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Abstract. A hemp-based composite filament (CF) for a fused filament fabrication (FFF) process was developed. The designed filament is based on hemp particles obtained from stack used for cannabidiol (CBD) production and PLA, a bio-based, biodegradable, recyclable plastic. The rheological properties of virgin PLA grains, commercial PLA, and hemp-PLA filaments were analyzed. Then, hemp powder was produced and separated according to particle sizes (75-150 µm and 150-300 µm). The hemp ratio used was 5% and 10% by weight. Next, filaments were extruded from a mixture of virgin PLA grains and hemp powder. Mechanical characteristics of standard specimens were determined. Also, the shape and size of hemp particles were observed. The extrusion temperature was the most prominent parameter. Created 3D-printed parts were more ductile. Moreover, the developed filaments showed lower viscosity that was inversely proportional to the size of the hemp particles and directly proportional to the hemp ratio particles in the composites. The effect of particle size was a more influential factor on viscosity than the hemp ratio in the composite. The ultimate tensile strength (UTS) of the newly designed filaments was lower but the elongation before failure was higher when compared to commercial filaments.

Keywords: Hemp, Composite, Additive Manufacturing, FFF, PLA.

1 Introduction

With increasing concerns about climate changes, making manufacturing more environmentally friendly is the focus of many manufacturers. Thus, the maximum use of biobased, biodegradable, reusable, and recyclable materials is highly desirable.

FFF [1] is a manufacturing process and a technology that falls into the Material Extrusion category of additive manufacturing (AM) [2]. In FFF, a continuous filament is fed into a heated movable extruder head of a 3D printer. The extruder melts the filament, pushes it through a nozzle as a bead and deposits it on the gradually built work piece, layer by layer. The deposited material solidifies into an object of a desired shape. FFF uses thermoplastics like polylactic acid (PLA) which is environmentally friendly (biobased and biodegradable). Although PLA is a biobased material with good mechanical properties, it is brittle. Adding filler materials to PLA can be an effective way to overcome this problem. Different additives (but not hemp) were used to make different types of PLA composite filaments (CFs) [1]. This work uses hemp as the filler material. The objects produced from this new CF should be less brittle than the objects created from pure PLA filament. Before using hemp in the composite, some preparation steps, such as separation of unwanted portions of the plant (decortication) and producing small particles (pulverization), are usually required.

This work focuses on designing hemp-PLA CF containing different hemp particle/powder ratios as well as varying the particle sizes used in the composite. By doing so, improvements in brittleness of the material are analyzed and the changes in strength and elastic properties of the manufactured specimens are studied.

2 Literature Review

According to the American Society for Testing and Materials (ASTM) standard terminology for AM technologies ASTM F2792-12a, AM can be defined as “the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies” [2]. Materials used for AM are polymers with associated composites [3] – [7]. For common applications, PLA is the most frequently used material. It is a polymer exhibiting high mechanical strength, high melting temperature, renewability, biodegradability, and biocompatibility [6]. However, the high brittleness of PLA is a major hindrance in its wide-spread use. To overcome the challenges regarding the brittleness of PLA, blending PLA with various materials was attempted. Introduction of different additives at different amounts is described in [5] where hemp is considered as the material to blend with PLA to develop a CF that may produce high quality objects. The mechanical behaviors become more favorable for AM when hemp is used within a certain limit in the composite [3], [4].

Dogra *et al.* [3] addressed changes in mechanical behaviors due to load of hemp fibers at 10 wt.% and filament deposition geometry. They obtained 20% increase in UTS. Some researchers investigated the changes in mechanical properties due to the change of hemp ratio powder (with fixed particle size) as filler in the composite [4]. In [5], the influence of varying infill angles and different crystal structures on changes in the mechanical properties were studied.

