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Perspective Chapter: Composites Manufactured by Stereolithography

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Abstract

Stereolithography (SLA) is a widely utilized rapid additive manufacturing process for prototypes and proof-of-concept models with high resolution. In order to create structurally sound components using SLA, reinforcement needs to be incorporated in the UV-based resins typically used. However, the introduction of reinforcement into vat-based SLA printers has had limited success due to a host of processing challenges including the creation of a homogeneous resin mixture and UV-inhibiting constituents. The effectiveness of using a dual curing system, consisting of a photo and thermal initiator, for the additive manufacturing of carbon fiber short-fiber composites via vat photopolymerization, was investigated. The necessary processing parameters were developed that resulted in successful printing and curing of composites at a 5% fiber volume. Manufacturing with reinforcements that have different densities from the resin creates separation issues, either suspending to the top or settling to the bottom. Following the approaches discussed in this chapter, an even distribution of short fibers was achieved throughout SLA printed samples using a modified commercial printer. Separation was overcome by inducing a continuous flow of reinforced liquid resin in the printer vat during printing. This flow field adaptation allows commercial SLA printers the ability to produce composite parts with different densities of the constituents utilized.

Keywords: stereolithography, composites, carbon fiber, fiber glass, and dual cure

1. Introduction

A current drawback of additive manufacturing (AM) parts is that the material properties of the parts produced are much lower than that of parts manufactured using traditional manufacturing such as milling, injection molding, and traditional composite manufacturing methods [1–3]. If the material properties of the parts produced using AM could be increased to be similar with that of traditional manufacturing methods, a new era of design could be opened up. This would be accomplished by the ability to use AM to make parts that could not be produced using any other methods due to their complex geometry. With the advent of computer-aided design (CAD) software, the design process was changed, but limitations of what can be made in the virtual world versus what can be manufactured in the real world still exist. With the incorporation of AM into the final production processes, the

complexity of the geometries that could be manufactured increases. This increase in complexity of part geometry can allow for a decrease in the over complexity of the part, subassembly, or whole assembly, along with helping to relieve supply chain issues. For instance, by combining multiple parts into one, the need for several fasteners can be eliminated. This decreases the number of parts needed, number of components to analyze, and possible points of failure.

An appealing advantage of vat photopolymerization over material extrusion processes, such as fusion deposition modeling (FDM), is the ability to manufacture parts that have isotropic material properties [4]. For parts produced using FDM, the part has the properties of the material in the plane of printing, but perpendicular to that it becomes dependent on the mechanical adhesion of the polymer layers to each other for the part's mechanical properties [4]. For parts manufactured using vat photopolymerization, it is possible to produce parts that have near isotropic mechanical properties [4]. Although the part is produced in a layer-by-layer process, as like in FDM, the thermoset polymer is not completely cured within each layer before the part is raised and the next layer is printed. This allows for unreacted polymer functional groups in a previous layer to react with the polymer curing in the current layer being printed. Because of the ability of vat photopolymerization to produce parts with near isotropic properties, the orientation of the part while printing does not depend on what direction force will be applied to the finished part, but what orientation of the part will optimize the printing process.

One of the limiting factors of vat photopolymerization is the material properties of the resins used to create parts. The parts produced using these resins are often weak and brittle, limiting their use for many end-use structural applications [5]. One method of improving the properties of a material is the incorporation of a reinforcement material in the creation of a composite. Short-fiber composites have traditionally been produced via injection and compression molding. By using short fibers as a reinforcement, the same manufacturing method used for polymers can be used to form the composites, but with increased material properties [6].

Short-fiber composites usually find their applications in situations where isotropic material properties are desired, typically manufactured via injection or compression molding, but the manufacturing processes can influence the fiber orientation due to the flow of the material during manufacturing final material properties [7]. While the flow-induced alignment can be taken advantage of to some extent, it can be limited due to the requirements of the mold design and can be an undesired effect when isotropic properties are desired [8].

With short fibers already in widespread use as a reinforcement material for traditional manufacturing methods, such as injection and compression molding, they have found their way into use for additive manufacturing methods as well [1, 3, 9–19]. For FDM there are numerous types of reinforcements ranging from nanoparticle to continuous fiber, of both natural and synthetic materials, which are currently being researched and available for sale on a commercial level [1, 3, 16]. Whereas FDM-based methods have a number of publications in the area of short-fiber composite characterization, the area of vat photopolymerization manufactured composites is lacking in published studies and available data using carbon fiber as a reinforcement.

There have been various nanosized reinforcements studied as a method of increasing the material properties of vat photopolymerization manufactured parts such as: cellulose nanocrystals (CNC), multi-wall carbon nanotubes (MWCNTs), and silver nanoparticles (AgNPs) [12–14, 18]. Feng et al. [14] used lignin-coated cellulose nanocrystals (L-CNC) at 0, 0.1, 0.5, and 1 weight percent with an acrylic matrix. The research was carried out using Form+1 (Formlabs, Somerville, MA), which is a bottom-up desktop vat photopolymerization printer. At a loading of 0.5 wt.% L-CNC,

there was an increase in the tensile strength and Young's modulus by 3% and 5%, respectively [14]. This was achieved only after a thermal post-cure being carried out on the specimens with the non-post-cured specimens showing unimproved or reduced properties depending on the loading of L-CNC [14]. The decrease in material properties that was seen at higher weight percent was attributed to poor dispersion of the L-CNC and poor adhesion between the L-CNC and matrix [14].

