 0.7 g/cm^3 [5]. Mengeloglu and Matuana compared neat rigid PVC and rigid PVC/wood-flour composites produced with chemical foaming agents (CFA's). They found that the PVC/wood-flour foams had improved ductility and comparable impact resistance to neat PVC [6].

There are many aspects of extrusion foaming that must be considered. Morreale et al analyzed and compared the rheological behavior of foam extruded biodegradable polymers to traditional polymers. They outlined the effects of humidity on the foaming process of certain bio-derived polymers [7]. Schroeck outlines six fundamental rules that must be considered during chemical foam sheet production. He provides information on selecting the right foaming agent for the polymer, the amount of foaming agent, the temperature profile of the extrusion line, the screw configuration, and the screen and die selection [8]. Understanding the effects that reinforcing materials and foaming agents have on the morphology of the composite is at the helm of research in this field. Wang et al examined the effect that different foaming temperatures had on the densities and microstructures of expandable microsphere/epoxy foams. They discovered high precuring extent and high foaming temperatures yielded homogeneous cell distribution. The cell distribution was correlated to the compressive strength of the foam composites [9]. Zepnik et al examined the extrusion behavior and subsequent morphologies of organic cellulose ester foams. It was shown that thermoplastic cellulose acetate demonstrated good expansion behavior at the die using HFO 1234e as a low global warming blowing agent and talc as nucleating agent [10].

Based on the research previously stated, the purpose of this study is to combine AM and extrusion foaming technologies and understand the effect of micro-cellulose fibers (MFC) on the foaming process, density, and mechanical properties of additively manufactured biocomposites. MFC-polylactic acid (PLA) feedstock pellets of varying MFC content (5, 10, 15 and 20 wt.%) were used to produce parts using big area additive manufacturing (BAAM) and tested to determine the effect of fiber content on density and mechanical properties of AM bio-composites.

EXPERIMENTAL

1. Materials

Cellulose microfibers (TC750) were obtained from CreaFill™ (Chestertown MD). CreaFill™ TC750 micro fibrillated cellulose fibers are specified as 20-30 micron in width and approximately 700 microns in length. The loose density of the fibers is 20-30 g/L. The dry-base fibers are also specified by the manufacturer as to be approximately 99.6 % pure cellulose. These cellulose microfibers were used to create a thermoplastic mixture out of PLA that were obtained from Techmer PM. The HIFILL PLA (1949, 1914, 1915, 1916, and 1917) had varying percentage infills of micro fibrillated cellulose: neat, 5%, 10%, 15% and 20% fill, respectively. For the added foaming agent (FA), Nouryon Expancel microspheres 930 MB 120 were used.

2. Additive Manufacturing

All the PLA pellets were dried at 63 ℃ for a minimum of 4 hours to reduce moisture content. A gravimetric blender was used to premix the FA with MFC-PLA pellets at the desired ratio (4 wt.%), and the mixtures were fed directly into the Big Area Additive Manufacturing (BAAM) through a vacuum system. However, due to unforeseen issues (static build up in the pellets), the material needed to be hand fed into the BAAM extruder in batches instead of through the vacuum lines. The printing parameters used in BAAM system are listed in **Table 1**. A high throughput screw which minimizes residence time and allows for lower printing speeds was used for avoiding degradation of the material from extended heat exposure. Each PLA blend was printed into a two-bead wall 25.4 cm tall hexagon with 45.7 cm wide walls.

Table 1: 3D printing parameters used for MFC-PLA bio-foam composites

Build Sheet Temp.	*100 ℃*	Tip	*205 ℃*
Barrel 1	*145 ℃*	Layer Height	*75-85 mm*
Barrel 2	*150 ℃*	Bead Width	*102 mm*
Barrel 3	*175 ℃*	Layer Time	*2:51 mins*
Barrel 4	*190 ℃*		

3. Density Measurements

The densities were measured following ASTM D792 standard. Small samples were cut using a bandsaw and all burrs were removed before testing to ensure minimal bubbles on the samples to achieve more accurate density measurements.