3 Experimental Environment

In this research, hemp stalk grown for cannabidiol (CBD) is processed into powder without decortication. Such a plant is cut into pieces which are further reduced in size in a pelletizer, and finally, the pellets are pulverized into powder by a planetary ball mill. The powder is separated according to the particle sizes by sieve processing. The in-house produced hemp powder is fed through a progression of sieves of continuously smaller mesh sizes. Then, the mass of the material deposited on each sieve is measured as a fraction of the total mass of the powder or granular material. In this work, categorization and separation of the hemp powder is performed so that hemp particles of different size ranges are used for developing hemp-PLA CFs. To create CFs, the hot-melt filament extrusion process is used.

Rheological tests measure deformation of material affected by the applied stress and provide an analysis of change of the internal properties of the material due to the applied force. One of the methods to study these properties is to measure viscosity and normal stress differences [7]. In this research a capillary rheometer is used. It consists of a straight tube or capillary and a piston inside the capillary. The material to be tested is loaded or fed into the cylindrical capillary. The temperature during the test is maintained constant. The material is allowed some time to melt inside the capillary. After the material melts, the piston is moved at a controlled speed pushing the material through a die opening at the end of the capillary. The capillary used in this research is circular, thus it is a subject to Ryder-Bagley correction. The pressure of the capillary is measured at the inlet of the capillary. Apparent shear rate is computed by using the speed of the piston and dimensions of the piston and the capillary. The apparent shear stress can be calculated by using the pressure and dimensions of the capillary, thus, the apparent viscosity can be calculated from the apparent shear rate and apparent shear stress [7]. In this work, apparent viscosity curves are generated by repeating the tests at different temperatures. The circular capillary provides the best results at higher stresses. Therefore, the pseudoplastic behavior of polymer melts can be well defined by this capillary [7].

Corrections. In the case of the circular capillary, the pressure sensor cannot be inserted inside of the capillary due to the geometrical shape of the rheometer. At the inlet of the capillary the deformation causes error while measuring the pressure, consequently, Ryder-Bagley correction is required for calculating the shear stress. Also, Since Newtonian equations are used for calculating non-Newtonian behavior of the polymer melts while calculating the shear rate, Weissenberg-Rabinowitsch correction, is applied [7].

4 Methodology

In this section, a procedure for hemp particle separation according to particle sizes, the equipment used for extrusion of filament, and the equipment for creating samples for experimental analysis, with associated procedures are described. In addition, the scientific instruments used for rheological and mechanical testing with accompanying experimental methods and procedures are addressed. Finally, sample preparation and microscopy procedures are described.

Hemp Particle Separation by Size. The in-house produced hemp powder is separated into batches according to particle sizes by using a soil test machine and a stack of four sieves (425, 300, 150 and 75 µm) with the 425 µm sieve on top. After loading, the machine runs for about 10 minutes. Then, from each stage, powder is collected, weighed, and recorded.

Filament Extrusion. The in-house produced filament is extruded from 3D850 PLA pellets manufactured by Filabot. Also, a mixture of 3D850 PLA and hemp powder at different ratios and different particle sizes is used. A Filabot's EX2 filament extruder equipped with a 1.75 mm diameter nozzle is used to manufacture the filament. To remove moisture from 3D850 pellets, the pellets are dried overnight at 40 ºC. Then, the pellets are poured into the hopper of the filament extruder. For extruding hemp-PLA CF, pellets and hemp powder are mixed by shaking the mixture inside a glass bottle for a few minutes. The hemp/PLA mixture ratio is 5/95 and 10/90 by weight. The extrusion temperature is kept at 172.5 ºC. The extrusion speed is set to the low setting. The extruded filament is wound manually onto a spool.

Rheological Tests. Samples are prepared in batches of 9 grams. The sample size usually varies from 8 to 10 grams. For PLA pellets (pre-filament stage) the preparation of batches is performed by simply taking 9 grams of material from a larger lot. When testing filament samples, filament is first cut into pieces about 0.5 cm long and then 9 grams of those small pieces are used as a batch. Dynisco Rheometer Model 7002 is used to perform rheological tests. Model 7002 has two barrels for material loading. As a result, two batches can be tested at the same time to obtain more precise data.