Sandoval et al. [12] investigated a composite made from MWCNTs at 0.025 and 0.1 weight percent with an epoxy-based matrix using the commercial resin, DSM Somos® WaterShed™ 11,120. A top-down printer, the 3D Systems SLA-250/50 machine (3D Systems, Rock Hill, SC) was modified from a 47 liter vat to a 500 ml vat with the sweeping mechanism removed, and a peristaltic pump was used to recirculate the resin mixture [12]. The research looked at the increasing tensile strength and fracture strength of the resin. For 0.025 wt.% of MWCNTs, an increase in tensile strength of 5.7% with an increase in fracture strength of 26% was reported. While at 0.10 wt.%, an increase of 7.5% and 33% in tensile and fracture strength, respectively, was reported, but it was pointed out that at the higher loading of 0.1% MWCNTs, there were issues with agglomeration of the MWCNTs [12]. The elongation at break decreased 28% for the MWCNTs reinforced resin, and the fracture mode was reported as a brittle-type verse as more of a ductile failure mode that was seen in the pure resin [12].

Short glass fibers have been studied more as reinforcement materials for vat photopolymerization in part due to the decrease in opacity when compared with that of carbon fiber [3]. In one study, Cheah, C. et al. [19] looked at using short glass fibers 1.6 mm in length at various fiber volume fractions of 0, 5, 10, 15, and 20% and a urethane acrylic matrix, DeSolute SCR310. The experiment was carried out for comparing molded and 3D printed samples. Although the paper does not state what machine was used to print the samples, it can be inferred that a top-down style was used [19]. Cheah et al. saw improvements for all fiber volumes, with increased mechanical properties achieved by increasing fiber amount, and part shrinkage can be reduced. For a fiber volume of 20%, they were able to achieve an increase in tensile strength of 24% and an 80% increase in the Young's modulus [19]. The top-down vat photopolymerization machine that was employed resulted in the manufacture of composites that were close to unidirectional in fiber orientation due to the scraping step in between layers [19]. While the creation of unidirectional composites is desirable in some applications, the leveling step would prevent the printing of an isotropic part and therefore could limit potential applications and restrict the printing process based on how the part must be printed.

Along with short glass fibers, there have also been studies that have looked into the use of continuous glass fiber as a reinforcement in vat photopolymerization. Karalekas et al. [2] placed a single layer of nonwoven glass fiber mats, of various thicknesses, within specimens produced using vat photopolymerization. This was done by pausing the printer at a predetermined build height, placing the mat of the specimen, and resuming the print [2]. Karalekas et al. were able to show an increase in the Young's modulus, but a decrease in tensile strength for thinner mats. For the thicker mats, the Young's modulus was shown to decrease; this was contributed to the inability for the photopolymer to fully cure within the thicker mats [2]. While this study was able to show that continuous glass fibers could be placed into the part for reinforcement, the fact that it was added by hand during the build process is inefficient, especially if multiple layers of fiber are to be used in the manufacturing of a part, and would be difficult for the manufacturing of complex parts.

Some research has been carried out using continuous carbon fiber by Gupta et al. [17] where to overcome the issues of fully curing the part, a dual curing system was used. The dual curing system employed a photo initiator for initially curing the

Figure 1.
Dual curing system.

fiber and matrix in the desired geometry and a thermal initiator to cure the remaining resin. While Gupta et al. were able to show that the system was fully cured, they did not report any information on the material properties of the composite produced and appeared to have limited success in incorporating the initiator into the liquid resin [17]. The ability for the thermal initiator to cure the areas that the UV light cannot, due to the opacity of the carbon fiber, could be a promising method of incorporating carbon fiber into vat photopolymerization produced, shown in **Figure 1**.

There are a host of complications from suspending fiber to achieving optimal cure with opaque fibers hindering the UV light. Some success has been achieved by introducing glass fibers into vat printers, while struggling to keep a homogeneous resin mixture as the fibers settle to the bottom of the print bed [20].

SLA composite parts have been approached with different tactics in the past. Some success has been achieved in the smaller particle reinforcement with chemical and rheological approaches. For filler-sized particles, approaches such as suspension with shear thinning polymers have been attempted to produce SLA ceramics [21, 22]. Another tactic used is surface modification of the filler to reduce conglomerations and improve the stability of the dispersion [23]. Other research has shown that certain fibers can be aligned and suspended via shear flow or electric field induction [24–27]. However, using a more common and larger fiber does not allow all these techniques to be applied and requires a different approach.

Fiber suspension is a critical and complicated issue when looking at the disparaging density ranges of fibers to resin combinations. If a homogeneous resin bath cannot be maintained throughout the print, the resulting parts will either have no reinforcement or possibly too much reinforcement to successfully print. An adaptation to a Moai 130 SLA vat printer was designed in this study to provide a homogeneous reinforced resin bath for printing using standard printing parameters. The adaptation ensures the glass fiber is suspended in the build plate region of the vat for the entirety of any print allowing a homogeneous composite component to be manufactured.

