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I, Dineshwaran Vijayakumar, hereby submit this original work as part of the requirements for the degree of Master of Science in Mechanical Engineering.

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Manufacturing Carbon Nanotube Yarn reinforced Composite parts by 3D Printing

A thesis submitted to the Graduate School of University of Cincinnati in partial fulfillment of the requirements for the degree of

Master of Science in Mechanical Engineering

In the Department of Mechanical and Materials Engineering of the College of Engineering and Applied Sciences

By
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ABSTRACT

Fused filament fabrication (FFF) is a 3D printing technology that translates plastic filaments into three-dimensional parts. Presently, there is an unmet demand to translate this technology into a full-scale manufacturing process. With advancements in hardware components and build preparation software, the main component that has been holding back progress in 3D Printing industry is the filament material. The majority of the plastic filaments in the market lack performance characteristics such as strength, durability and electrical properties. Reinforcing the standard plastic filaments with a strong multifunctional nanomaterial like Carbon Nanotubes (CNT) will drastically improve the capabilities of 3D Printed parts. In this research, several techniques were tested to implement custom fibers into standard plastic filaments. An innovative filament production system was developed to produce CNT yarn reinforced filaments. CNT yarn and Nomex filaments successfully demonstrated the ability to be 3D Printed.
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Chapter I

INTRODUCTION

3D Printing technology provides the ability to transform complex digital designs into real products. This technology has been primarily used in Rapid prototyping from the time it was first commercialized the 1980s. Rapid prototyping was an intelligent solution in the initial stage of production as it provides the designers and engineers an opportunity to identify the defects, challenges, form and fit. This also immensely reduced the production costs in terms of labor, time and resources. During this phase, the market for 3D printing was primarily driven by the need for rapid prototyping in order to improve the production efficiency. In the past decade, rapid prototyping has slowly evolved into a complete manufacturing process, with the inclusion of certain post processing techniques. A variety of thermoplastic polymers such as ABS, PLA, PETG, Polycarbonate, Nylon etc. have been used as the filament materials. Parts made of these materials may not be suitable for many practical applications as they have poor durability and undergo deformation when exposed to mechanical and thermal stresses. This has restricted 3D Printing applications to mainly research and development and low key prototypes that serve an educational purpose rather than being functional. The present competitive manufacturing environment demands engineering grade materials with higher part accuracy at lower cost with low upkeep and maintenance. The technology advancements has led to inexpensive electronics, smarter software programs and highly precise machine components. The only real factor that has been holding back progress is the availability of high performance filament materials.

In 2009, the 3D Printing revolution started as some of the key patents expired which were held by Stratasys, one of the biggest 3D Printing companies [17]. The patents mentioned here are pertinent
to a 3D Printing technique called Fused Deposition Modelling (trademarked by Stratasys) or Fused Filament Fabrication (FFF). The working principle of FFF is quite simple. A long continuous plastic filament is melted and deposited in thin layers, one on top of the other eventually building the final part. An open source 3D printing community was started by enthusiasts and technically inclined individuals. This led to the creation of mechanical designs, software, firmware and even filament extruders. Self-starters and entrepreneurs started building machines and released the plans and software programs on online digital repositories like GitHub. Local manufacturers started selling kits for some of these low cost printers, and the hobbyist market started growing rapidly. Fused filament fabrication (FFF) emerged as a commercially successful additive manufacturing technique due to its ability to produce customized parts at an affordable cost. Simple designs and basic parts that were otherwise only available commercially were being made in garages at home. At present, 3D Printing is a billion dollar industry with an enormous market potential [18]. Several startup companies and small scale printer manufacturers are successfully running their businesses catering a large and diverse group of users. Large scale companies and tech giants like Microsoft, Google and Autodesk are also investigating heavily in 3D Printing and its applications.

