A Novel Multimaterial Additive Manufacturing Technique for Fabricating Laminated Polymer Nanocomposite Structures

The objective of this research is to develop a novel, multimaterial additive manufacturing technique for fabricating laminated polymer nanocomposite structures that have characteristic length-scales in the tens of millimeters range. The three-dimensional (3D) printing technology presented in this paper combines the conventional inkjet-based printing of ultraviolet (UV) curable polymers with the deposition of either aligned or random nanoscale fiber mats, in between each printed layer. The fibers are first generated using an electrospinning process that produces the roll of fibers. These fibers are then transferred to the part being manufactured using a stamping operation. The process has been proven to manufacture multimaterial laminated nanocomposites having different 3D geometries. The dimensional accuracy of the parts is seen to be a function of the interaction between the different UV-curable polymer inks. In general, the addition of the nanofibers in the form of laminates is seen to improve the mechanical properties of the material, with the Young's modulus and the ultimate breaking stress showing the most improvement. The pinning and deflection of microcracks by the nanoscale fiber mats has been identified to be the underlying mechanism responsible for these improved mechanical properties. The thermogravimetric analysis (TGA) reveals that these improvements in the mechanical properties are obtained without drastically altering the thermal degradation pattern of the base polymer. [DOI: 10.1115/1.4029263]

Keywords: laminated nanocomposites, electrospinning, inkjet-based additive manufacturing, 3D printing

1 Introduction

Conventional fiber-reinforced composite materials are typically comprised of aligned microscale reinforcements (e.g., glass, carbon, or Kevlar fibers) dispersed in a polymer matrix [1]. The engineering products/parts made out of these composite materials are typically manufactured in the form of laminates that consist of a sequence of unidirectionally reinforced plies laid one on top of the other [1,2]. In the case of these products/parts, both the orientation of the microscale fibers in each ply and the ply lay-up sequence are tailored to achieve the desired laminate properties [2]. With the recent discovery of various forms of nanoscale fibers [3–5], there is a need to extend this approach toward the manufacture of laminated polymer nanocomposite structures with desired properties. The potential applications of such structures include...
artificial muscles and body parts for surgeon training, directional viscous dissipation dampers, and self-healing transparent laminates.

The most common technique of fabricating polymer nanocomposites is by the shear mixing of nanoscale fibers into a polymer matrix [6–8]. While this approach has been shown to improve the properties of the nanocomposites, it does not result in the alignment of the fibers in the matrix. This lack of alignment limits the extent of attainable improvements in the properties of the nanocomposite [9]. Alignment of nanoscale fibers in a polymer matrix has been accomplished using techniques, such as spin-coating (i.e., shear-based alignment), and the use of electric and magnetic fields [10,11]. While these techniques have been used successfully to fabricate thin-film composite samples having aligned nanoscale fibers, they are not suited for the scale-up needed to manufacture 3D laminated polymer nanocomposite structures. Additive manufacturing (AM) techniques that use polymer deposition offer a feasible scale-up solution [12]. While studies have demonstrated 3D printing using polymer microdroplets containing nanofillers, this technique does not result in alignment of the fibers within the matrix and is therefore unsuitable for manufacturing laminated polymer nanocomposite structures [13,14].

This paper presents the development of a novel, multimaterial additive manufacturing technique for fabricating laminated polymer nanocomposite structures with characteristic lengths that are in the tens of micrometer range. This new manufacturing technique combines the conventional inkjet-based 3D printing of UV curable polymers along with the deposition of nanofiber mats that are manufactured using an electrospinning process. The process has been proven for both aligned as well as randomly oriented multimaterial laminates.

The remainder of this paper is organized as follows: Section 2 describes the proposed manufacturing process cycle for fabricating laminated polymer nanocomposite structures, followed by Sec. 3 that presents the design details of the setup. Sections 4 and 5 discuss the selection of the prototype geometries/materials and the manufacturing outcomes, respectively. Section 6 presents the results from the thermomechanical property characterization studies. Finally, Sec. 7 presents the specific conclusions that can be drawn from this work.

2 Proposed Manufacturing Process Cycle

Figure 1(a) outlines the proposed process cycle to manufacture 3D multimaterial laminated polymer nanocomposite structures. The process first involves the manufacture of the roll of nanofibers using an electrospinning operation. Both aligned as well as randomly distributed nanofibers can be generated by appropriate design of the collector electrode. Once the nanofiber rolls have been manufactured, they are mounted on to a custom designed inkjet-based AM setup (refer to Sec. 3.2 for details) to print the 3D part.

The sequential processing steps involved in the manufacture of the laminated polymer nanocomposite are as follows (Fig. 1(a)):

- Step 1: Prepare a roll of nanofibers (aligned or randomly oriented) to be used during the 3D printing process;
- Step 2: Use the inkjet nozzles to print a layer of UV-curable polymer ink;
- Step 3: Expose the printed layer of polymer ink to UV light;
- Step 4: Dry the cured polymer surface using a heat lamp (optional);
- Step 5: Use a numerically programmed cutter to cut a section of the roll of nanofibers to the desired geometry of the layer;
- Step 6: Stamp the section of nanofibers on the dry polymer surface; and finally
- Step 7: Repeat steps 2–6 for each layer as needed.