2. Equipment and processing

2.1 Opaque reinforcement

A Moai Laser vat photopolymerization printer manufactured by Peopoly, and purchased from MatterHackers, (Lake Forest, CA) as a DIY kit, was assembled and calibrated. The Moai is a bottom-up printer that uses a 405 nm 70-micron spot size laser and is based on an open-sourced design. The photopolymer resin used in this

research was Moai Standard Clear resin, by Peopoly purchased from MatterHackers (Foothill Ranch, CA). It is an acrylic-based photopolymer designed to work with the Moai printer being used in this research.

The primary carbon fiber used was Toray T-700. The fiber was purchased from Composite Envisions (Wausau, WI) as a chopped 3 mm fiber and comes sized for epoxies. The fiber was then milled in a Retsch Rotor Beater Mill SR 300 (Retsch GmbH, Haan, Germany) using a 120 μm screen. The milled fiber was then sieved using a stack of screens, with a stacking sequence of 2 mm, 250 μm , 106 μm , and 76 μm . The fibers were collected in between the 106 μm and 76 μm screens. A sample of fibers were observed using an Axovert 40Mat (Carl Zeiss AG, Oberkochen, Germany), with images obtained by a ProgRes C10plus camera (Jenoptik AG, Jena, Germany), to determine the average length along with the length distribution. The processed fibers were then placed in an oven at 80°C and dried for a minimum of 8 hours before use. The distribution of the length of 300 fibers of the milled Toray fibers had an average length $74.1 \pm 40.2 \mu\text{m}$, and the distribution of the measured lengths is shown in **Figure 2**.

A variety of thermal initiators were investigated in order to identify the optimum thermal initiator to be used in a dual cure system. The thermal initiators were evaluated based off of the thermal initiators solubility with the resin system, the stability of the resin system at room temperature, and the temperatures needed for post-curing of the samples. The thermal initiators investigated were Dilauroyl Peroxide (Luperox LP), Cumene Hydroperoxide, Dicumyl Peroxide, Tert-Butyl Peroxybenzoate (Luperox P), Benzoyl Peroxide (Luperox A98) and were purchased and used as received from Sigma-Aldrich® (St. Louis, MO).

To prepare the resin system, the resin and fiber were first mixed with a high-speed mixer and then sonicated for 5 minutes. After sonication the thermal initiator was added and mixed again with a high-speed mixer. The resin system was then degassed in a vacuum chamber and then immediately used to manufacture samples.

For all samples that are manufactured using the 3D printer for this research, the longitudinal axis of the parts was varied in the x-axis of the printer to examine the effects of part orientation relative to the build surface. For all samples prepared, the finished parts were washed in ethanol after being removed from the build

Figure 2.
Milled Toray T-700 fiber length distribution.

platform. This allows for the removal of any uncured resin, and in the case of the fiber-reinforced samples any loose fibers from the surface. The supports that were generated during the printing process are left in place at this time to support the sample while it was being post-cured.

The neat (non-fiber-reinforced) samples were post-cured in an in-house built cure oven, consisting of three 25 Watt LED UV (405 nm) light banks, a heating element, and a rotating platform. The temperature and the time for the post-cure can be adjusted by the use of proportional-integral-derivative (PID) controller. For the neat samples, a temperature of 80°C was used while being exposed to the UV light for 1 hour. All fiber-reinforced samples were post-cured using a VWR Forced Convection Oven (VWR International, Radnor, PA), with the temperature and times determined from the DSC results. After post-curing the supports were removed from the sample, and the area where the supports were attached was sanded with increasingly finer grits of sand paper, ranging from 60 to 600, with care taken to preserve the sample geometry, which varies depending on the desired testing. This was done to diminish the effects of surface defects (due to support material) on the tested samples.

Composite and neat specimens were printed using a Moai 130 inverted SLA printer with the acrylic vat. Printing was performed using factory settings of the Moai 130, with one exemption. The peel step time was extended to allow more time for the higher viscosity resin mixture to flow in the printed area between layers. A standard Peopoly UV acrylic-based SLA resin was utilized as the resin of choice for both the neat specimens and composite specimens.

2.2 High-density reinforcement

A higher-density short-fiber reinforcement, E-glass fiber procured from Fiber Glast Development Corporation (Brookville, OH), was also studied. Fiber glass was selected for its high degree of transparency to UV light to not reduce the effectiveness of the UV cure. Reinforcing the resin while still allowing for good initial cure from the printer and achieving optimal polymerization through post curing was a goal. The particular glass fibers were 0.8 mm fibers denoting that the fibers have a possible length up to 0.8 mm and smaller, resulting in a mean length of 230 μm .

When manufacturing the neat specimens, no unique changes to the printing process occurred. The resin was simply poured into the vat and printing commenced per standard operating procedure for the Moai 130. The composite resin consisted of 85% resin and 15% fiber glass by volume. The composite resin batches were high-speed mixed and degassed prior to introducing the resin to the printer. The viscosity of the neat resin was found to be 517 Pa*s and the composite mixture was 950 Pa*s using a Brookfield DV-II+ Pro Viscometer. This study focused on 15% fiber volume fraction, as higher fiber loading further increased the viscosity, causing premature recirculating pump failures.

