Characterizing short-fiber-reinforced composites produced using additive manufacturing

Marcus Ivey, Garrett W. Melenka, Jason. P. Carey and Cagri Ayranci*

Facility of Engineering, Mechanical Engineering, University of Alberta, Edmonton, Canada

Abstract  Material extrusion additive manufacturing (MEAM), a sub-branch of three-dimensional (3D) printing is growing in popularity. Test specimens were 3D-printed using commercial polylactic acid (PLA) filament, and PLA filament reinforced with short-carbon fibers (PLA/CF). As-printed specimens and specimens that were annealed at three different temperatures, then subjected to tensile testing. The internal microstructures of the samples were also examined. The effects of the short-carbon fiber fillers on the mechanical properties of 3D-printed PLA were investigated, and the effects of the annealing process on polymer crystallinity and mechanical properties. The annealing process was shown to increase the crystallinity of both sample groups, though no statistically significant effect of annealing on mechanical properties was observed. The tensile properties of the PLA and PLA/CF filaments showed that the addition of carbon fibers to the PLA filament led to a significant increase in elastic modulus of the MEAM samples.

Keywords  Material extrusion additive manufacturing, Annealing, Mechanical testing, Differential scanning calorimetry (DSC), Short-fiber composite, Optical extensometry

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Introduction

The implementation of additive manufacturing techniques, like three-dimensional (3D) printing has increased substantially due to the advent of low-cost, open-source printers. Additive manufacturing process can be sub-divided into seven categories. The first three: material extrusion, material jetting, and powder bed fusion utilize thermal reaction bonding as state of fusion during production. Remaining four: binder jetting, material jetting, vat photopolymerization, and sheet lamination utilize chemical reaction bonding as state of fusion during production. Among these, material extrusion has become very popular due to the ability to rapidly perform design cycle iterations with relatively low cost materials and with short print times. Material extrusion will be referred as Material Extrusion Additive Manufacturing (MEAM) in this manuscript. MEAM is also known as fused deposition modeling (FDM) in the literature. In MEAM, a polymeric filament is fed to the machine in a controlled manner. This filament passes through a hot chamber (extruding head) and molten. The melt is pushed out of the nozzle of the machine and deposited layer-by-layer until the desired shape/dimension is achieved. Most MEAM 3D printers allow for materials to be produced using a variety of thermoplastic materials, such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), or polyamide (Nylon®). Lately, more advanced MEAM 3D printing filaments have become available. Some examples of advanced MEAM 3D printing filaments include PLA filaments combined with powdered metals, wood-based filaments, high flexibility filaments (thermoplastic polyurethane), shape memory filaments and graphene, Carbon Nanotube, and carbon fiber-reinforced 3D printing filaments. New advanced 3D printing filaments offer a wide variety of surface finishes as well as mechanical, thermal, and electrical properties.

Several authors have evaluated the mechanical properties of conventional 3D printed components, however, little work has been done on the plethora of new advanced 3D printing filaments. Broader applications of components/parts manufactured using additive manufacturing are required in the industry and research circles; however, the use of non-reinforced polymer filaments with low elastic and mechanical properties of MEAM process limit MEAM's progress. In this
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The goal of this study is to evaluate the mechanical properties of two MEAM 3D printing filaments; examine the efficacy of a post-print annealing procedure; and examine the internal microstructure of 3D-printed parts. This study used a conventional PLA thermoplastic filament, while the second filament was a PLA plastic reinforced with short-carbon fibers (PLA/CF). These two filaments were compared to determine if short-fiber reinforcement has an effect on the mechanical properties of 3D-printed components.

Post-manufacturing heat treatment, i.e. annealing, of polymeric materials is gaining increasing importance in the research circles similar to metallic components. Consequently, this study also explored the effect of a post-printing annealing procedure. In annealing of polymers, a semi-crystalline polymer is heated up to a temperature below its melting point, $T_m$, and held at that constant temperature for a period of time, before cooling to ambient temperature. This heat treatment alters the thermal history of the polymer, resulting in changes to its physical and mechanical properties. Annealing can be used for the relief of residual stresses left over from manufacturing, and can also lead to secondary polymer crystallization, as well as changes to molecular mobility.

The effectiveness of the process is highly dependent on the selection of annealing time and temperature.