Measuring viscosity at varying temperatures is a step-by-step process. According to the ASTM D445 standard, the barrel temperature must remain constant while measuring viscosity. Therefore, for each temperature, a new experiment is performed and thus the changes in viscosity at different temperatures are recorded. During tests, the viscosity data are recorded at a specific shear rate and a specific piston speed. The data collection points are automatically generated by the rheometer controlling software, Lab Kars. In the barrels of the rheometer, two different dies are used. The diameter and die entrance angle of the dies are the same, 1 mm and 180º respectively. The height of one die is 10 mm, while the height of the other is 20 mm.

Mechanical Tests: Tensile, Flexural, and Hardness Tests. To perform tensile, flexural, and hardness tests, specimens are 3D printed with natural PLA filament, hemp-PLA CF and PLA filament derived from hemp. 3D printers used to print these specimens were MakerBot Replicator 2 with non-heated bed, MakerBot Replicator 2x with heated bed, and Dremel 3D45 with heated bed. ASTM D638 standard was used for creating specimens for tensile testing. Specimens are 3D printed without rafts. The travel speed of the nozzle is set to 100mm/s and 120mm/s, print speed set to 30mm/s and 50mm/s, and layer height set to 0.5 mm and 0.1 mm for MakerBot and Dremel, respectively. For both printers, nozzle temperature is set to 210 ºC, and infill is set to 100%. For both the Dremel and the MakerBot Replicator 2x printers, the bed temperature is set to 40 ºC. The filament diameter was 1.75 mm.

The tensile test is performed using an Instron Universal Testing Machine 1123. The speed of the crossbar movement in the Instron equipment at the crosshead control panel is set to 0.2 inch/minute. The flexural test is performed in a similar way to the tensile test on the same testing machine.

Rex Durometer Type D Model 1600 (using ASTM D2240 standard) is used to measure the hardness of the 3D printed specimens.

Microscopic Analysis. To analyze the structure of studied filaments, microscopic analysis is performed. A small piece of filament is cut and placed into a holder or a mount specially made for this purpose. A Primotech MAT optical microscope from ZEISS is used. The reflected light stage, 50x objective, and 10x eyepiece provide 500x magnification. Zen Blue Edition software for the microscope is used to take photographs of the cross-sectional areas of filament samples. The necessary dimensions are tagged to analyze the filament structures.

5 Experimental Results and Analysis

FFF uses thermoplastic polymers. PLA, a thermoplastic obtained from natural sources, is particularly popular because it is strong, biodegradable, and easily recyclable. However, it is also brittle. Here, the hemp-PLA CF is designed to increase the ductility of parts produced by FFF. There are two extrusion processes involved, i.e., manufacturing of filament and FFF. Each process has parameters limiting the design of filament. The extrusion of a mixture of PLA pellets and hemp powder through a 1.75 mm diameter nozzle requires certain material viscosity and thus allows only a narrow range of temperatures for extrusion. Similarly, to prevent nozzle clogging during FFF, the extrusion of filament through a 0.4 mm diameter nozzle requires certain material viscosity and a certain size, distribution, and ratio of hemp particles in the hemp-PLA composite. In this work, the hemp powder used was produced from whole hemp plants (excluding leaves and roots) by cutting the plants into small pieces with a woodchipper, then pelletizing the plants with a Filabot pelletizer, and finally pulverizing the pellets with a planetary ball mill.

In this section, the experiments performed according to the methodology described in the previous section are presented and analyzed. The results of a comparative study of commercially produced filament (PLA, and hemp-PLA 15/85 composite) and in-house produced filament (PLA, hemp-PLA 5/95 and 10/90 composite with variable size particle distributions) are provided. Process parameters like temperature (directly influencing viscosity), hemp particle sizes (influencing 3D printer nozzle clogging), and hemp/PLA ratio (influencing viscosity) are determined.