With the composite resin system mixed and degassed, the resin was introduced to a modified vat. The resin tank in the Moai 130 SLA printer was adapted to allow for a flow field in the print region. Inlet ports were fixed to the front of the vat, and outlet ports were fixed to the back of the vat. A diagram and picture setup can be seen in **Figure 3**. This setup allows for a constant flow and circulation of resin mixture with a changeover rate faster than the settling of the fibers in the resin.

Pumping the abrasive resin mixture was accomplished using a 12-volt peristaltic pump. The peristaltic pump utilized 6.4 mm inner diameter tube, which was also the same as the vat connections and made for a seamless transition to recirculate the resin mixture. At max output the motor could achieve 400 ml/min with a hose inner diameter (ID) of 6.4 mm.

Figure 3.
 Diagrams of pumping setup.

After the printing process was complete, the prints were washed with ethanol to remove any UV resin buildup. The print supports were kept in place until after being post cured. To ensure a full cure, all prints were placed in a UV oven for 60 min and 60°C. The oven consisted of a three 25 W LED UV lights and a heating element. The specimens were placed on a rotating platform in the oven. The rotation of the bed allowed for an even distribution of UV Light.

3. Testing and results

3.1 Opaque reinforcement characterization

3.1.1 Testing

The selected thermal initiators were evaluated experimentally via differential scanning calorimetry (DSC) in accordance with ASTM E2160 [28]. The testing was carried out from 25–180°C at a ramp rate of 10°C/min, using a Q20 DSC (TA Instruments, New Castle, DE). For each sample, two runs were carried out. The first was of an uncured sample, and the second was a sample that had been UV cured by placing the DSC pan in the UV cure oven 25.4 mm away from the light source for 1 minute at room temperature. This was done to determine the thermal initiators' onset temperature and to experimentally determine if any reactions are occurring after UV curing. The samples were tested at a fiber volume (V_f) of 5% and a thermal initiator content of 1 wt.% of thermal initiator. The neat Moai resin was also included to determine if there is any activation of the photo initiator at elevated temperatures. Graphs produced from the DSC data were made using TA Universal Analysis (TA Instruments, New Castle, DE).

Tensile testing was carried out using an Instron 5567 load frame (Instron, Norwood, MA), a 25.4 mm extensometer, and a 2 kN load cell. The load frame was controlled and data collected using Bluehill software (Instron, Norwood, MA). While there are no ASTMs directly concerning 3D printed materials, all tensile testing will be carried out referencing ASTM D638 [29] and ASTM 3039 [30]. The specimen geometry was of the type IV according to ASTM D638 [21]. The type IV specimen was chosen due to the limiting size of the build plate (130 × 130 mm) of the Moai printer being used to conduct this research. All samples were tested at a constant cross-head rate of 1 mm/min, so failure of the specimen occurred within 1–10 minutes of testing, per ASTM D3039 [30]. The flexural testing was carried out

using an Instron 5567 load frame (Instron, Norwood, MA) with a 2 kN load cell. The load frame was controlled and data collected using Bluehill software (Instron, Norwood, MA). The flexural testing, referencing ASTM D790 [23], was carried out as a three-point bending utilizing center loading, with specimens having a span-to-thickness ratio of 16:1 and a cross-head rate of 1 mm/min. For each sample, five specimens were tested. The maximum tensile strength and Young’s modulus were found as specified in ASTM D638 Section 11.2 and 11.4 respectively, and the maximum flexural strength and flexural modulus were found as specified in ASTM D790 Section 12.2 and 12.5, respectively [29, 31].

Scanning electron microscopy (SEM) was utilized to examine the fracture surface of tested samples. This will allow for examination of the fracture surface in determining failure types and to evaluate the dispersion and the orientation of the fibers within the sample [32]. Samples were attached to cylindrical aluminum mounts with colloidal silver paste (SPI Supplies, West Chester, Pennsylvania, USA). The specimens were sputter coated (Cressington 108auto, Ted Pella, Redding, California, USA) with a conductive layer of gold. Images were obtained with a JEOL JSM-6490LV scanning electron microscope (JEOL USA, Inc., Peabody MA, USA); energy-dispersive X-ray information was collected at an accelerating voltage of 15 kV using a Thermo Scientific UltraDry Premium silicon drift detector with NORVAR light element window and Noran System Six imaging system (ThermoFisher Scientific, Madison WI, USA).

3.1.2 Results

In order to fully cure all of the resin within the sample, the use of a dual cure system that uses both a photo initiator and a thermal initiator was investigated. The results of the DSC testing are shown in **Figure 4** (non-UV-cured samples) and **Figure 5** (UV-cured samples) are summarized in **Table 1**.

Based off of the results from the thermal initiator testing, Luperox P was chosen as the thermal initiator to be evaluated for the dual cure resin system and was determined to be effective at a 0.5 wt.%. The 10 hour half-life is the temperature at which half the content of the peroxide is lost after 10 hours. Making all of these peroxides a stable option for the processing will still have peroxide available during the thermal post curing process.

Figure 4.
DSC results for samples without UV curing.

Figure 5.
DSC curves for samples after UV curing.