The proposed integration of conventional inkjet-based 3D printing technology with an electrospinning-based nanofiber generation process not only makes it feasible to manufacture 3D laminated polymer nanocomposite structures but it also opens up a new frontier in nanocomposite design. The above manufacturing process cycle can be easily adapted to print multiple polymeric inks and nanofibers into the same laminated nanocomposite structure to achieve hitherto unattainable material properties in the laminates.

In addition, the proposed manufacturing process allows for a relatively straightforward scale-up to print macroscale laminates containing nanofibers. This can be done by repeating the stamping operation over a larger area. Furthermore, the nanofiber loading in the laminate can be easily varied by varying the frequency of the stamping operation (Figs. 1(b) and 1(c)). For a given number-density of nanofibers in a roll, the highest loading of the fibers in the laminate can be obtained by stamping the fibers after depositing every single polymer layer, as seen in Fig. 1(b). This loading of nanofibers in the laminate can be reduced by reducing the frequency of the intermittent stamping operation, as shown by the cross-section of the sample in Fig. 1(c).

Fig. 1  Manufacturing process cycle for fabricating laminated polymer nanocomposite structures: (a) outline of process cycle, (b) cross section showing higher density of nanofiber mats, and (c) cross section showing lower density of nanofiber mats
3 Setup Design Details

The overall manufacturing setup consists of two separate systems, viz.: (1) the fiber collection system (FCS) and (2) the 3D printer system. The FCS was used to generate rolls of nanofibers both in the aligned and the randomly oriented form by using the electrospinning process [15]. These rolls were then transferred to the custom-built 3D printer unit so as to proceed with the manufacturing process cycle described in Sec. 2. The remainder of this section describes the design of each of these two systems. It should be noted here that while these two systems are physically separate, they can be easily integrated into a single unit for scale-up.

3.1 Fiber Collection System

3.1.1 Principle. Far-field electrospinning is a commonly used process for manufacturing different types of polymer nanofiber mats [15]. In this process, the polymer of interest is first dissolved in a solvent and this solution is then loaded into a glass syringe with a metallic needle. An electric field (V = 5–35 cm) is then applied between the tip of the needle and a collector electrode located at a distance of ~5–35 cm from the needle. The applied electric field deforms the liquid droplet to first form a Taylor cone [16], which then breaks down to release a jet of the polymer solution. The jet then undergoes a whipping motion that causes the thinning of the polymer jet to generate polymer fibers with diameters as low as 100 nm [15]. A syringe pump is used to maintain a constant flow rate of the polymer solution. Both randomly oriented as well as aligned nanofibers can be generated by modifying the geometry of the collector electrode [17].

3.1.2 Collector Plate and Electrode Design. Randomly oriented nanofibers have been easily generated by using a flat plate electrode design [15]. However, the generation of aligned nanofibers requires shaping of the electric field lines to enable the alignment. While parallel plate electrodes have been proven in the literature to yield aligned nanofibers [17], those designs have only allowed for small area (~10² mm²) deposition of the nanofibers, which is significantly smaller than the total coverage area of ~10⁶ mm² required to manufacture the rolls. Furthermore, the nanofibers get attached to the stationary electrode, thereby making it unsuitable for the manufacture of the nanofiber rolls needed for the proposed process. Therefore, there is a need to design a unique collector plate and electrode combination that not only allows for the alignment of the nanofibers but also for the manufacture of nanofiber rolls that could cumulatively span a 25 mm × 40 mm area of coverage for the aligned nanofibers. The larger length (L) of the electrodes was designed to expand the effective area covered by electric field lines. The length was limited to 100 mm since simulations with L > 100 mm showed no further expansion of the covered area. The radius R of the collector plate was also a critical design parameter that helped distribute the field lines more uniformly over the collector surface. For a flat collector plate (i.e., R = infinity), there is a distinct agglomeration of the field lines at the center of the fiber collection region (Fig. 2(d)). This is due to the fact that for such a collector, this center region has the shortest distance between the needle and the collector. Such an electric field would result in uneven distribution of the nanofibers in the roll and should therefore be avoided. The addition of a curvature helps the field lines at the center to be distributed evenly across the fiber collection region (Fig. 2(c)).