5.1 Hemp Separation Based on Particle Size – Sieve Analysis.

The in-house prepared hemp powder is categorized according to the particle sizes using a soil test machine and different sieve sizes. The mass distribution of a hemp powder sample obtained via a process described in the previous section is presented in Table 1. The percentages of various particle sizes can be controlled by the duration of grinding and the rotation speed of the planetary ball mill used in pulverization. Again, due to the nozzle clogging limitations, hemp particles of sizes above 300 μm were not used.

Table 1. Sieve Analysis

Sieve Number	Particle size (μm)	Mass (g)	Percentage of particles
40	Above 425	0.5	0.33%
50	Above 300	42.9	28.24%
100	Above 150	62	40.82%
200	Above 75	43.8	28.83%
Pan	Below 75	2.7	1.78%
Total		151.9	100%

5.2 Rheological Tests

Virgin PLA. The first material that is tested in the rheometer is virgin PLA provided as granules by Filabot. The tests are repeated at temperatures ranging from 180 ºC to 230 ºC with 5 ºC steps between set points. Fig. 1 provides precise results for each experiment. It is evident that the viscosity of the material decreases with the increase in temperature. Also, the viscosity decreases with an increase in shear rate. Moreover, it can be observed that as the temperature increases the change in viscosity decreases with the increase in shear rate. Specifically, at temperatures of 210 ºC and higher, the increase in shear rate produces small changes in viscosity.

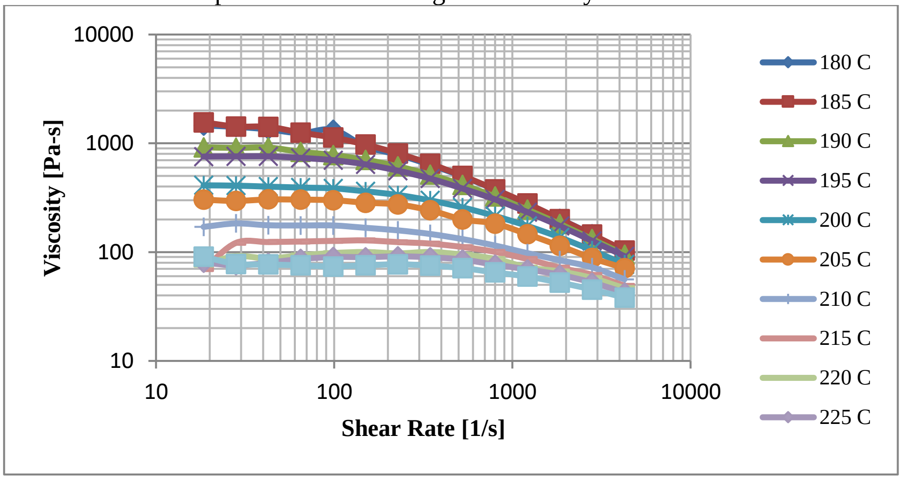

Fig. 1. Viscosity of virgin PLA granules with respect to shear rate and varying temperature

It can be noted that according to Fig. 1, few points at the lower shear rate do not comply with the notion of decreasing viscosity with increasing shear rate. These discrepancies can be explained by the fact that those points during the rheological tests were created with an insufficient amount of material inside the barrel for a valid test. Namely, during testing, data points are created from right to left. The erroneous points are included for completeness. The viscosity of fluid is measured at a given shear rate at a fixed temperature. For a viscosity measurement to be meaningful, the shear rate must be defined.