As such, printed samples used in this study were annealed at temperatures of 30, 60, and 90 °C above the glass transition temperature ($T_g$) to examine the effect of annealing on MEAM 3D-printed components. Finally, the microstructures of the 3D-printed parts were examined to assess the quality of the 3D printing process and compare the microstructural features of components printed with both the PLA and PLA/CF filaments. Presently a comparison of the effect of short fiber reinforcement in 3D printing filament does not exist in literature; nor has the effect of a post-print annealing procedure been examined. This study uses commercially available 3D printing filaments to examine the effect of short-fiber reinforcement and annealing on the mechanical properties.

**Methods**

**Materials and methodology**

Two 3D printing filaments were used in this study. One filament consisted of PLA plastic filled with 15% carbon fiber reinforcement (3DXMax CFR Carbon Fiber Reinforcement PLA Filament, 3DXTech, Wyoming, MI, USA). Manufacturer information did not specify, whether carbon fiber loading was by volume or weight percent; however, as indicated in the following sections a microscopic study is conducted as part of this study to determine the fiber area fraction. The second filament was a conventional PLA filament (Natural PLA MEAM 3D Printing Filament, 3DXTech, Wyoming, MI, USA). Both filaments are 1.75 mm in diameter.

All samples used in this study were manufactured using an open-source 3D printer (RoVa3D 5 Extruder MEAM 3D Printer, ORD Solutions, Cambridge, Ontario, Canada). Test samples were designed using a computer-aided design package (SolidWorks 2015 SP4.0, Dassault Systems, Waltham, MA) and then exported as stereolithography files (STL). The sample geometry was created according to ASTM D638-14 using a Type V geometry with a specimen thickness of 2 mm. The critical dimensions of the specimens are shown in Fig. 1.

The STL files were imported into an open-source g-code generation software package (Slic3r 1.2.9, slic3r.org). The printing parameters used for all samples in this study are detailed in Table 1. As shown in Table 1 all samples were printed with two external shells around the perimeter of the dogbone geometry. As well, all samples were printed with 100% infill where the infill was printed by alternating 0° and 90° layers. A schematic of the internal structure of the dogbone samples is shown in Fig. 2.

**Figure 1** Schematic of Type V dogbone specimen geometry

![Figure 1](image)

**Table 1** MEAM 3D printing parameters.

| Parameter                     | Value       |
|-------------------------------|-------------|
| Nozzle size (mm)              | 0.5         |
| Nozzle temperature (°C)       | 200         |
| Bed temperature (°C)          | 85          |
| Print speed first layer (mm/s)| 30          |
| Print speed subsequent layers (mm/s) | 35 |
| Layer height (mm)             | 0.1         |
| Number of shells              | 2           |
| Infill percentage (%)         | 100         |
| Infill pattern                | 90 degrees rectilinear |

The external shell of the test sample and alternating 0/90° infill layers are shown.

**Figure 2** Internal structure of the MEAM 3D-printed samples. The external shell of the test sample and alternating 0/90° infill layers are shown.

![Figure 2](image)
PLA is a well-known hygroscopic material. In this study, effect of humidity was not investigated as it is well-documented for PLA. The specimens were tested after sufficient amount of time of preparation (at 24 ± 5% relative humidity) to allow saturation of the materials to eliminate the effect of humidity as a parameter.

Annealing procedure
The MEAM 3D-printed specimens were subjected to annealing heat treatments post-manufacturing. Turng and Srithep indicated that when annealed at 80 °C PLA reached 49% crystallinity in 30 min; therefore, in this study an annealing time more than 30 min was targeted to ensure the samples attained a similar degree of crystallinity.\(^{14}\) Annealing was done by placing MEAM 3D-printed specimens in a pre-heated oven (Thelco Model 28, GCA/Precision Scientific, Chicago, IL, USA) and holding at constant temperature for a period of 2 h. Specimens were not placed under any dimensional constraints during annealing and the oven atmosphere was uncontrolled. Both PLA and PLA/CF specimens were subjected to annealing. Three different annealing temperatures were chosen based on their relationship to the glass transition temperature, \(T_g\), of the filament. Annealing temperatures were 85, 115, and 145 °C, which correspond to 30, 60, and 90 °C above \(T_g\), respectively, based on a \(T_g\) of 55 °C for both the as-received filaments, which was determined and based on preliminary thermal analysis of the PLA and PLA/CF filaments. Five specimens were annealed for each material and temperature combination, and five specimens of each material were prepared without annealing in their as-printed (AP) state. The sample annealing temperatures, 3D printing filament and number of test samples is summarized in Table 2.