Holding the dimensions of the collector plate and the electrode constant (as in Fig. 2(a)), the static copper electrodes were modified to take the form of two rolls of thin copper tape that were...
chosen as the reinforcement phase in this study [18]. Nylon 6 pel-

The take-up reels B and D (Fig. 3(c)) were attached to an ultrahigh molecular weight polyethylene (UHMWPE) backing for the fibers (reel C). Reel A had two strips of copper tape (acting as parallel plate electrodes during the nanofiber generation) that were supported on a paper backing. The copper tape, along with its paper backing, was dispensed from reel A and traveled over two tensioning rollers before reaching the collector plate (Fig. 3(b)). As the copper tape passed over the collector plate, it collected the aligned nanofibers generated by the electrospinning unit. Once the nanofibers were deposited in between the two strips of copper tape, the paper backing on the copper tapes was taken up by the collector reel B, whereas the copper strips laden with the aligned nanofibers proceeded to be attached to an ultrahigh molecular weight polyethylene backing (being dispensed from reel C). At the end of the nanofiber generation process, reel D held the nanofibers that were then loaded onto the collector plate electrode to generate randomly oriented nanofibers [15].

### 3.1.3 FCS Design

Figure 3 shows the details of the nanofiber collection system that used the above collector plate and electrode design, in conjunction with a dynamic parallel plate electrode configuration with a reel-to-reel architecture, to manufacture the aligned nanofiber rolls. As with a conventional far-field electrospinning setup, the FCS had a syringe pump with a dispensing syringe, which had a metallic needle tip that served as the positive electrode (Figs. 3(a) and 3(b)). The ABS plastic collector plate was positioned directly opposite to the needle. Two copper tape rolls of width 5 mm were used as the ground electrodes to enable the alignment of the nanofibers.

In order to facilitate the manufacture of the nanofiber rolls, a nonconducting roller frame that automates the fiber roll production (Fig. 3(c)) was implemented. As seen in Fig. 3(c), the design consisted of two dispensing reels, one for the copper tape electrode (reel A) and the other for the ultrahigh molecular weight polyethylene (UHMWPE) backing for the fibers (reel C). Reel A had two strips of copper tape (acting as parallel plate electrodes during the nanofiber generation) that were supported on a paper backing. The copper tape, along with its paper backing, was dispensed from reel A and traveled over two tensioning rollers before reaching the collector plate (Fig. 3(b)). As the copper tape passed over the collector plate, it collected the aligned nanofibers generated by the electrospinning unit. Once the nanofibers were deposited in between the two strips of copper tape, the paper backing on the copper tapes was taken up by the collector reel B, whereas the copper strips laden with the aligned nanofibers proceeded to be attached to an ultrahigh molecular weight polyethylene backing (being dispensed from reel C). At the end of the nanofiber generation process, reel D held the nanofibers that were then loaded onto the 3D printing system (Fig. 3(c)). A DC motor was used to drive the take-up reels B and D (Fig. 3(c)).

### 3.1.4 Nanofiber Production Results

Nylon 6 nanofibers were chosen as the reinforcement phase in this study [18]. Nylon 6 pellets (3 mm) and formic acid (reagent grade >95% to be used as solvent) were purchased from Sigma-Aldrich™ and used as received. A polymer solution concentration of 30 wt.% was fed from the horizontally oriented 30 ml capacity glass syringe (Multi-Fit™) fitted with a 25 gauge blunt-end needle. A constant flow rate of 0.2 ml/h was controlled with a syringe pump (Razel™ R99-EJM). A positive voltage ranging from 18 to 20 kV was applied directly to the needle by one positive electrode of a high-voltage, direct-current power supply (Glassman High Voltage, Inc., High Bridge, NJ). These nanofibers were electrospun both into random as well as aligned mats. Representative samples of randomly oriented (fiber A) and uniaxially aligned nanofibers (fiber B) are shown in Figs. 4(a) and 4(b), respectively. The mats were produced en mass and collected on the reel D in the FCS (Fig. 3(c)). In order to manufacture randomly oriented mats, a single 100 mm × 40 mm copper electrode was fixed to the collector plate and a paper tape (40 mm wide) was made to follow the same path as shown for copper tape in Fig. 3(b). The fibers were then subsequently collected on the paper tape.

### 3.2 3D Printing System

Figure 5 outlines the design of the custom-built 3D printing system that was used for manufacturing the laminated nanocomposite structures. The system consisted of the following key components: (1) a multinozzle inkjet-based polymer dispensing unit that was used to deposit the UV-curable polymer; (2) a fiber layering system (FLS), which took the nanofiber reels from the FCS and stamped them onto the part being printed; (3) a surface preparation system comprised of the UV source and the heat lamp; and (4) the substrate mount. As depicted in Fig. 5, the system is comprised of an Aerotech™ five-axis linear motion system. Axes 1 and 2 (Aerotech ANTi180 stages) provide the 2D motion for the substrate, axis 3 (Aerotech ATS100 stage) held the inkjet dispensing nozzles and provided vertical movement to build-up layers, and axes 4 and 5 (Aerotech PRO115 stages) carried the FLS. Axes 1 and 2 had a positional accuracy of ±100 nm, and all the remaining axes had a positional accuracy of ±250 nm.
±1 μm. The UV source and the heat lamp were mounted on pneumatic slides attached to the granite frame of the 3D printer. A kinematic coupling-based pallet design was implemented to hold the substrate during the printing process [19]. The entire system was mounted on a granite table to ensure sufficient damping. Table 1 summarizes the overall specifications of the 3D printer. The remainder of this section outlines the details of the each of the subsystems of the 3D printer.