Commercial Hemp-PLA 15/85 Composite. The rheological property tests for the commercial hemp-PLA composite are performed for the temperatures from 180 ºC to 215 ºC with steps of 5 ºC between set points. As in the previous test, the results are similar except that in the case of hemp-PLA composite, viscosity cannot be studied at temperatures higher than 215 ºC as the material's viscosity is too low to obtain accurate readings. The manufacturer of the filament has recommended the filament use at temperatures of 190 ºC and higher. Flow curves at 195 ºC, 200 ºC and 205 ºC show little dependence on shear rate, i.e. the filament behaves as a Newtonian fluid.

Commercial Natural PLA. The rheological property tests for commercial natural PLA are performed for temperatures from 190 ºC to 215 ºC with the temperature steps of 5 ºC between set points. The flow curves show similar results as in the previous case.

Comparison of Viscosities with Different Compositions and Particle Sizes of Hemp in Hemp-PLA CF. Rheological experiments are conducted with filament samples prepared in the laboratory. These samples are extruded through a Filabot EX2 extruder. Hemp-PLA 5/95 CF with hemp particle sizes ranging from 150 to 300 µm is produced and tested at 190 ºC. In addition, hemp-PLA 10/90 CF with hemp particle sizes ranging from 75 to 150 µm is manufactured and tested at 190 ºC. Finally, PLA filament (without hemp or any other additive) extruded in the lab from PLA pellets is tested as well. Our previous research determined (using thermogravimetric analysis) that the commercial hemp-PLA CF is 15/85 with hemp particle sizes ranging from 25 to 30 µm. Fig. 2 shows flow curves of the above-mentioned CFs compared at 190 ºC.

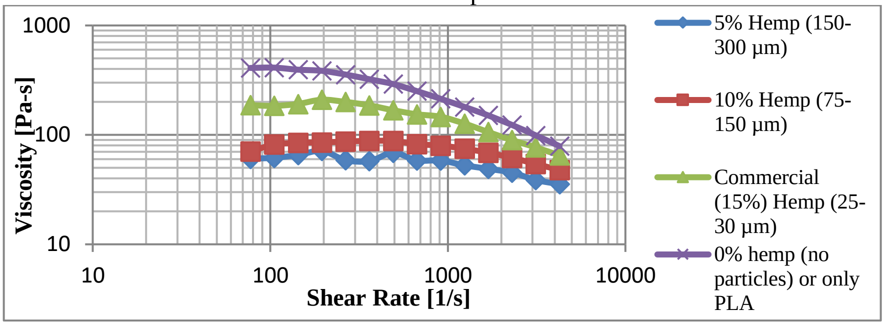

Fig. 2. Viscosities with different compositions and hemp particle sizes

The composite with the lowest hemp ratio contains the largest size particles and shows the lowest viscosity. This suggests that the viscosity is much more dependent on particle sizes than the hemp ratio at the ratios studied. When the particles are large, the viscosity is low. Conversely, when the particles are small the viscosity is high. This means that the smaller hemp particles can bond with the PLA polymer better than the larger hemp particles. Therefore, the rheological test results for pure PLA filament samples show the highest viscosity and the results for 5/95 hemp-PLA CF with the largest particle size show the lowest viscosity. Furthermore, The curves of Fig. 3 prove that the composites having smaller particles exhibit higher viscosity. It is apparent that the viscosity of 5/95 hemp-PLA having hemp particle sizes in the range 75 -150 µm is higher than the one having hemp particle sizes ranging from 150 to 300 µm.

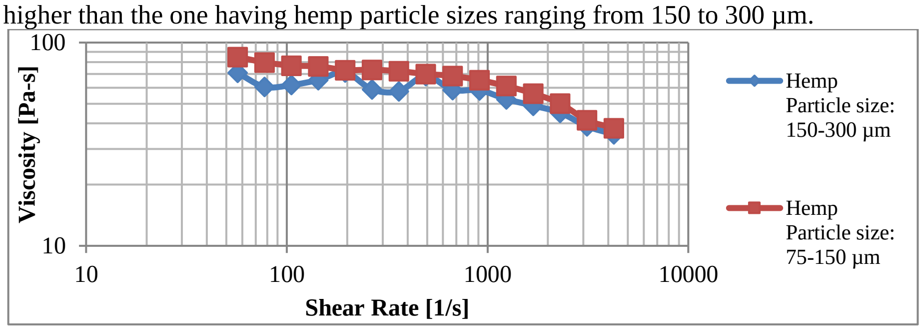

Fig. 3. Viscosities of 5/95 hemp-PLA CF samples with different hemp particle sizes