Thermal Initiator	Onset temperature (°C)	10 Hour half-life (°C) [33]
Luperox P	115.99	104
Dicumyl Peroxide	116.83	114
Cumene Hydroperoxide	104.01	135

Table 1.
Thermal initiator onset temperature from DSC curves.

The fiber volume consistency results are summarized in **Table 2**. The top section of the samples has a higher fiber volume than what the resin mixture was designed to have (5% V_f). This is due to the lowering of the bed plate into the vat trapping more fibers in between the sample and bottom of the vat than desired. The reason believed for the samples to have lower and similar fiber volume gradients despite the different print times is that the area around the sample being printed becomes depleted of fibers as the sample is printed. This slowly lowers the fiber volume of the sample as it is going through the printing process.

Because the flexural specimens have a larger cross-sectional area throughout the entire specimen, the fiber gradient appears more pronounced. Similar burn off testing was carried out with the tensile specimens with the exception that only the two ends of the specimen were tested. The average difference in the fiber volume of the top and bottom portions of the tensile specimens changes by on average of 0.8% for the specimens printed in the 90° orientation. This lower difference could be due to the varying specimen geometry, or that due to their large size, less specimens were printed at the same time to keep the print time short. This allowed for more spacing between the specimens and could have prevented the fiber from becoming depleted from around the specimens being printed.

To aid in sample identification, the follow naming scheme will be implemented for the remainder of this paper. It will consist of the main material parameter being looked at along with the layer height and print orientation. The lettering is in Ref. to the material parameter: M is Moai resin as supplied, LP is Moai resin mixed with thermal initiator (Luperox P), and C consists of carbon fiber, thermal initiator (Luperox P), and Moai resin. The number following the lettering is the layer height

Layer height (μm)	Print time (hours)	Top (% V _f)	Middle (% V _f)	Bottom (% V _f)
100	3.0	5.23 ± 0.02	4.84 ± 0.10	3.57 ± 0.27
50	5.25	5.45 ± 0.15	4.50 ± 0.13	3.88 ± 0.01

Table 2.
Summarized fiber volume consistency results for flexural samples.

(100 μm or 50 μm). The number following the hyphen is the angle (0° or 90°) between the longitudinal axis of the sample and the build platform during the manufacturing process. The summarized results of the tensile and flexural testing are shown in **Table 3**. The samples are identified with a superscript in the first column and identified with the superscripts of other groups in which significant statistical difference between the results was found via an ANOVA analysis and post-hoc Tukey HSD test at a 95% confidence interval. The samples are compared across four different groups: 0° orientation, 90° orientation, 100 μm layer height, and 50 μm layer height.

When comparing the Young’s modulus of the samples, there was an increase of 21% between the M100-0 and CF100-0 samples and an increase of 27% for the M50-0 and the CF50-0 with an increase in Young’s modulus for the CF50-0 samples when compared with the CF100-0 of 5%. While showing only 4% increase between the LP100-0 and CF100-0 samples and 13% increase for the LP50-0 and CF50-0, evidence of the weak interfacial properties of the short-fiber composite samples can be seen in **Figure 6**.

In **Figure 6**, the smooth channels left behind from the carbon fiber in A, the clean (lack of bonded matrix material) fibers present in B, and the smooth holes in B are all signs of weak interfacial properties due to poor bonding between the matrix and fiber [6, 34]. This limits the ability for the matrix to transfer stress to the fibers and therefore reduce its overall properties [6]. If the composite had better interfacial properties, there would have been evidence of fiber breakage, which was not present in any of the SEM images taken [6, 34].

Sample	Tensile strength (MPa)	Young’s modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
M100-0	58.9 ± 5.0	2.72 ± 0.06	86.0 ± 9.5	2.52 ± 0.07
M100-90	66.1 ± 0.4	2.87 ± 0.05	96.2 ± 1.7	2.42 ± 0.01
M50-0	43.4 ± 7.7	2.81 ± 0.15	82.2 ± 11.2	2.42 ± 0.05
M50-90	64.6 ± 1.6	2.89 ± 0.12	100.8 ± 3.4	2.62 ± 0.06
LP100-0	36.9 ± 7.9	3.17 ± 0.15	27.9 ± 5.4	2.34 ± 0.15
LP100-90	27.6 ± 22.5	3.17 ± 0.26	14.6 ± 3.0	2.47 ± 0.21
LP50-0	50.3 ± 7.7	3.04 ± 0.11	23.9 ± 3.7	2.55 ± 0.23
LP50-90	68.8 ± 5.9	2.83 ± 0.01	13.2 ± 0.6	2.50 ± 0.20
CF100-0	52.4 ± 3.7	3.29 ± 0.29	84.9 ± 4.3	2.59 ± 0.06
CF100-90	41.4 ± 2.6	3.39 ± 0.52	66.1 ± 0.5	2.31 ± 0.11
CF50-0	50.6 ± 6.6	3.46 ± 0.17	43.4 ± 5.5	2.64 ± 0.12
CF50-90	11.69 ± .28	2.92 ± 0.01	19.4 ± 2.5	2.58 ± 0.16

Table 3.
Summarized tensile and flexural testing results.

Figure 6.
Fracture surface of CF50-0 (A) X200 and (B) X250 magnification.