### 3.2.1 Multinozzle Inkjet-Based Polymer Dispensing Unit

In order to dispense UV curable polymer inks that serve as the matrix of the nanocomposites, an inkjet-based polymer dispensing system from MicroFab™ was integrated into the above motion platform. As shown in Fig. 5 (items a-b), the system comprised of four piezoelectric microneedles (MicroFab™ MJ-ABL series) with their ink reservoirs, a pneumatic controller (MicroFab™ CT-PT4), and JetDrive III drive electronics to trigger each of the nozzles. The presence of multiple nozzles not only allowed for the printing of different inks in the same part but it also allowed for the selection of different nozzle diameters in the 20–120 μm range. In order to print microdroplets using this system, the pneumatic controller was first used to create the meniscus needed to eject consistently sized droplets [20]. Once the proper meniscus had been formed, the piezo-electric nozzles were triggered using specific voltage patterns that were input to the JetDrive III controller using the JETSERVER software. The size of the droplets being released from the nozzles was measured using a CCD camera (Fig. 5) in conjunction with the APHELION™ image analysis software.

### 3.2.2 Fiber Layering System

The inset on the top right hand side of Fig. 5 depicts the FLS system that was used to lay down nanofibers to create the nanocomposite plies. As shown, the system was comprised of two reels, viz., the feed reel and the take-up reel (item e) that were attached to axes 4 and 5 using a mounting plate. The reels were driven by a pair of servomotors that were controlled using an Arduino microcontroller. The reels of the FLS were interchangeable with those on the FCS allowing for the loading of the nanofiber rolls. The rolls obtained from the FCS were comprised of nanofibers attached to a UHMWPE backing. To increase the bend radius of the UHMWPE backing, rollers were provided both at the entry and the exit of the stamping region (item f in Fig. 5). The stamping region (item f in Fig. 5) of the FLS was a rectangular region of 50 mm × 100 mm size made of high-density foam that provided the stamping force for depositing the nanofibers.

Integral to the functioning of the FLS was the tungsten carbide cutting tool (item g in Fig. 5) that was used to cut the nanofibers into the required shape for each layer, before the stamping operation. The circular cutter was mounted on axes 1 and 2 and had an outside diameter of 60.2 mm and an edge radius of 5 μm. The holder for the cutter had an in-built servomotor that allowed for the cutter to undergo 90 deg rotations. This rotary actuation of the cutter combined with 2D motion provided by axes 1 and 2 allowed for the cutting of nanofibers in different geometries. Figures 6(a)-6(d) depict the cutting and the subsequent stamping of the nanofibers by the FLS. Depending on the 2D pattern of the fibers needed for each layer, a tool-path planning software is first used to program the motion of the cutter for every layer (Fig. 6(a)). Figure 6(b) depicts this implementation in the form of two orthogonal positions of the carbide cutter corresponding to cuts 1 and 2 in Fig. 6(a). After that the FLS (mounted on axes 4 and 5 in Fig. 5) in lowered on to the substrate to deposit the fibers. The speed of stamping was maintained at 600 mm/min on stages that have a 1 μm positional accuracy. As seen in Figs. 6(c) and 6(d), the fibers get released according to the patterns cut on each layer.

### 3.2.3 Surface Preparation System—UV Cure and Heat Lamp

To facilitate the manufacture of 3D parts using UV curable inks, it
was critical to have a UV curing station built into the 3D printer. A Dymax\textsuperscript{TM} BlueWave 200 curing spot lamp and rod lens combination was used as the UV source for this 3D printer (item i in Fig. 5). The rod lens was suspended at a height of 25 cm from the surface of the substrate. This resulted in a coverage area of 161.3 cm\textsuperscript{2}, with an intensity of $\sim$30 mW/cm\textsuperscript{2}, which is sufficient for curing thin layers of commonly used UV curable polymers [21]. A protective shield was designed around the UV lamp in order to prevent the ink from curing in the inkjet reservoirs and the microdispensing nozzles. The enclosed UV lamp was mounted on a pneumatic slide (item i in Fig. 5) to enable its actuation during the UV curing step.

In addition to the exposure to UV light, some UV curable polymers, such as SU-8, require a subsequent heating step to fully cure the surface layer [22]. Other commonly used polymer inks from Sartomer\textsuperscript{TM} require a heating step to remove the oily residue left behind due to the UV curing process [23]. To accommodate the printing of such polymers, a 250 W heat lamp was also integrated into the system (item j in Fig. 5). An insulating shield was put into place to protect the critical components of the printer from the heat. The lamp and shielding assembly were actuated vertically using the same air slide that actuated the UV curing system (item i in Fig. 5).