4. Specimen Preparation and Mechanical Testing

The additively manufactured hexagons were cut into 6 panels (one for each side) using a bandsaw and panels were sent to Huskin Machining Company, LLC for cutting compression and tensile testing specimens. The ASTM standards for rigid cellular plastics (D1621 and D1623) were followed for the specimen dimensions and mechanical (compression and tensile) testing. Because of the limited wall thickness of the printed hexagons, the dimensions of the compression testing specimens had to be scaled down following the aspect ratios in ASTM D1621 standard. Six cubic compression testing samples from each formulation at both y- (printing) and z- (interlayer) directions were cut as shown in **Fig. 1** and tested at 0.033 mm/s up to 13% strain. The tensile testing samples were cut following the ASTM D1623 standard dimensions in both y- and z-directions as shown in **Fig. 2**. While all the compression tests were completed and are shared in this manuscript, the tensile testing is still in progress.

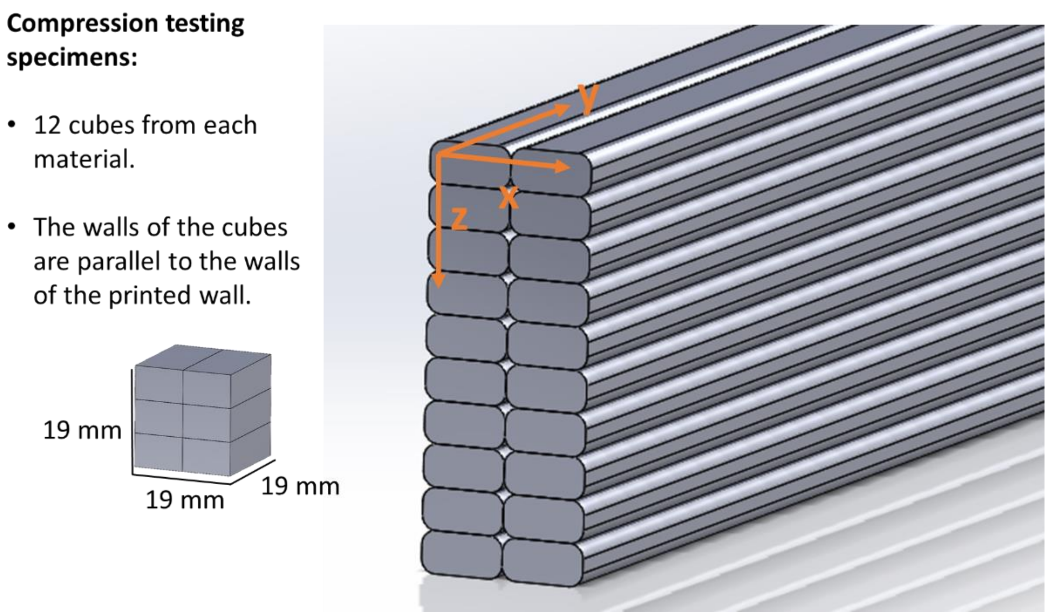

Figure 1. The compression testing specimens that are cut from printed foam hexagon walls. Six of the specimens were tested in y- (printing) direction, and the other six specimens were tested in z- (interlayer) direction.