However, when the hemp particle sizes are the same, the hemp ratio in the composite plays the primary role in determining the composite's viscosity. In that case, the larger the hemp ratio in the composite the higher the viscosity. In Fig. 4, the hemp particle sizes in both composites are the same, i.e. 75-150 µm, but the 10/90 hemp-PLA composite shows higher viscosity than the 5/ 95 hemp-PLA composite.

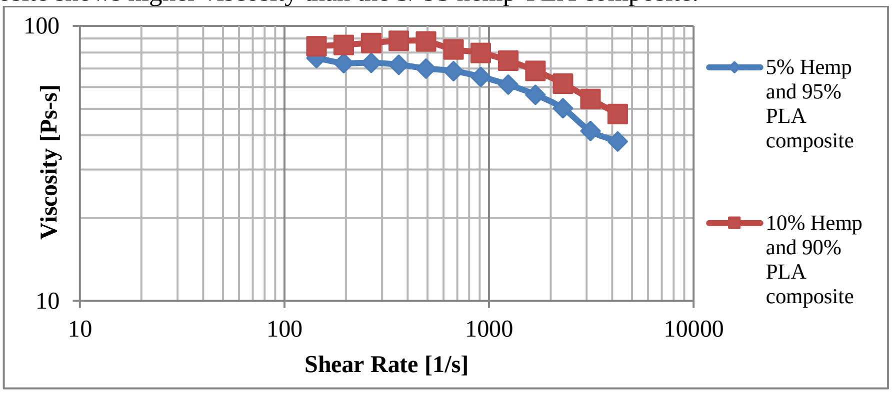

Fig. 4. Viscosities of 5/ 95 and 10/90 hemp-PLA CF, hemp 75-150 µm

5.3 Mechanical Tests

Tensile Test. The Dremel 3D printer with heated bed was used to create the standardized specimens. The tensile test was performed on the specimens produced from different commercial and laboratory-developed filaments. The test results show that all stress-strain curves are similar and that the UTS values are also close. The average UTS value for these specimens is about 40.7 MPa. The average UTS for commercial hemp-PLA filament was about 41.7 MPa. Also, it was observed that the laboratory-prepared filament samples produce specimens with lower UTS than the commercial ones. However, the elongation before failure is much higher for the laboratory developed hemp-PLA CFs. Although the specimens from commercial filament show the higher UTS value, the highest elongation before failure was seen for specimens from the laboratory-developed filament, more specifically by 5/95 hemp-PLA CF, where the strain value of 0.0615 is 55.69% higher than the average strain of the commercial filament made specimens (0.0395). Therefore, the laboratory developed filaments are more suitable for applications where the elongation before failure is more important than UTS.

Flexural Test. Three-point bending tests are performed to observe the behavior of the specimens under bending load. The goal is to determine similarities and differences among the patterns for specimens made of different filament materials. The experiments finish when the strain reaches 0.2. Although the maximum stresses at strain 0.2 differ depending on the material types of the specimens, the stress strain curves for the flexure tests have similar patterns. Therefore, the effect of applying a bending force is expected to be similar for all specimens.

Hardness Test. The hardness of the printed specimens printed from above-mentioned filaments is measured to analyze the quality of the builds in terms of brittleness. Fig. 5 shows that the specimens 3D printed from commercial hemp-PLA composites have the highest hardness, while the laboratory-developed 10/90 hemp-PLA composites have the lowest hardness and the highest ductility.