#### Table 2  Test sample filament and annealing temperatures.

| Sample filament | Annealing temperature (°C) | Number of samples |
|-----------------|-----------------------------|-------------------|
| PLA             | N/A                         | 5                 |
| PLA             | 85                          | 5                 |
| PLA             | 115                         | 5                 |
| PLA             | 145                         | 5                 |
| PLA/CF          | N/A                         | 5                 |
| PLA/CF          | 85                          | 5                 |
| PLA/CF          | 115                         | 5                 |
| PLA/CF          | 145                         | 5                 |

#### Figure 3  MEAM 3D-printed Type V samples; (a) PLA, (b) PLA + CF

Experimental characterization

Physical measurements
Prior to performing mechanical tests on the MEAM 3D-printed test samples all critical dimensions of the samples were measured. The dimensions \(W\), \(W_{N}\), and \(T\) were measured using a micrometer (0 – 25 ± 0.01 mm Micrometer, Mitutoyo, Kawasaki, Japan). Sample dimensions were required in order to determine the cross-sectional area of the printed samples and to evaluate the consistency of the 3D printing process. A total of 40 samples were used for dimensional measurements. Three measurements for each test sample were collected for all measured critical dimensions.

Thermal analysis
Differential scanning calorimetry (DSC) was conducted in order to characterize the relative initial crystallinity of the test specimens subjected to different thermal histories through 3D printing and annealing. DSC tests were conducted on the as-received filament, as-printed material, and annealed material for both the PLA and PLA/CF materials. Samples ranging from 3.0 to 4.6 mg in mass were extracted from 3D printed specimens using a scalpel. Samples were loaded into the DSC instrument (DSC Q100, TA Instruments, USA), and subjected to the following heating program. Temperature was equilibrated at 25 °C, then held isothermally for 3 min. The temperature was then ramped at a rate of 2 °C/min up to 200 °C, while recording time, temperature, heat capacity, and heat flow at a sampling rate of 12 Hz.

Heat flow data were used to determine the initial degree of crystallinity of the various specimens to investigate the effects of the annealing process. The cold crystallization temperature, \(T_c\), enthalpy of cold crystallization, \(\Delta H_c\), melting temperature, \(T_m\), and enthalpy of fusion, \(\Delta H_m\), were measured from the heat flow curves using commercial software (TA Universal Analysis, TA Instruments, USA). Equation (1) was used to calculate the initial crystallinity of the DSC test specimens.\(^{35}\) In this equation, \(\Delta H_f\) is the enthalpy of fusion of 100% crystalline PLA, which was selected to be 93.1 J/g,\(^{35}\) and \(W_f\) is the weight fraction of fibers in the polymer. For the PLA specimens, \(W_f\) is zero, as there are no fibers in the polymer.

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\%DOC = \frac{\Delta H_m}{\Delta H_f (1 - W_f)} \times 100 \quad (1)
\]

Microstructural analysis
Microstructural analysis was conducted on the PLA and PLA/CF filament materials and 3D-printed test specimens using an optical microscope (BX61, Olympus, USA). For the PLA/CF filament, fiber and void area fractions, as well as fiber length and diameter were measured from microstructural images. The printing quality and layer morphology of the printed specimens were also examined.

Longitudinal and transverse cross-sections were analyzed for the PLA and PLA/CF filament samples, and 3D-printed specimens were sectioned transversely for analysis, at the location shown in Fig. 4. Samples were potted in an epoxy resin (ColdCure, System Three Resins, Inc., Auburn, WA, USA), and ground and polished in preparation for microstructural
analysis. Grinding was done using 320 grit, followed by 600 grit sandpaper, and polishing was done using a 9 μm diamond slurry, then a 6 μm diamond slurry, and finished with a 0.05 μm alumina suspension.

Fiber and void area fractions in the PLA/CF filament were measured from microstructural images using algorithms written in MATLAB (MATLAB, The Mathworks, USA). Images were taken from multiple cross-sections of filament at 20x magnification. In the images, the carbon fibers appeared as bright objects on the relatively dark background made up by the PLA matrix, and fiber area was segmented based on contrast. The segmented fiber area was divided by overall image area to obtain fiber area fraction. A total of 30 images were processed, and the average fiber area fraction was found. Void area fraction was determined using a similar contrasting method. Images were taken from multiple cross-sections of filament at 10x magnification, in which the voids appeared as relatively dark spots in the images. A power law transformation was applied to the images as a pre-processing step to improve contrast between the voids and the remaining filament material, allowing the void area to be segmented by contrast. The segmented void area was divided by overall image area to obtain void area fraction. 23 images were processed, and the average void area fraction was found.