When comparing the modulus of the carbon fiber samples printed at different layer heights (100 µm and 50 µm), the increase in modulus of 5% can be attributed to the partial alignment of the fibers in the loading direction. The CF100-90 has a higher modulus than the CF50-90 samples. While this would be expected if the material was going from isotropic material to a special orthotropic material due to fiber alignment, it is not the case for these samples due to cracks being present in the CF50-90 samples [6]. The alignment of the fibers via layer height is demonstrated in **Figure 7** with the yellow arrows highlighting the various fiber orientations.

When comparing the strength of the Moai resin samples, the samples printed in the 90° print orientation for the Moai resin have a higher strength when compared with the same samples printed in the 0° print orientation. This is due to the effects of the support material being removed and leaving behind notches in the specimen. These notches then act as small stress concentrators resulting in lower strength of the sample [35]. Due to these effects, the Moai resin samples tested at a print orientation of 90° are a better representation of the actual ultimate tensile strength of the neat resin material. The samples tested with just the thermal initiator (Luperox P) added also showed flaws the contributed to a lower tensile strength result. These are from cracks that were present on the surface of the samples, which originated during the thermal curing process. These cracks originated from the volumetric shrinkage that occurs during the post-curing process as the degree of conversion within the system increases [36].

Figure 7.
Fracture surface of (A) CF100-90 and (B) CF50-90 specimens.

The lower strength of the carbon fiber samples is due in part to the end effects of the fiber reinforcement acting as stress concentrators within the composite [6]. This is caused by the large number of very short fibers (much less than the critical length) in the distribution of the lengths, seen in **Figure 2**, being present in the sample [6]. The strength of short-fiber composites is also affected by the length of the carbon fiber being used. To get the maximum amount of reinforcement from the carbon fiber, the fiber needs to be over a critical length to maximize the load transfer between the fiber and matrix [6]. The shorter length of the fibers ($76\text{ }\mu\text{m}$) being used is below the critical length needed for the system ($433\text{ }\mu\text{m}$ using a shear lag model) [6]. This results in the load not being fully transferred to the fiber and limiting the composites performance [6].

Overall the flexural modulus of the samples was not improved by the addition of the carbon fiber. This could be primarily due to the lower fiber volume (5%) of the samples, causing them to have results similar to that of the neat resin samples. During the flexural testing, the specimens are subjected to the more complex stress state (compressive, tensile, and shear) when compared with the tensile testing [28, 29].

The effect of the fiber volume gradient that was present in the samples would also have a more pronounced effect of the results when compared with the tensile testing. For the tensile specimens, the gage section had similar fiber volume amount within the measured section. Among the flexural specimens, the whole specimen (within the span length) is tested allowing for failure to occur in the regions of lower fiber volume.

For the flexural testing, the samples are subjected to compressive, tensile, and shear stresses that lead to the multiple failure mechanisms affecting the flexural properties of material [29]. The tensile stresses can lead to fiber breakage and debonding, while compressive stresses can lead to fiber shear and/or buckling and kinking [29]. The fibers exhibited characteristics indicating poor interfacial strength between the fiber and matrix. This along with the low fiber content and weak shear properties of carbon fiber would lead to the failure of the flexural testing to coincide more with that of the compressive type failures, which are governed more by the matrix properties [6, 37, 38].

The samples made with just Luperox P added showed the same type of surface cracking after post-curing as was seen in the tensile samples. This led to them having the weakened flexural strength as seen in the tensile samples made of the same constituents. The carbon fiber samples exhibited poorer flexural strength than the neat Moai resin samples due to the effects of the fiber ends acting as stress concentration, weak interfacial properties, low fiber content, and the presence of voids [6].

3.2 High-density reinforcement characterization

3.2.1 Testing

Printed specimens were characterized for density, 3 pt. flexure, notched fracture toughness, and dynamic mechanical analysis (DMA). The testing conducted is to illustrate the performance enhancements and the quality of cure and consistency of the resulting composite parts.

Density calculations were performed to ensure the fibers were evenly dispersed, following ASTM D792-13 Test Method A [39]. An Ohaus Adventurer (Ohaus Corp., Parsippany, NJ) scale was used to weigh four sections from four different specimens. Using a Mettler Toledo (Mettler Toledo, Columbus, OH) density determination kit, the density comparison was conducted between samples printed using the

flow process and one specimen without resin flow. Where A is the weight of the sample in air, B is the weight of the sample in water and the density of water and air with subscripts O and L respectively to calculate the density of the samples.

$$\rho = \frac{A}{A-B}(\rho_O - \rho_L) + \rho_L \quad (1)$$

The flexural testing was carried out using an Instron 5567 load frame (Instron, Norwood, MA) with a 2 kN load cell. The load frame was controlled and data collected using Bluehill software (Instron, Norwood, MA). The flexural testing, referencing ASTM D790 [31], was carried out as a three-point bending utilizing center loading, with specimens having a span-to-thickness ratio of 16:1 and a cross-head rate of 1 mm/min. For each sample, five specimens were tested and the maximum flexural strength and flexural modulus were found as specified in ASTM D790 Section 12.2 and 12.5, respectively [29, 31].