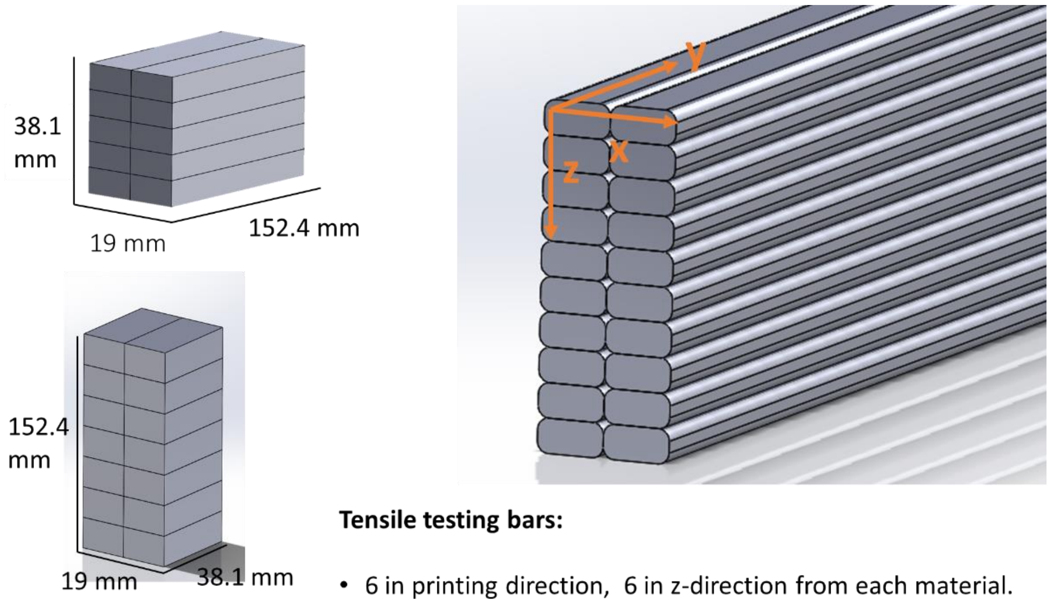

Figure 2. The tensile testing specimens that are cut from printed foam hexagon walls.

RESULTS & DISCUSSION

1. Foam extrusion of cellulose-PLA formulations

The goal of this study is to understand the impact of the presence and content of microfibrillated cellulose (MFC) on the density, microstructure and mechanical properties of 3D-printed bio-foam materials. For this purpose, commercially available micro-scale cellulose fibers have been acquired and compounded by Techmer PM at 5, 10, 15 and 20% (by weight) MFC content.

To investigate the effect of fiber content and extrusion speed on foaming behavior, initially a set of extrusion experiments were conducted using the extruder of Big Area Additive Manufacturing (BAAM) system without layer by layer printing process. For the extrusion experiments, foaming agent (FA) and MFC-PLA pellets (~2.5 kg) were premixed at 4 wt.% FA ratio and dried. During the experiments, the premixed pellets were hand fed to the BAAM system, extruded at three different extruder speeds (i.e., 100, 200 and 300RPM) and extrudate of each formulation was collected for a duration of 1 min. The images of piles of extruded foam beads collected and a small section of the bead out of the batch of selected formulations at 200 RPM extrusion speed are given in **Fig. 3**.

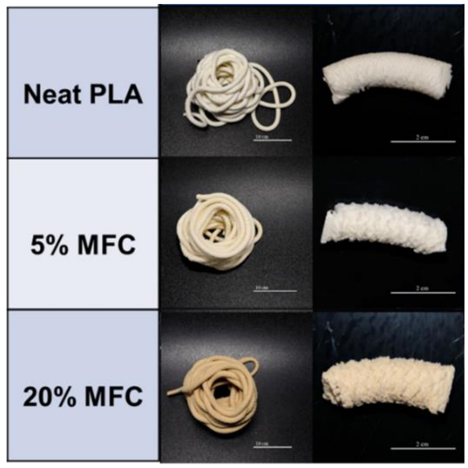

Figure 3. Images of extruded foam piles collected and a small section of the bead out of selected formulation using MFC+PLA pellets with 4% foaming agent content at varying MFC content and at 200 RPM extrusion speed.

From each batch, at least 5-6 sample pieces were taken and their densities were measured following ASTM D792 standard. The densities measured are given in **Table 2**. Although it was difficult to draw a certain trend from the initial data, lowest density values were reached with the presence of 20 % MFC. While the extrusion speed had the expected impact on the density of neat-PLA and 5 % MFC+PLA samples (i.e., density decreased with increasing extrusion speed), the impact was observed to be more complicated on the samples containing higher MFC content. While more data have to be collected prior to drawing any certain conclusion, it is clear that the presence of cellulose fibers affects the foaming behavior during extrusion. First, it is important to note that the cellulose fibers theoretically have a higher density (1.5 g/cm^3) than neat PLA blend (1.24 g/cm^3) used in this study; thus, normally a slight increasing effect in density is expected with the addition of cellulose fibers. Also, the presence of cellulose fibers may possibly be limiting/slowing down the expansion of the spheres, as well as damage some of the spheres during foaming process either due to an increase in viscosity or physically blocking them. While this might explain the change in foaming behavior with extrusion speed, another possible explanation for the decrease in density at higher speeds for neat or low fiber content PLA can be the die swell behavior. The drop in density might be because of expansion of PLA due to die swell, rather than the further expansion of the Expancel spheres. At higher fiber levels, cellulose fibers might be limiting the die swell behavior preventing further expansion of PLA matrix.