Carbon fiber diameter and length in the PLA/CF filament were also measured from microstructural images. Diameter was measured using an algorithm written in MATLAB (MATLAB, The Mathworks, USA), which identified circular objects in the images corresponding to transverse cross-sections of the fibers, and returned the diameter of these objects. 30 images taken at 20x magnification were processed, and the average fiber diameter was found. Fiber length was measured by hand from 18 images taken at 10x magnification. Only fibers that were parallel to the cross-section were measured to minimize false length measurements caused by angled fibers. A total of 170 fibers were measured, and the average fiber length was found.

**Mechanical measurements**

Tensile testing was conducted on the MEAM 3D-printed specimens according to ASTM D638. Type V dogbone specimens were 3D-printed from both the PLA and PLA/CF filaments, and subjected to the annealing treatments outlined in Table 2. Specimens were mounted into the test frame (MTS Model 810, Manufacturing Technical Solutions, Inc. (MTS), USA) equipped with a 100 kN load cell. Specimens were mounted into clamp-type grips which were tightened by hand. Testing was conducted to ultimate failure at a constant displacement rate of 1 mm/min. Load, cross-head displacement, time, and strain were recorded at a rate of 10 Hz.

An optical extensometry system was used to measure strain in the specimens during the tensile tests. A digital camera (Ace AcA3800 – 10gm, Basler AG, Ahrensburg, Germany) and lens (LM50JC10M, Kowa Optical Products Co. Ltd., Torrance, CA, USA) were used to acquire images of the specimens as they were subjected to tensile testing. Table 3 summarizes the experimental parameters related to the camera and lens assembly used for imaging.

The images were processed through a custom software application written in MATLAB (MATLAB, The Mathworks). The software measures strain by tracking the distance in pixels between two high-contrast locations over a series of images, and comparing this distance to the original gage length. When an image stack is loaded, a bounding box is selected by the user to specify the area of interest, and the software generates a plot of average vertical pixel intensity along the length of the bounding box. A curve consisting of two error functions is fit to the intensity plot, and the contrast marks are identified as the locations where large changes in intensity occur. Fig. 5 shows an example of the measurement system applied to a tests specimen. Using this method, strain can be measured without contacting the specimen, which avoids stress concentrations that could arise when using a conventional extensometer.

Contrast marks were painted onto the surface of the test specimens to facilitate optical extensometry measurements. A gage length of 7.62 mm (0.300 inches) was taped off in the center of the specimens, and the exposed portions of the sample were spray-painted. Black paint was used on the natural PLA specimens, which were clear to white in color, and white paint was used on the PLA/CF specimens, which were black in color.

**Results**

**Dimensional accuracy of printer**

The dimensional accuracy of the ORD Solutions MEAM 3D printer was evaluated for both the PLA and PLA/CF filaments used in this study. The critical dimensions 7 and 5W of the test samples, shown in Fig. 1, were used to assess the dimensional accuracy of the 3D printer. A t-test was used to compare the nominal sample dimensions to the measured sample dimensions. A p-value of < 0.05 was used as the criteria for determining if a statistically significant difference exists between the nominal and measured sample dimensions. The resulting average sample measurements and comparison with nominal
undergo cold crystallization during the DSC testing, indicating that a maximum degree of crystallinity had been achieved.

Microstructural analysis

The general microstructures of the PLA and PLA/CF filaments, including both transverse and longitudinal filament cross-sections, are shown in Fig. 7. The PLA filament shows a round cross-section with smooth edges (Fig. 7(a) and (b)). The PLA/CF filament (Fig. 7(c) and (d)), however, is not as round and appears to have a rougher surface finish. Carbon fibers are visible in the PLA/CF filament as white features in the micrographs. The PLA/CF filament also contains relatively large internal voids compared to the PLA filament, which appear as dark spots in the micrographs. Fig. 8 shows a close-up of the transverse and longitudinal sections of the PLA/CF filament, revealing that the carbon fibers are generally well aligned with the filament extrusion direction, and are well distributed throughout the entire filament cross-section. The voids are also well distributed throughout the filament, and are generally circular in shape, suggesting they are a result of air bubbles formed during extrusion.