Since the beginning of 3D Printing explosion, several different types of filaments have been tested and printed successfully. Many different process parameters had to be tweaked on the machines to come up with optimal printing conditions for most filaments. Hardware changes like adding a heated build platform and a part cooling fan were also required. But the printed parts seemed to lack one major quality, which is the durability. Real life plastic products are usually subjected to different environmental conditions like high temperature, moisture and in some cases chemicals like disinfectants and cleaners. Engineering grade materials like PEEK, Teflon and Ultem (trademark PEI resin) that are currently used in these end use products were not easy to print on
desktop machines due to their high operating temperature and enclosed chamber requirements. Additives or Filler materials seemed to be promising solution as they have the potential to improve not only mechanical but also electrical, magnetic, optical and thermal properties. Several companies started experimenting by dispersing powdered additives and nanomaterials like Carbon fiber, graphene and Carbon nanotubes into the polymer solution [8-12]. These additives were blended with thermoplastic polymers by means of dispersion. Depending on the type of additive used, the filaments contained anywhere between 0.1 to 5% filler by weight. These filaments displayed marginal improvement in mechanical properties but posed a lot of challenges including nozzle erosion, clogging and poor surface quality. The fundamental problem behind this issue is the method of mixing these additives into the thermoplastic material. The filament when squeezed through the liquefier, experiences a lot of thermal stresses that may lead to extrusion issues. Ineffective or poor dispersion can cause localized agglomeration and as a result, these additives to stick to the walls of the nozzle during the printing process. This results in nozzle clogging, similar to the clogged arteries where the blood flow is inhibited. Furthermore, these filaments do not significantly improve the material properties as fillers are usually in a discontinuous state with a low volume fraction in the printed part. This suggests that a better form of reinforcement, like a thread, fiber or yarn will be required for the 3D Printing process.

The aim of this project is to design, fabricate and print continuous Carbon Nanotube (CNT) yarn reinforced filament on a FFF type printer. Reinforcing the standard polymer filament with continuous yarn will drastically (order of magnitude) improve its capabilities such as high strength, electrical and thermal conductivity. Continuous fibers exhibit excellent load transfer from material when compared to its powdered counterparts. The uniform stress distribution will minimize stress concentrations and failures in certain parts of the material. 3D Printing continuous carbon fiber
and similar fibers are presently available but they do not offer multifunctional capabilities. CNT yarn has incredible pliability excellent flexibility which is ideal for producing complex geometries. As the 3D printing industry is growing rapidly, it is imperative to enhance the quality and performance of the filament material. In this research, a new type of wire coating filament extruder will be designed and developed to produce customized composite filaments. Prototypes and sample parts will be 3D Printed to establish the capability of producing multifunctional composite products.