Table 2. Average densities of extruded foam beads of MFC+PLA pellets at 4% foaming agent content at varying MFC content and at different extrusion speeds.

Average Density (g/cm^3)		4% Foaming Agent Content			
Extruder Speed (RPM)	**Neat PLA**	**5% MFC+PLA**	**10% MFC+PLA**	**15% MFC+PLA**	**20% MFC+PLA**
100	0.410	0.532	0.342	0.316	0.258
200	0.370	0.435	0.453	0.408	0.308
300	0.356	0.347	0.538	0.285	0.219

2. Big area additive manufacturing of printed bio-foams and characterization

After initially focusing on the foaming behavior of MFC-PLA feedstock during extrusion at different MFC contents and extrusion speeds, next we focused on printing bio-foams to understand the impact of MFCs on the printing process and mechanical properties. Although the initial printed articles were quite non-uniform, we achieved uniform foam articles after several process modifications. Non-uniform transfer and feeding of the FA and MFC-PLA pellet premixtures into the extruder was the main reason for irregular printing, which was temporarily resolved through hand feeding. Also, low extruder speeds had to be used, i.e., below 75 RPM, to achieve uniform printing. The problem with higher extrusion speeds was the poor layer time (too low), which caused the wavy layers. Low layer time does not allow for sufficient cooling of the previously deposited layer causing it to have a low viscosity and yield strength by the time new layer is deposited. Therefore, when the new layer is being deposited, the previous layer randomly moves causing a loss of dimensional stability. Therefore, lowering extrusion speed and increasing the layer time helps with this problem; however, longer layer time leads to higher residence times for the material inside the extruder and extended exposure to high process temperatures, which in return causes the degradation of both the FA and PLA pellets and poor mechanical properties. To overcome this problem, the screw in the BAAM system was replaced with a high throughput screw, allowing for lower extrusion speeds, minimizing the residence time. After resolving the issues related to non-uniform printing, representative hexagons with 25.4 cm height and 45.7 cm side dimensions were additively manufactured out of all MFC-PLA formulations and at a FA content of 4%. **Fig. 4** shows the images of the selected formulations during printing in BAAM system.

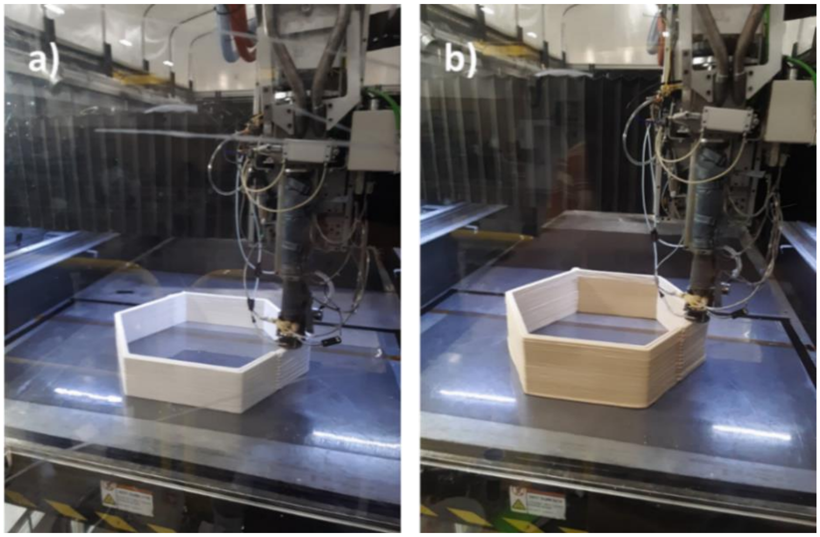

Figure 4. BAAM Printing of foam hexagons using a) neat PLA, b) 20% MFC-PLA formulations at 4% foaming agent content.