Table 4 Dimensional accuracy of the ORD solutions 3D printer.

| Sample | Average (standard deviation) width (WN) | % difference | p-value | Average (standard deviation) thickness (TN) | % difference | p-value |
|--------|----------------------------------------|--------------|---------|--------------------------------------------|--------------|---------|
| PLA    | 3.44 (0.17)                            | 9.12         | <0.001  | 1.95 (0.04)                                | 2.3          | <0.001  |
| PLA /CF| 3.47 (0.03)                            | 8.19         | <0.001  | 1.95 (0.07)                                | 2.25         | <0.001  |
Table 5 Summary of initial crystallinity based on DSC results.

| Specimen          | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $\chi_c$ (%) |
|-------------------|------------|---------------------|------------|---------------------|--------------|
| PLA – filament    | 105.9      | 24.0                | 145.2      | 26.3                | 2.4          |
| PLA – as-printed  | 102.9      | 22.4                | 145.0      | 25.7                | 3.5          |
| PLA – 85 °C       | 98.5       | 2.6                 | 150.4      | 22.6                | 21.5         |
| PLA – 115 °C      | –          | 0                   | 145.1      | 24.3                | 26.1         |
| PLA – 145 °C      | –          | 0                   | 148.7      | 28.0                | 30.1         |
| PLA/CF – filament | 98.4       | 19.3                | 151.7      | 22.5                | 3.9          |
| PLA/CF – as-printed| 98.0      | 20.3                | 151.5      | 22.8                | 3.1          |
| PLA/CF – 85 °C    | 93.1       | 7.5                 | 150.4      | 20.5                | 15.6         |
| PLA/CF – 115 °C   | –          | 0                   | 151.1      | 24.7                | 29.7         |
| PLA/CF – 145 °C   | –          | 0                   | 146.4      | 25.2                | 30.3         |

Figure 6 DSC results for (a) PLA specimens, (b) PLA/CF specimens

Figure 7 Comparison of PLA and PLA/CF filament microstructures: (a) PLA transverse cross-section, (b) PLA longitudinal cross-section, (c) PLA/CF transverse cross-section, (d) PLA/CF longitudinal cross-section
good consolidation of the layers. Variations in layer thickness can also be observed.

Micrographs taken from the as-printed PLA/CF specimens are shown in Fig. 10. Fig. 10(a) shows the overall morphology across the specimen thickness. Both small and large voids are visible throughout the sample cross-section. The small voids are likely a product of the pre-existing voids in the as-received filament material, while the large voids may indicate jamming of the extruder nozzle during printing. The edge morphology is less consistent than for PLA samples, showing large variations in geometry from top to bottom. Furthermore, the top and side surfaces of the specimen appear rough and non-uniform. Note that the fibers in the shell region are oriented in the same direction, and the bottom layer appears to be thicker than the rest, as with the PLA sample. Fig. 10(b) shows a close-up of the infill, which clearly shows the alternating 0/90 orientation of the layers, as indicated by the alignment of the fibers. Layer consolidation appears to be generally good, however, variations in layer thickness is observed, similar to the PLA samples.

The microstructures of PLA and PLA/CF samples annealed at 145 °C were examined and compared to the as-printed microstructures. In both cases, annealing appeared to result in improved consolidation of the 3D-printed layers. A comparison of as-printed and annealed PLA microstructures is shown in Fig. 11. Fig. 11(a) shows the as-printed sample, where clear boundaries between individual print layers can be seen. Fig.

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### Table 6 Summary of image analysis measurements on micrographs of PLA/CF filament.

| Measurement               | Average (± standard deviation) |
|---------------------------|--------------------------------|
| Fiber area fraction, $A_f$ | 7.7 ± 0.5%                     |
| Void area fraction, $A_v$  | 12.1 ± 2.0%                    |
| Fiber diameter, $d_f$ (μm) | 7.4 ± 0.6                      |
| Fiber length, $l_f$ (μm)   | 125.2 ± 53.0                   |

Fiber geometry and fiber and void area fractions in the PLA/CF filament were quantified using image analysis of the micrographs; the results are summarized in Table 6. Fiber area fraction, $A_f$, void volume fraction, $A_v$, and fiber diameter, $d_f$, were relatively consistent between the different images, while fiber length, $l_f$, varied substantially. An example of fibers selected for length measurement is shown in Fig. 8(b).