### 3.2.4 Substrate Mount

The substrate mount should be one that not only supports the manufacture of the part but also allows for off-line inspection of the part as it is being built. The off-line inspection step involves taking the part-off of the 3D printer and characterizing its surface under an interferometer or laser scanning device. In order to maintain the part build accuracies after inspection, it is critical that the repositioning of the part into the 3D printer is done with submicron accuracy. In order to ensure submicron repeatability in the positioning of the substrate, a kinematic coupling-based pallet design was chosen for the substrate mount. The substrate of choice (silicon or glass) is mounted on an interchangeable pallet (item k in Fig. 5) that is connected to the 2D motion platform (axes 1 and 2) through a kinematic coupling obtained from Bal-Tec\textsuperscript{TM}, Inc. The coupling has a repositioning accuracy of $\pm$100 nm. The use of such kinematic couplings has been successfully demonstrated in similar applications involving microscale machine tools and microfactories [19].

### 4 Prototype Geometries and Materials

In order to demonstrate the capability of the 3D printer, two different printing geometries were chosen, viz.: (1) a pyramidal geometry to demonstrate the multimaterial printing capability and the accuracy of the new manufacturing process and (2) a dog-bone geometry to measure tensile properties of the nanocomposite laminates.

#### 4.1 Pyramidal Geometry

Two pyramidal prototypes were chosen for this study, viz.: (1) a two-material part comprised of one UV curable polymer and nylon nanofibers and (2) a three-material part comprised of two UV curable polymers and nylon nanofibers. Target drawings for the two-material and the three-material pyramidal prototypes can be seen in Figs. 7(a) and 7(b), respectively. Both pyramids have a square base (20 mm $\times$ 20 mm) and a height of 10 mm. For the three-material part, the UV curable ink used for printing was switched at a height of 4 mm from the base (Fig. 7(b)).

The pyramidal geometry was chosen for the following reasons:

- Printing time reduction for tall parts: A pyramid allows the part to be tall while using a third of the ink needed for a cubic part. This allows for a taller part to be printed in a shorter period of time.
- Edge definition: For most 3D printed parts, the only visible edge definition is around the base of the part where the outline is first created. However, for the pyramidal geometry there are many visible edges, the most significant being the inclined edges that connect the corners of the base to the tip of the pyramid. These inclined edges are created one layer at a time thereby making consistency over the course of the entire printing process to be of paramount importance.

### Table 1 3D printer specifications

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
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<tr>
<td>Motion axes</td>
<td>(1) Linear position stages</td>
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<tr>
<td></td>
<td>* Axes 1–2: Aerotech ANT180 stages, $\pm$ 100 nm</td>
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<tr>
<td></td>
<td>* Axis 3: Aerotech ATS100 stage, $\pm$ 1 (\mu )m</td>
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<td></td>
<td>* Axes 4–5: Aerotech PRO115 stages, $\pm$ 1 (\mu )m</td>
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<td></td>
<td>(2) Rotary axes for the tungsten carbide cutter (servomotor)</td>
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<td></td>
<td>(3) Pneumatic linear slide for the UV curing and heating station</td>
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<tr>
<td>Inkjet system</td>
<td>Four MicroFab\textsuperscript{TM} dispensing nozzles (MJ-ABL series, 50–120 (\mu )m diameter) with ink reservoirs, a pneumatic controller (MicroFab\textsuperscript{TM} CT-PT4), JetDrive III drive electronics and CCD camera for droplet size analysis</td>
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<tr>
<td>UV cure station</td>
<td>Dymax\textsuperscript{TM} BlueWave 200 curing spot lamp and rod lens combination with UV shield</td>
</tr>
<tr>
<td>Heat lamp</td>
<td>250 W heat lamp with insulating shield</td>
</tr>
<tr>
<td>FLS</td>
<td>Servomotor-based reel-to-reel system</td>
</tr>
<tr>
<td>Substrate mount</td>
<td>Kinematic coupling-based pallet</td>
</tr>
<tr>
<td>Build volume</td>
<td>100 mm $\times$ 100 mm $\times$ 50 mm</td>
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![Image](http://micronanomanufacturing.asmedigitalcollection.asme.org/)
both the working volume of the printer and the speed of the manufacturing process. Therefore, the dog-bone geometry (Fig. 8) was chosen as the second prototype for the nanocomposite laminates. Therefore, the dog-bone geometry (Fig. 8) was chosen as the second prototype for the nanocomposite laminates. The dimensions of the specimen were chosen taking into account both the working volume of the printer and the speed of the manufacturing process.

4.2 Dog-Bone Geometry. While the pyramidal geometry allows for the demonstration of the multimaterial printing capability and the accuracy of the manufacturing process, it does not lend itself to the testing of the material properties of the laminated nanocomposites. Therefore, the dog-bone geometry (Fig. 8) was chosen as the second prototype for the nanocomposite laminates. The dimensions of the specimen were chosen taking into account both the working volume of the printer and the speed of the manufacturing process.