Notch fracture testing was carried out using ASTM D5045 [40] standard with an Instron 5567 load frame and a 2kN load cell. Single-edge-notch bending (SENB) specimens were created as rectangular bars 7 mm × 13 mm × 63 mm. These bars were notched post processing using a vertical mill and a final fine crack initiated with a razor blade. Five neat and five reinforced samples were tested and post-test measured using a Keyence VHX-7000 Digital Microscope for the crack length determination.

Glass fiber is highly transparent to UV light, but DMA was performed to ensure that each part was optimally cured. To perform this, ASTM D5418-15 [41] was followed. Three samples of both neat and glass fiber-reinforced specimens were printed. Dual cantilever DMA was chosen because the T_g can easily be evaluated at the peak of the tan(δ) curve. Each sample was printed at 60 mm × 13 mm × 4 mm to fit in the dual cantilever grips. A TA Instruments DISCOVERY DMA850 was used with a temperature range of 30–150°C, a frequency of 1 Hz, an amplitude of 15 μm, and a heating rate of 1°C/min.

3.2.2 Results

As observed in other research attempts, the high-density fiber glass quickly settles to the bottom of the print. This results in components that have the desired reinforcement at the beginning of the print, but little to no reinforcement after the glass settles to the bottom of the VAT and is unable to flow into the print area. The printer does not have a swipe step or means of resin movement, which allows the fibers to settle to the bottom. With the fiber on the bottom, the fiber free resin is allowed to flow back into the print area with very few fibers present. Therefore, the density of the composite will vary from the top of the print to the bottom of the print without a pumping system. When examining the samples, a gradient of fibers/density could easily be seen without a microscope with the specimens printed without flow.

Comparison of glass content and distribution between prints with no pump and pump can be seen in **Figure 8**. The fiber distribution is consistent from the start to finish for the specimen printed with the pump providing a flowing resin mixture. **Figure 8B** is the end of the print and **Figure 8D** is the beginning of the part but after the scaffolds had already been printed. Similarly, **Figure 8A** is the end of the print and **Figure 8C** is the start of the part but after the scaffolds. It can be seen that even at the start of the part, there is very little glass in the part and diminishes to nearly no fiberglass by the end of the print. No discernable differences were found when

Figure 8.
A, end of print with no pump; B, end of print with pump; C, start of print with no pump; D, start of print with pump.

Process	Density g/cm ³
No pumping	1.26
Sample 1	1.39
Sample 2	1.40
Sample 3	1.39

Table 4.
Densities of specimens examined.

observing parts printed with the circulation pump. **Figure 8** images are taken using a Keyence VHX 7000 digital microscope (Keyence Corp of America, Itasca, IL).

Table 4 shows the density averages of the specimens printed. The theoretical density of the composite specimens at 15% fiber volume fraction, assuming no voids, was 1.42 g/cm³. The three samples that used the pumping system only had a 1.4% deviation from the target density. As predicted, the density of the no flow specimen was much lower as the majority of the volume did not have any fiberglass present. The composite specimens created with the flow field were consistent and very close to the theoretical density.

For fracture toughness, the Keyence microscope was used to measure the crack length in each specimen. The calibration factor was then calculated for the SENB specimen, and this factor ensured that each specimen was comparable. This calibration factor is denoted as $f(x)$ and takes the geometry of each specimen into account. In this equation K_{IC} is the fracture toughness, P_Q is the max flexure load, B is the thickness at the crack and, W is the width at the crack.

$$K_{IC} = \left(\frac{P_Q}{BW^{\frac{3}{2}}} \right) f(x) \tag{2}$$

An increase in fracture toughness of 32.5% was observed when adding 15% glass fiber to the resin. These results can be observed below in **Figure 9**. This is a tremendous improvement to one of the historically low properties of a UV curable resin. Also, the standard deviation narrowed in the results when testing reinforced specimens, providing a more consistent performing product.

The increase in fracture toughness by addition of short fibers is not uncommon, and the difference in fracture surface helps discuss the increase. **Figure 10A** is the nearly perfectly smooth brittle failure of the Neat specimen, and **Figure 10B** shows the reinforced fracture surface. The reinforced fracture surface exhibits a multitude of fracture surface redirections because of the obstructing fibers, greatly increasing the fracture surface area. Fiber pullout can also be seen on the surface providing increased toughness and ductility.

The flexural results are a great indicator of a part's quality and encompass the overall performance of the resulting composite. One of the most obvious improvements is the reproducibility of the results that can be seen in **Figure 13**. By introducing fiberglass to the system, there was not only a substantial improvement in modulus but overall a more predictable performance was obtained. During testing, crazing could be observed on the tensile side of the flexural specimen during the plastic deformation portion of the test on just the reinforced specimens. Abrupt brittle failure occurred on all the neat specimens with each specimen having multiple fracture surfaces. The change in the average maximum flexural stress, average flexural modulus, and average max strain is shown in the graphs below (**Figure 11**). The addition of the 15% fiberglass increased the

Figure 9.
Average fracture toughness of neat and glass-reinforced samples.

Figure 10.
Fracture toughness surface: A, neat; B, fiberglass.

Figure 11.
Comparison of neat and glass fiber-reinforced samples of: Modulus, flexure strength, and flexure strain.