Micrographs taken from the as-printed PLA specimens are shown in Fig. 9. Fig. 9(a) shows the entire specimen thickness and the morphology at the edge of the sample. Small voids can be seen between the passes of the two shell layers, and the width of the shell layers appears to be inconsistent from the bottom to the top of the sample. The bottom layer of the sample is thicker than the remaining infill layers, and it appears that the sample is wider at the bottom relative to the top, which may be indicative of over-extrusion. Fig. 9(b) shows a close-up of the infill of the specimen, and reveals reasonably
Mechanical measurements results

Representative plots of stress vs. strain for the PLA and PLA/CF specimens subjected to the various annealing treatments are shown in Fig. 12. The average results (± standard deviation) for elastic modulus, ultimate strength, and ultimate strain are reported in Table 7. The results show that annealing has little
is not a clear trend which correlates annealing temperature to an improvement in mechanical properties.

Discussion

Microstructural analysis revealed that the PLA/CF filament and printed samples contained a higher quantity of large voids when compared to the PLA filament and printed samples. The voids in the as-received filament were likely a result of bubbles formed by air entrained during the addition of the carbon fiber to the PLA base material. The larger voids present in the printed PLA/CF samples may be attributed to clogging of the extruder nozzle during printing, due to the presence of carbon fibers in the filament. Reducing or eliminating these voids should lead to improved mechanical properties of the final part.

A one-way ANOVA was used in order to determine if the 3D printing filaments used in this study had a statistically significant effect on the mechanical properties of the printed test specimen. A p-value of 0.05 was used as the significance criteria. The results from the statistical analysis are summarized in Table 8. Figure 13 demonstrates the effect of MEAM 3D printing filament and annealing temperature on mechanical properties. From Table 8 and Fig. 13(a) it can be seen that there is a statistically significant difference between the PLA and PLA/CF filaments for both elastic modulus and ultimate tensile strength. Fig. 13(a) demonstrates that the PLA/CF filament results in a significant increase in the elastic modulus of a MEAM 3D-printed part compared to a conventional PLA filament. Table 8 demonstrates that the annealing temperature applied to the MEAM 3D-printed samples has a significant effect on elastic modulus and ultimate tensile strength for both PLA and PLA/CF printed samples, however, Table 8 shows that although there is a statistically significant difference between annealed samples there is not a clear trend which correlates annealing temperature to an improvement in mechanical properties.
consolidated in the as-printed PLA and PLA/CF samples, with major gaps appearing only at the boundary between the shell and infill. Dimensional accuracy was poor at the edges of the 3D-printed samples for both the PLA and PL/CF materials, revealing one of the limitations of this type of MEAM 3D printing process.

DSC measurements revealed that annealing of the PLA and PLA/CF specimens caused an increase in sample crystallinity, which is consistent with previous work annealing PLA and PLA composites.18-21 The low degree of crystallinity of the as-printed filament and as-printed samples can be attributed to relatively rapid cooling of the experienced by the polymer, which does not allow enough time for any significant crystallization to occur, due to the slow nucleation and crystallization rates of PLA.17,24,25 For the as-printed filaments, this rapid cooling would have occurred during the extrusion process, while for the as-printed specimens, the rapid cooling is experienced due to the cooling fans used to solidify the polymer after it has been deposited. DSC test results showed that for a constant annealing time of 2 h, increasing the annealing temperature led to a higher degree of crystallinity, up to a maximum value of around 30% for components printed with both PLA and PLA/CF materials. In addition to a temperature dependency of crystallinity, previous work on injection molded PLA specimens has also shown a time dependency of crystallization kinetics.23 While this time dependency was not investigated in the present work, future testing incorporating a range of annealing times as well as temperatures may help to further refine the annealing process for the 3D-printed filament materials used in this work.

Previous studies have shown that for injection molded PLA and PLA composites, the increased degree of crystallization obtained through annealing can lead to improvements in mechanical properties.7,20,22,23 However, in the current study, ANOVA results showed no statistically significant difference in strength or elastic modulus for samples subjected to different annealing conditions. This may be partially due to the 3D-printed structure of the specimens, which has been shown to produce lower tensile properties than equivalent injection molded parts.21 The majority of the specimens failed in a similar location along the gage length, which may indicate the presence of a stress concentration created during the printing process, resulting in premature failure and masking potential annealing effects on strength. It should also be noted that though no statistically significant difference was found, the average elastic modulus for the annealed PLA and PLA/CF samples were higher than their as-printed averages. Testing a larger sample size would help to further investigate this relationship; however, any change to modulus due to annealing will likely be minimal compared to the effect of introducing carbon fibers to the PLA.