4.3 Material Selection. Table 2 summarizes the material and prototype selections made as part of this study. Nylon 6 was selected as material for the nanofibers (Fig. 4) since it is commonly used for electrospinning applications and has also been proven as a good reinforcing phase for composite applications [18]. The nanofibers chosen for the pyramidal part were of random orientation (fiber A—Fig. 4(a)). For the dog-bone specimens, both aligned (i.e., fiber B) as well as randomly oriented nanofibers (i.e., fiber A) were used for comparing the material property trends.

Two commercially available UV curable polymers were selected as the matrix for the composite laminates, viz.: (1) a mixture of 85% by weight of SR531 (a low viscosity monofunctional acrylate monomer manufactured by Sartomer™, Inc.) and 15% by weight of photoinitiator, Irgacure 500 (BASF, Inc.); and (2) FullCure®930 TangoPlus™, a popular UV curable ink manufactured by Stratasys, Inc. [24]. These UV curable polymers will be referred to as polymer A and polymer B, respectively, for the remainder of this paper. In addition to being commonly used by the rapid prototyping community, these polymers were also chosen because of the relative ease of cleaning them in their uncured state using acetone and water. This meant a fairly easy cleaning step for the inkjet nozzles.

5 Manufacturing Outcomes

5.1 Off-Line Testing Parameters. Before the printing of a 3D part, it is critical to arrive at the printing parameters that enable the formation of uniform layers with well-defined edge resolution. For a given ink and nozzle diameter, a key parameter that dictates the overall accuracy of the part is the spacing between successive droplets. If this spacing is too small, then too many droplets will be deposited, resulting in poor edge resolution. A spacing that is too large will result in the creation of voids (i.e., an area devoid of ink) in the material. Therefore, it is important to conduct preliminary tests to determine the optimal spacing between the droplets. The preliminary tests should be performed on the same substrate surface to be used for the final manufacture of the part.

Figures 9(a)–9(f) depict the results from such a study conducted for polymer A printed on a silicon surface. Preliminary tests revealed that the use of a 120 μm diameter nozzle results in a droplet of 312 μm diameter after spreading. Figures 9(a)–9(f) depict the results from a test done to print a rectangular area using eight different interdroplet spacing values between 65% and 90% of the printed droplet diameter. The dotted line in the images depicts the intended edge of the printed layer. As seen in Figs. 9(a) and 9(b), the smaller spacing values of 65% and 70% are seen to result in an overflow of the material that destroys the accuracy of the edge being printed (Figs. 9(a) and 9(b)). On the other hand, larger spacing values of 85% and 90% are seen to result in voids within the rectangular area of interest (Figs. 9(e) and 9(f)). The tests revealed that the optimal spacing was in the 75–80% range (Figs. 9(c) and 9(d)). While this range is dependent on the properties of the UV curable polymer ink and the substrate, it was generally observed during the preliminary trials that maintaining spacing in the 75–80% of the final droplet diameter resulted in well-defined edges for both of the UV curable polymer inks.

5.2 Two-Material and Three-Material Prototypes. The two-material prototype consisted of one UV curable polymer ink (polymer A) and randomly oriented nylon nanofibers (fiber A). Figures 10(a)–10(c) depict the time-evolution of the pyramid during various stages of the manufacturing process. As seen, the prototype has well-defined edges. The total manufacturing time for the two-material prototype was 17.5 h while using a single 120 μm inkjet nozzle. Figure 10(d) depicts the cross section of the part as seen under the Zeiss™ scanning electron microscope. Each layer is seen to have a consistent height of 40 μm for the composite material. A close-up of the layer transition areas clearly shows the presence of the nanofibers (inset of Fig. 10(d)). Such consistent layer heights were not seen for the case of pure polymer samples, thereby leading to the hypothesis that the presence of these fibers ensured uniform spreading characteristics of the polymer inks across multiple layers.

The three-material pyramid prototype consisted of a combination of polymer B and the randomly oriented nylon nanofibers for the first 4 mm height of the part, followed by a combination of polymer A and the randomly oriented nylon nanofibers for the remainder of the part. The time-evolution of the part can be seen in Figs. 11(a)–11(e). The total manufacturing time for this part was 22 h while using a single inkjet nozzle. The increased manufacturing time was attributed primarily to the generation of the different path-planning files and the cleaning of the nozzle that was needed.
when switching between the polymer inks. While the cross section of the three-material prototype was observed to be similar to that seen in Fig. 10(d), across both the polymers, the edge resolution results were different for the two polymers. As seen in Fig. 11(f), for the initial 4 mm height of the part containing polymer B and the nanofibers, the pyramid has fairly straight edges. However, the edge geometry is seen to deviate for the remainder of the part comprised of polymer A and the nanofibers. This difference is attributed to the higher extent of shrinking that polymer A undergoes after curing.