1.1 3D Printing Nanomaterials
The 3D Printing materials market is rapidly growing as the technology is now adopted across different industries. The rising demand for mechanically stronger and versatile materials has promoted the different formulations of feedstock filament. Incorporating additives in the standard plastic filament such as PLA and ABS has produced good results in terms of properties and aesthetics. Manufacturers like ColorFabb [5] and Protopasta [6] are selling composite filaments that contain PLA with metallic fillers such as copper, bronze, brass, stainless steel and iron particles. Non-metallic fillers like wood, cork, and glow-in-the-dark materials have also been successfully used as additives. With some additional post processing, the parts made with these filaments find great use in the design, architecture and prop making industries. Over the last couple of years, a few companies have also started incorporating nanomaterials like powdered carbon nanotubes (CNT) and graphene, and also short carbon fiber are being developed for FFF 3D printing. 3DXTech [9] has been selling carbon nanotube reinforced with ABS, PETG and Ultem materials. Small companies like Functionalize [10] and Arevo labs [12] are also producing CNT reinforced filaments. The most recent announcement has been the FilaOne™ GRAY, from Avante Technology that claims to be UV resistant, water repellant with mechanical properties similar to
Polycarbonate material [8]. There is just one company in the market that produces graphene reinforced filaments called Black Magic 3D [11]. Nanomaterial reinforced polymer composites have been popular for several years and has been exclusively used in automotive and aircraft industries. These composites were fabricated using traditional methods such as Resin transfer molding, film stacking, Pulltusion etc. With 3D Printing process becoming more commonplace, a few groups have studied the Printed parts made of nanomaterial reinforced filaments. Students from University of Tennessee [4] analyzed the influence of Multiwall CNT and graphene as additives in standard PLA parts. Graphene when added in 0.2% by weight showed a 47% increase in tensile strength, a 17% increase in modulus, and 12% increase in energy absorbed upon fracture. On the other hand, Multiwall CNT of 0.1% by weight shows an increase of 41% in tensile strength, 16% in modulus, and 9% in impact strength [4]. Postiglione et al. [13] investigated the influence of electrical properties on adding multi-walled CNTs to a PLA blend. They developed a variation of FFF process called Liquid Deposition Modelling to print microstructure scaffolds. The electrical conductivity of the nanocomposite peaked to 100 S/m at a high concentration of MWCNT (about 5% by weight) [13]. High performance additives such as carbon fiber, in the form of chopped fibers, short fiber and particulates were also tested as potential reinforcements. Ning et al. [14] investigated the effect of mechanical properties on carbon fiber reinforced ABS parts. As observed in the previous researches, carbon fiber reinforcements increased tensile strength and Young's modulus with increased fiber length and volume fraction up to 10% [14]. Smaller particulates seemed to improve the toughness of the parts. There was one major drawback noted by reinforcing short fibers, which is porosity. Increase in volume of carbon fiber reinforcements led to a higher chance of fracture along the interface. These results are suggestive of the multifunctional capabilities of CNT reinforcement in 3D Printed parts. The material properties are far superior when compared to the standard fillers materials and including carbon fiber.
In 2014, a company called Markforged from Cambridge MA [7] launched an advanced 3D Printed that can print composite materials. Mark One can print continuous carbon fiber with Nylon matrix producing very strong parts. This printer turned out to be a game changer in the 3D Printing and composite material industry. At present they can print Carbon fiber, Kevlar and Fiberglass with a proprietary nylon material. The latest version Mark Two even comes with a chopped carbon fiber reinforced nylon material. The printed parts are mechanically strong with high strength to weight ratio but does not exhibit multifunctionality. Several other open source projects on printing wires and fibers have been going on for a few years in the RepRap community [15] [16]. However, there has not been any established process to practically implement these techniques at a larger scale.

CNT yarn is multifunctional, pliable and has excellent flexibility in terms of producing complex geometries. The nanotube yarn carries the load across the component whereas nanotube and graphene fillers only reinforce the material locally and provide only a modest improvement in properties. Also, electrical conductivity will not be limited to the hopping mechanism of electrical conduction that occurs when using powder nanotubes. Recently, John M. Gardner et al. [3] from NASA published a paper on 3D Printing high density CNT yarn with high temperature engineering grade plastics. This paper demonstrated the ability to print multifunctional Carbon nanotube fibers on low cost desktop printers. The printed fiber strands were very close to each other making turns at a radius of 2.5mm [3]. However, the mechanical properties of the printed parts were very less than predicted due to the poor wettability of the Ultem matrix on the CNT fibers. Theoretically, CNT yarn should provide an order of magnitude improvement in material properties compared to printing parts using standard plastic filament. The Filament manufacturing process should be designed to ensure the good wettability and fiber-matrix bonding. This will directly influence the mechanical properties of final product. In addition, true 3D printing of complex parts is possible
using CNT yarn because the yarn is pliable and can be bent in any direction and even tied in knots without losing strength. Hence, this hybrid filament will be superior when compared to its counterparts that are made with carbon fibers, suspended nanoparticles, and powdered reinforcements. This project aims to investigate and produce new knowledge in the field of 3D printing using continuous carbon nanotube yarn integrated within a polymer matrix material. CNT yarn reinforced plastic parts will uncover new opportunities in the field of additive manufacturing.