Though mechanical properties were not significantly improved by annealing, there exist other benefits associated with annealing, such as increased heat deflection temperature19 and residual stress relief.11 In addition, annealing appeared to improve print layer consolidation, though further testing of the bond strength between print layers is required to quantify this improvement. Despite these potential benefits, previous studies have indicated that over-annealing should be avoided, as it can lead to warpage of the polymer due to high degrees of recrystallization.19-21 In this study, no discernable warpage was observed in the annealed specimens. Further study would be necessary in order to determine the annealing parameters to cause warping in the 3D-printed specimens used in this study.

The results from the mechanical tests for the MEAM 3D-printed samples demonstrate that the carbon fiber reinforced MEAM 3D-printed parts exhibited a greater elastic modulus than conventional PLA 3D-printed parts.

The addition of short carbon fibers to conventional PLA plastic will result in an increase in mechanical properties due to the high elastic modulus of carbon fiber. The elastic modulus of a short fiber reinforced plastic can be predicted using Equation (2), which is the Halpin-Tsai equation for short fiber composites.26 This equation shows that short fiber reinforced materials as a function of the length (l) of short fibers, diameter (d) of the short fibers, the volume fraction of fibers (Vf), elastic modulus of the plastic (Ei), and elastic modulus of the fibers (Ef).

\[
\frac{E}{E_i} = \frac{1+2(1-\eta_f)V_f}{1-\eta_fV_f} \left( \frac{E_f}{E_i} \right) + 2(l/d)(1-\eta_f) \left( \frac{E_f}{E_i} \right)
\]

Example parameters for a short fiber reinforced PLA plastic are summarized in Table 9. Using the parameters shown in Table 9 and Equation (2) the predicted elastic modulus for a fiber reinforced PLA plastic is 9.92 GPa. The introduction of short carbon fibers into PLA plastic results in an elastic modulus which is approximately 3.4 times greater than the elastic modulus of conventional PLA plastic.

As predicted, the results in Fig. 13 and Table 8 show that all carbon fiber reinforced MEAM 3D-printed parts had a greater elastic modulus than the conventional PLA plastic parts. The average elastic modulus for all PLA 3D-printed parts was 3.51 GPa while the elastic modulus for the carbon fiber 3D-printed parts was 6.26 GPa, resulting in a 1.78x increase. It has been shown that the elastic modulus of MEAM 3D-printed parts is typically lower than injection molded parts.4,5 MEAM 3D-printed parts exhibit a lower elastic modulus than injection molded components due to the orientation of plastic fibers within the sample structure, voids present, and incomplete bonds between layers in the MEAM 3D printed structure. This explains the difference in the predicted elastic modulus for carbon fiber reinforced PLA (9.92) versus the experimentally determined elastic modulus (6.26 GPa).

Conclusions

This study examined the effect of different MEAM 3D printing parameters and the effect of applying a post-printing annealing procedure on the mechanical properties of MEAM 3D printed parts. These parameters were examined with the goal of improving the mechanical properties of the MEAM 3D-printed structures using commercially available 3D printing filaments. The results from this study demonstrated that the addition of short carbon fibers to PLA filaments results in an improvement in the elastic modulus of the printed samples. The effect of annealing was also examined. Annealing of the PLA and PLA/CF samples caused an increase in crystallinity, up to a maximum value of 30%, with
higher annealing temperatures corresponding to a higher degree of crystallinity. Annealing has been demonstrated to improve the mechanical properties of injection molded plastics; however, in this study an improvement on the mechanical properties of annealed MEAM 3D-printed samples was not found. Despite this finding, annealing did appear to improve consolidation of the printed layers, however further study is required to understand the significance of this effect.

The dimensional accuracy of the MEAM 3D printer used in this work was evaluated, and it was found that the thickness and width of the specimens showed significant deviations from the intended geometry. Microstructural images also showed large variations in overall sample dimensions, particularly in terms of sample width. Specimens printed from the PLA/CF filament contained many large voids, which were most likely a result of the print nozzle clogging due to the presence of the carbon fibers in the filament.

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