Table 3 presents the metrology data obtained on both of the parts using a Keyence™ LJ-G030 laser sensor. As seen, the overall errors are the highest along the X axis measurement for both the prototypes. Since the primary printing motion was along that axis, it was suspected that the overshoot in the positioning of the stages contributed to this error. The three-material prototype was seen to have higher errors both along the Y and the Z axes of the part. In addition, it also had double the error in the inclination angle. This was attributed to the dissimilarity in the curing responses of the two polymers A and B. The metrology results point to the need for careful selection of the polymer combinations for 3D laminated nanocomposites. Another source of geometric error comes from the current technique of first depositing an entire layer of UV-curable polymer and then curing it. Given the time taken to print a single layer (due to the use of a single nozzle), this delay in curing causes an “ink run-off” effect at the edges, which affects the geometrical accuracy of the part. To address this issue, the next design iteration of this 3D printer will attempt to combine both the curing and the inkjet printing process, as it is done in commercial 3D printers.

6 Material Property Characterization

The dog-bone specimens were used to characterize both the tensile properties as well as the thermogravimetric signature of the laminates.

### Table 2 Material and prototype selection

| UV Curable polymers | (1) Polymer A: SR531, a low viscosity monofunctional acrylate monomer manufactured by Sartomer, Inc. + 15% by weight Irgacure 500 photoinitiator
|                     | (2) Polymer B: FullCure™ TangoPlus™, a popular UV curable ink manufactured by Stratasys, Inc. |
| Nanofibers          | (1) Fiber A: randomly oriented nylon fibers
|                     | (2) Fiber B: aligned nylon fibers |
| Pyramidal geometry  | Two samples:
|                     | (1) Polymer A + fiber A: pyramidal two-material prototype
|                     | (2) Polymer A + fiber A + polymer B: pyramidal three-material prototype |
| Dog-bone geometry   | Six samples:
|                     | (1) Polymer A
|                     | (2) Polymer A + fiber A
|                     | (3) Polymer A + fiber B
|                     | (4) Polymer B
|                     | (5) Polymer B + fiber A
|                     | (6) Polymer B + fiber B |

6.1 Tensile Test Results for Laminated Nanocomposites. In order to characterize the mechanical properties of these laminated nanocomposites, tensile tests were conducted on the dog-bone specimens (Fig. 8) using a 5582 Instron™ tensile testing machine. A pull rate of 30 mm/min was used along with a load-cell sampling frequency of 600 Hz. A total of six materials were tested and their results are summarized in Table 4.

As seen in the experimental data, the polymer B-based nanocomposites appear to be most sensitive to the addition of the nylon.
nanofibers. The presence of the nylon nanofibers is seen to result in a 54–69% increase in the elastic modulus of the laminate for polymer B, whereas for polymer A the increase is in the 9–15% range. In general, the presence of the aligned nanofibers is seen to improve the elastic modulus values. With the addition of the nanofibers, the ultimate tensile stress values are seen to increase for the polymer B-based nanocomposites, indicating a better load transfer to the nanofibers. In general, this is also seen to result in a decrease in the percentage elongation at break for polymer B-based materials. For polymer A-based composites, the trends seen in the mechanical properties other than the Young’s modulus are not that distinct.

Figures 12(a)–12(c) depict images of the fractured surfaces seen for the polymer B-based materials. The plain polymer sample surface (Fig. 12(a)) has more of a brittle failure as indicated by the fairly smooth fracture surface with little to no ductile tearing. For the layered composite with randomly oriented nanofibers incorporated in it, (Fig. 12(b)) the nanofibers are not clearly visible along the interface of the printed layers, since they are not necessarily oriented perpendicular to the fractured surface. However, the evidence of their presence is seen in the form of the crack deflection patterns seen on the surface. As seen in Fig. 12(b), the crack is seen to go along path AB crossing from the printed layer 1 to layer 2. It is then pinned at B (interface of printed layers 2 and 3) and deflected along the path BC. After being pinned at C, it is again deflected along CD, which is closer to the interface between printed layers 2 and 3. Such a pattern of crack arrest and deflection is known to dissipate more energy during the failure process [25,26] and is likely to be the reason for the higher breaking stress of 0.881 MPa observed in the layered composite (Table 4).

### Table 3: Metrology results

<table>
<thead>
<tr>
<th></th>
<th>X (mm)</th>
<th>Y (mm)</th>
<th>Z (mm)</th>
<th>Inclination angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desired values</td>
<td>20</td>
<td>20</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>Two-material prototype</td>
<td>18.75</td>
<td>19.73</td>
<td>10.01</td>
<td>45.01</td>
</tr>
<tr>
<td>Average error</td>
<td>6.25%</td>
<td>1.31%</td>
<td>0.16%</td>
<td>1.21%</td>
</tr>
<tr>
<td>Three-material prototype</td>
<td>18.87</td>
<td>20.64</td>
<td>10.11</td>
<td>46.71</td>
</tr>
<tr>
<td>Average error</td>
<td>5.65%</td>
<td>3.20%</td>
<td>1.13%</td>
<td>3.80%</td>
</tr>
</tbody>
</table>

The above mechanism is more clearly seen in action in the aligned composite (Fig. 12(c)). In this case, the presence of the aligned nanofibers is seen visibly at the interface of the different layers. As seen, the crack PQ originating in layer 1, after being pinned by the nanofibers at Q (interface of printed layers 1 and 2), is seen to deflect along two paths. The path QT travels along the interface between layers 1 and 2, whereas the path Q–R–S ultimately reaches layer 4. Crack arrest and deflection are seen very clearly at various points along the crack.