1.2 Patent Survey

3D Printing has been around for more than three decades. During this time many patents were filed by the innovators and big corporations. A patent or copyright allows a company to take their idea into the commercial market thereby creating new opportunities and businesses. This ultimately fosters innovation and competition. However, the recent growth in the 3D Printing industry was a result of some of these important patents expiring. This led innovators and makers to start tinkering with the desktop 3D printers and open source hardware. Some of them started reinventing the technology by implementing innovative materials and mechanical design. As a result, a variety of new patents have been filed which can potentially open up a broad spectrum of application for 3D Printing.

Earlier in 2014, Mark et. al. [19] launched an advanced 3D printer called Mark One that can print continuous carbon fiber composite. This is one of the first machines that can print continuous fibers as opposed to the standard homogenous plastic filaments and plastic filaments with fillers. This patent describes a method for manufacture fiber-reinforced composite parts that have a continuous fiber tow in a solidifying matrix material. The nozzle head design included in the patent is capable of dispensing the towpreg on the build platform. The printing process follows a CAD-generated
deposition path with an aim to minimize the points at which the fiber towpreg has to be chopped. The reinforcement fiber in the composite part is aligned along at a minimum of one specified direction. However, this patent does not specifically mention the usage of continuous carbon nanotube yarn.

Another patent filed by the same company describes the method for toolpath generation for building composite parts. Mark et al [20] propose a method for generating three-dimensional toolpath instructions wherein the 3D model will be split into parts being filled by the continuous fiber reinforcement and parts being filled by the matrix material. They also mention that toolpaths of both the fiber and the matrix could be carried out in alternative layers or the same layer within the negative space of one contour. The printed parts may have reinforcements and matrix aligned in such a way to introduce very high strength to weight ratio. In addition, they also mention several ways to tack the continuous fiber material on the composite surface by using laser or electromagnetic radiation. Laying the fiber down on its place after deposition could be challenging and hence several points along the layup can be tacked on to the base which could be based on a preplanned pattern or it could go along the direction of the layup. The company has filed several other patterns which are in line with the current and future developments of their 3D Printer.

On a different approach, Kenneth Tyler [21] has proposed the concept of coextrusion in the 3D Printer extruder head. This method is very interesting as it facilitates the idea of in process combination two or more materials directly in the tool head where one is a continuous core. This idea could very well be expanded to liquid resins such as photopolymers and gels which has a great potential in the medical industry. The liquid resin/filler mixture can later be cured on the printer or offsite in a chamber by different sources. The toolpaths generated for this composite will be similar to that of the standard parts. There is also a possibility of having the core material which is
chemically, electrically, thermally or mechanically strong or combinations of two or more of these properties. Having the core element to have a unique property will help creating application specific toolpaths where the core performs a specific function in the printed object such as being electrically or thermally conductive.

Another patent in coextrusion comes from Richard Guillemette and Robert Peters [22]. They completely focus on different forms the co-extrusion process that can be incorporated into the toolhead. The feedstock filament structure may comprise separated layers or sections with more than one material. These filaments may be prepared by coextrusion, microlayer coextrusion or multicomponent/fractal coextrusion. In addition they propose using nozzle with multiple inputs and outlets, thereby the combination of 2 or more materials can happen either inside the toolhead or directly on the part. On-site mixing of the materials of different properties can potentially simplify or even eliminate post processing. The materials that can be used in this technique could span from aerospace grade epoxy resins to biocompatible gels, live tissues etc. Another possibility is to have two chemically reactive materials which can merge on site to form a whole new product as it is being printed. This is also a fairly neat way to implement coating of one material around another, where the central axis provides heat to melt the filament.

Chinese inventors Xiaoyong et al. [23] have taken the idea of fabricating fiber reinforced resin composite parts into additive manufacturing. Their claims are specific towards the design of a printer that can use continuous fiber along with either a plastic filament or resin. The fiber is fed from a tensioning device that can hold it stiff without kinking. This process essentially eliminates any need for a custom mold or pre-treated fiber prepreg tape. This can greatly reduce the cost and simplify the process chain. In addition, the ability to control the direction of the reinforcing fibers will help achieve the desirable properties along the load bearing direction. Having the ability to
change this across different heights of the part is another advantage. This means that different sections of the same composite can be strong in different directions of loading.