Once the printing of all the formulations were completed with the new screw and at the optimized conditions, samples were cut to measure densities. Six samples were taken from each sample, and densities were measured. The density values and standard deviations are given in **Table 3**. Although the density initially increased with the presence of cellulose fibers at 5%, as previously observed the density decreased with further increase in cellulose content. Considering the higher density of cellulose fibers (1.5 g/cm^3) compared to PLA (1.24 g/cm^3), decrease in density with increasing cellulose fiber content shows that cellulose fibers clearly affect the foaming behavior and mechanism. It is also important to note that the density measurements carried out on as extruded beads yielded lower values than the ones from printed hexagons, especially at high MFC loadings. This shows that the beads are possibly compressed during printing while they are still hot and soft with the deposition of next layer on the top of them. Therefore, the process can possibly be further optimized to achieve lower densities optimizing the printing parameters such as layer time.

Table 3. Average densities of printed MFC+PLA pellets at 4% foaming agent and at varying MFC contents.

Material	**Avg d (g/cm^3)**	**Std Dev (σ)**
Neat-PLA	0.398	0.016
5% MFC-PLA	0.441	0.015
10% MFC-PLA	0.423	0.026
15% MFC-PLA	0.408	0.022
20% MFC-PLA	0.380	0.028

Once the density measurements were completed, the cubic samples cut out from the hexagons (**Fig. 1**) were compression tested in both y-(printing) and z-(interlayer) directions to understand the impact of MFC content on mechanical properties of printed MFC-PLA foams. Compression yield strength and modulus values are given in **Fig 5**. It was observed that the compressive strength initially increased in both y- and z- directions with the addition of MFCs; however, it started to drop with the further increase in MFC content. It is important to note that the densities followed a similar pattern, which possibly have a significant impact on the mechanical properties. However, the change in strength was more significant than the change in density, demonstrating the effect of MFCs.