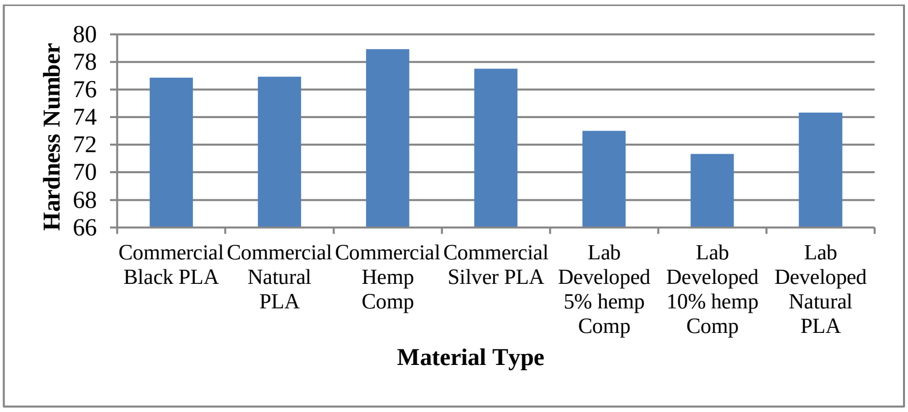

Fig. 5. Hardness for specimens printed from commercial and lab-developed filaments

Microscopic Images. An analysis of microscopic images provides important data on size, shape, amount, and distribution of hemp filler particles in PLA matrix of CFs developed in this work. As expected, the commercial natural filament does not contain any colorant particles while the commercial hemp-PLA CF contains hemp particles from 24 µm to 27 µm. The laboratory developed 5/95 hemp-PLA CF has particles sized from 150 µm to 153 µm while the laboratory developed 10/90 hemp-PLA CF contains 94 µm to 111 µm particles.

In this research, the hemp ratio used in composites has been kept up to 10% and the hemp particles to sizes smaller than 300 µm. Higher amounts of hemp and/or larger hemp particles could not be used in the CFs because such filaments tend to cause nozzle clogs during FFF.

6 Conclusions and Future Work

In this work, hemp powder obtained from stack left after harvesting for CBD was used to create hemp-PLA CF for FFF. Here, 5/95 hemp-PLA CF containing 75-150 µm hemp particles, 10/90 hemp-PLA filament containing 75-150 µm hemp particles, and 5/90 hemp-PLA filament containing 150-300 µm hemp particles were investigated. In addition, a pure PLA filament was extruded in the laboratory to compare its properties with both commercial PLA filaments and the newly designed hemp-PLA CFs. Extrusion temperature is the most prominent factor in designing a new CF.

The hardness of the specimens 3D printed from designed filaments is lower than the hardness of specimens 3D printed from a commercial PLA filament. The 10/90 hemp-PLA CF with 75-150 µm hemp particles has the lowest hardness as well as the brittleness.

The viscosity values of the newly designed CFs are lower than the viscosity values of commercial PLA filaments at any constant temperature. Therefore, these filaments exhibit better flow characteristics than the commercial ones and are, thus, easier to use in 3D printers. With an increase in the hemp ratio in the composite, the viscosity increases. However, the hemp particle size in the composite is a more dominant factor than the hemp ratio. The larger the particles the lower the viscosity.

The tensile strength of the designed CFs was found to be lower than that of the commercial ones, while the elongation before failure was higher.

Currently, the major limitation is the in-house produced hemp powder that is made from the whole hemp plant excluding the leaves. Future work could focus on special parts of the hemp plant, like bast fibers or hurd fibers for producing hemp powder which may lead to improved filament properties for 3D printing. The process could include full decortication leaving only hemp fibers that can be subsequently cut into lengths appropriate for AM. With such a setup, hemp particle geometry could be investigated, since in some composites longer and thinner particles may significantly influence the composite's characteristics.

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