Figure 12.
Flexural specimens: A, neat; B, fiberglass.

average flexure stress by 18%, increased the average modulus by 38%, and effectively did not change the average strain to failure.

The fracture surfaces can be seen in **Figure 12A** for the Neat specimen and **Figure 12B** for the reinforced specimen. The brittle failure on the neat specimens is very clean and consistent. While the fracture surface of the reinforced specimen shows signs of more cumulative damage. In **Figure 12B**, the tensile side of the flexural specimen on the right where the bright white shades on the surface can be seen and at the neutral axis going to the left the compression side shows a clear resin appearance. On the compression side of the specimen, there was little evidence of permanent deformation. On the tensile side, the specimen has crazing, which is the white portion of the specimens on the right side of the neutral axis. This microscopic evidence supports the results of increasing the modulus significantly and improving the toughness of the printed specimen by retaining the strain to failure of the neat polymer. The fibers are providing continued stress transfer and continuity beyond the polymers ability.

Figure 13 is the fracture surface from the **Figure 12B** on the tensile side of the specimen. The image shows clean fiber pullouts and areas of crazing. The fibers are not at a critical length where stress transfer is expected to be significant enough to fracture the fibers in the tensile. Also, seen in this image is the randomness of fiber orientation in the left to right directions, but rarely in the z-direction of the print, which is top to bottom. This orientation is due to the fiber length being greater than the print layer height, allowing for fiber alignment to be reduced to one plane.

Figure 13.
Flexural fracture surface at 200×.

Figure 14.
Neat sample 3 of DMA testing.

Figure 15.
Glass sample 1 of DMA testing.

To understand if the level of cure of the reinforced specimens was equal to the neat specimens, DMA was performed. The Tg was found using the tan(δ) curve. The neat resin was considered to be optimally cured by the recommended

manufacture processing and post curing of the resin, with the reinforced specimens receiving the same processing parameters. Examining the curves of the neat samples, the average Tg was found to 107.59°C. Sample 3 had the closest actual Tg to the average and can be seen below in **Figure 14**.

The three composite specimens yielded an average Tg of 109.19°C. Glass sample 1 had the closest Tg to this value, and the graph can be seen below in **Figure 15**. Adding fiberglass to a neat resin usually results in an improvement in Tg. It was found that by adding the glass fiber to the resin matrix, the Tg increased by 1.6°C. This increase in Tg does confirm that the specimens were comparably cured with and without the fiberglass reinforcement.

4. Conclusions

From the DSC results, it was determined that the neat Moai resin did not exhibit any curing due to thermal processing, but with the incorporation of a thermal initiator, the resin would cure both with and without prior UV curing. Luperox P was chosen as the thermal initiator that yielded the best results from the ones evaluated, from both processing and material properties perspective.

From the tensile testing results, the carbon fiber samples showed an increase in Young's modulus of 21% for a 100 µm layer height, and a 27% for a 50 µm layer height. The change in the modulus due to the lower layer height is due to the fibers being aligned in the loading direction within the sample. This demonstrates that manipulating a part's properties based off of fiber length and layer height could be possible. This increase was less than what was predicted by theoretical models. The lower modulus was thought to be caused by large distribution of fiber lengths and poor interfacial properties between the carbon fiber and matrix. These defects also lead to the carbon fiber samples having a lower tensile strength than the neat Moai resin samples. With improvements in these areas, the tensile properties of the composite could be further improved.

The flexural strength, flexural modulus, and fracture toughness showed no noticeable gains in material properties from the use of the carbon fiber reinforcement. For the flexural testing, this is thought to be because of the low fiber volume (5%) and high fiber volume inconsistency of the samples. While factors such as interfacial strength, fiber length distribution and volume consistency, and low fiber volume content lowered the effectiveness of the carbon fiber as a reinforcement, the main limiting factor is the fiber length itself. The shorter length of the fibers (76 µm) being used is below the critical length needed for the system (433 µm using a shear lag model) [6]. While it would be possible to incorporate fibers of this length into the resin and print parts, they could not have isotropic properties due to forced alignment of the layer height. The effects of fibers folding over within the layers could also affect the ability for the part to print successfully. This could be by limiting the amount of matrix material available to keep the layers attached to one and another. To avoid this, it would require a layer height at least as large as the fiber length itself. This is outside of the capabilities of even industrial grade vat photopolymerization printers, that typically print at around 200 µm on the top end of layer height [30]. The incorporation of carbon fiber and the subsequent shadowing of the photo initiator from the UV source would even further limit the depth of cure that could be achieved. So while it might not be feasible to use fiber with a length of 433 µm, increasing the fiber length and tightening the fiber length distribution would aid in increasing the material properties for the samples studied in this research.

Additive manufacturing of high-density reinforcement composites using SLA vat printing can be accomplished using the newly developed adaptation of flow

induction. Composites with reinforcements having largely disparaging densities can be homogenously manufactured with standard operational settings. This study proved out that the short glass fibers can be incorporated into a 3D printed part resulting in tremendous improvements in mechanical properties while maintaining print cure and consistency. This patent pending design (US Patent Application 63/073,260) can allow for 3D printing to continue to expand its offerings and capabilities.

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Conflict of interest

The authors declare no conflict of interest.

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