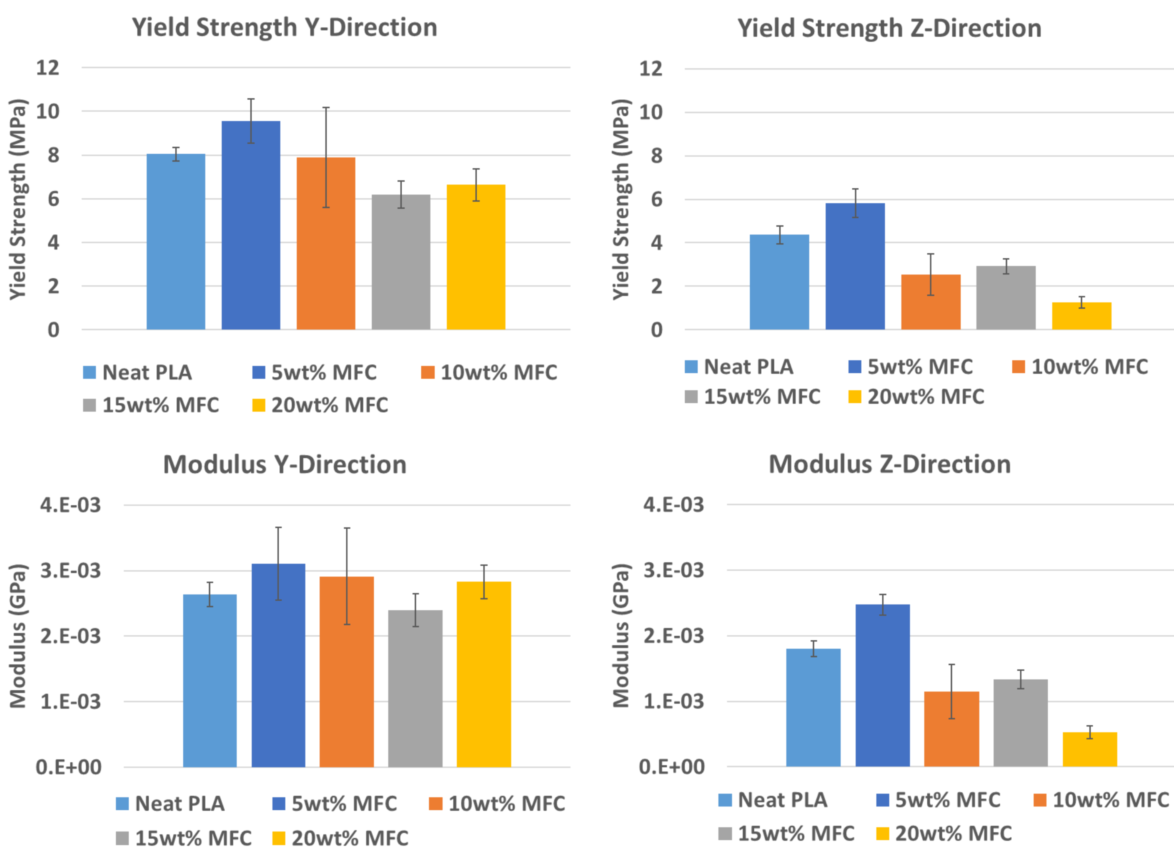

Figure 5. Mechanical properties of additively manufactured MFC-PLA bio-foams both in y-(printing) and z-(interlayer) directions at 4% foaming agent content.

Also, the decrease in strength in y-direction from 5% MFC content to 10% MFC content was minor compared to the decrease in z-direction. This can possibly be attributed to the saturation of polymer with cellulose fibers leading to poor adhesion between layers at higher fiber content. Also, another possible reason may be the impact of cellulose fibers on the cooling rate of deposited beads; however, this needs to be confirmed prior to drawing any conclusions in this regard.

The compressive modulus also followed a very similar trend to the compressive strength data. The only noticeable difference was the modulus of the higher MFC content bio-foams were relatively higher compared to neat-PLA foams. To understand the actual foaming mechanism and the microstructure, more detailed characterization of the samples has to be carried out. This work is still in progress and next steps will include tensile testing of printed foam articles, and microstructural analysis of the samples via SEM, X-ray CT and other characterization techniques.

CONCLUSIONS

Extrusion-based large scale additive manufacturing (AM) technology is rapidly growing and expanding to new application areas. Printing of lightweight materials via extrusion foaming is one of the emerging applications for large scale AM. For lightweight applications it is important to keep density low, while meeting the mechanical requirements. The goal of this study was to understand the impact of micro-fibrillated cellulose fibers (MFC) on the foaming behavior and the mechanical properties of additively manufactured parts. For this purpose, MFC-PLA feedstock pellets at varying MFC content (5, 10, 15 and 20 wt.%) were acquired and used for extrusion foaming studies at 4% expandable sphere foaming agent content. Initially, small quantities of formulations were extruded at varying speeds and the densities of beads as extruded were measured to understand the impact of extrusion speed and MFC content on foaming behavior of bio-foams. It was found that the presence of MFCs significantly impacted the foaming behavior of PLA leading to a decrease in density with increasing cellulose fiber content, although the density of cellulose fibers is expected higher than that of PLA. To achieve uniform printing, low extrusion speeds had to be used and it was observed that layer by layer printing process lead to relative increase in density, possibly due to the compression effect of newly deposited layer on the previously deposited layer while is still hot and soft. Compression tests showed that both the strength and modulus initially increased at 5% MFC content and started to decrease with further increase in MFC level. The changes in mechanical properties were more severe in z-(interlayer) direction compared to y-(printing direction). While this study demonstrated the impact of cellulose fibers on extrusion foaming behavior of printed foams, it is still in progress and more detailed study is needed to understand the foaming mechanism.

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