#### 6.2 Thermogravimetric Tests

Thermogravimetric analysis (TGA) is an important tool to identify the thermal stability of polymeric systems, particularly that of polymer blends [27]. Since the manufacturing process outlined in this paper can be used to combine different types of polymers in the form of nanofibers as well as UV curable polymer inks, a TGA was done to characterize the degradation behavior of nanocomposite laminates. Fifty micrograms of each of the dog-bone specimens was heated on a Parker Elmer thermogravimetric analyzer from 20 °C to 600 °C by ramping the temperature at the rate of 20 °C/min. During this heating process, the analyzer recorded the weight loss in the sample.

Figure 13 shows a representative thermogram (i.e., a plot of the surviving weight percentage of the sample versus temperature) and its derivative (wt.% change per °C). For the purposes of clarity, the plots are only presented for the temperature range of 100–600 °C, since no degradation of the materials was seen at temperatures below 100 °C. Black solid lines have been used for polymer B and black dotted lines have been used for the nanocomposite laminate comprising of polymer B + fiber A (randomly oriented nanofibers). The thermogram for nylon is plotted in red from Ref. [28]. Nylon is seen to be quite thermally stable with its degradation starting only around 440 °C. The curve for the base polymer B is seen to have a two-staged degradation process at temperatures of 320 °C and 420 °C, respectively. This is also clearly seen by the two peaks (regions a–b–c and regions c–d–e in Fig. 13) seen in the derivative of the thermogram.

Interestingly, while nylon itself has a higher degradation temperature, the presence of nylon nanofibers is not seen to transfer that property to the nanocomposite laminates. The thermogram signature for the nanocomposite (black dotted lines) closely mimics that of the base polymer B. This behavior was found to be independent of the degree of alignment of the nanofibers. A similar behavior was also noted for all of the polymer A-based materials. These measurements imply that the improvements in the mechanical properties of the laminates are obtained without drastically altering the thermal degradation pattern of the base polymer.
7 Conclusions

The following specific conclusions can be drawn from this work:

(1) A novel, multimaterial additive manufacturing technique has been developed for fabricating laminated polymer nanocomposite structures that have characteristic length-scales in the tens of millimeters range. The method combines an electrospinning process with the capabilities of a conventional inkjet-based 3D printing technology. The overall manufacturing setup consists of two separate systems, viz.: (1) the fiber collection system (FCS) and (2) the 3D printer system;

(2) The FCS uses a unique collector plate and electrode combination that not only allows for the alignment of the nanofibers but also for the manufacture of nanofiber rolls that could cumulatively span a total printed area of $4 \times 10^6$ mm$^2$.

The system has been demonstrated for manufacturing rolls with both randomly oriented as well as aligned nanofibers;

(3) The five-axis 3D printer primarily consists of a: (1) a multi-nozzle inkjet-based polymer dispensing unit that is used to deposit the UV-curable polymer inks; (2) a fiber layering system (FLS), which takes the nanofiber reels from the FCS and stamps them into the part being printed; (3) a surface preparation system comprising of the UV source and the heat lamp; and (4) the substrate mount;

(4) The proposed 3D printing process has been proven to manufacture laminated nanocomposites in various 3D geometries. The dimensional accuracy of the part is seen to be a direct function of the interaction between the different UV-curable polymer inks. The two-material part comprising of one UV-curable polymer ink and nylon nanofibers was seen to have better dimensional accuracy than the three-material part comprised of two UV-curable polymer inks and nylon nanofibers;

(5) In general, the addition of the nanofibers in the form of laminates is seen to improve the mechanical properties of the material with the Young’s modulus and the breaking stress showing the most improvement. Crack pinning and crack deflection have been identified as the underlying mechanisms responsible for these improvements;

(6) The thermogravimetric analysis reveals that the improvements in the mechanical properties of the laminates are obtained without drastically altering the thermal degradation pattern of the base polymer; and

(7) The manufacturing process outlined in this paper can be further improved in the following areas:

- The manufacturing time is directly proportional to the number of nozzles being used for the printing process. Currently, the system prints using one nozzle per polymer. The use of parallel arrays of inkjet nozzles will cut down on the processing time.
- Adding a rotary axis to the substrate will enable the manufacture of laminates with varying fiber orientation angles.
- In order to incorporate multiple fibrous materials into the same part, a fiber reel-magazine will have to be implemented, which can automatically load different reels onto the 3D printer. This would functionally be similar to an automatic tool-changer configuration used in modern machine tools.

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References