While all the above patents are focused on 3D Printing in specific, in the early 2000s, researchers from Auburn University have proposed a simple method to lay carbon nanotube fibers layer by layer with simple toolpaths. Bor Z. Jang et al. [24] have proposed a method for fabricating a composite structure that is composed of a matrix material and with carbon nanotubes (up to 50% by volume). There is at least one specific direction in which the nanotubes are aligned (substantially). The second method proposed is for making a continuous fiber-reinforced composite part that uses long continuous fibers to form a pre-impregnated towpreg. The toolhead will then deposit this towpreg on to the base material. The dispensing head is mounted on a device that is connected to a motion controller which can be regulated from a terminal. A computer program was used to generate simple toolpaths to move the tool head relative to the base member for several layers. The selected algorithm will keep the cut off points minimum to achieve the best possible reinforcement without losing strength.

Brandon Sweeney et al. [25] from the Texas Tech University developed a unique method to strengthen 3D printed parts made of carbon nanotube filaments. One of the drawbacks of the standard 3D Printing process is the bonding strength between layers or between individual strands laid down. This largely affects the strength of the part. These researchers have developed a microwave-induced heating system for parts made of CNT filled (or coated) plastic filaments. Carbon nanotubes (CNTs) have the ability to absorb microwave radiation which induces localized heating along the surface of the beads throughout the volume of 3D printer parts. When the parts are subjected to microwave radiation, the carbon nanotubes will heat and fuse the interface layers together, thereby improving the inter-bead diffusive bonding. This is an excellent way to post
process the 3D printed parts to impart overall mechanical strength and toughness. The microwave radiation should come from a controlled environment as the amount of radiation is directly proposed to the heat dissipated by the part. Excessive radiation can burn the nanotubes.

All the patents discussed above are quite different from the old and traditional patents proposed decades ago by the 3D Printing pioneers. Although they focus on standard 3D Printing process, the applications are very diverse. Novel and advanced products can be developed using the above technologies. It is also important to note that these patents do not explicitly discuss about the implementation of long continuous carbon nanotube yarn in the 3D printing process.
Chapter II

CARBON NANOTUBE REINFORCEMENTS

The multifunctional properties of CNTs makes them an excellent choice of reinforcement in composite parts. In the previous chapter, we discussed several ways CNTs were used in additive manufacturing industry. The powdered form was far more prevalent and the printed parts exhibited reasonably good properties. We believe that continuous reinforcement, in the form of thread or yarn will produce superior results when compared to its powdered counterparts. The composite parts made of continuous CNT yarn with possess greater strength and durability in addition to other excellent properties.

The nanoscale structure is primary factor that differentiates CNT yarn from conventional fibers such as carbon fiber. CNT yarn is strong, very tough, and conductive and cannot be easily cut or lose strength when woven or knotted because the nanotube diameter is small relative to a cutting edge or fiber bend radius. CNT yarn also does not fatigue because there are millions of nanotubes in the cross-section of a fiber held together van der Waals forces that are enhanced by twisting to increase friction. Cracks in the sense of breaking bonds do not happen but tube separation can occur along the direction of the highest resolved shear stress. These fibers are thus typically immune to fatigue and keep their flexibility at low and high temperature. The reactor used in this project uses a more fundamental multi-physics engineering approach to grow nanoscale materials and to assemble microscale material that has properties comparable to individual nanotubes. This scale-up importantly depends on synthesizing long atomically clean high quality straight nanotubes and assembling these into fiber.
2.1 Carbon Nanotube Synthesis

A new type of reactor called the Floating Catalyst reactor was developed by Dr. Mark Schulz et al. [38] at Nanoworld to grow long nanotubes with less impurities. This setup has been developed based on efforts from the NSF and Navy projects and unfunded work in collaboration with Dr. David Lashmore of UNH. The reactor uses multiple physical fields to precisely control the synthesis process and maintain equilibrium reactions. It will produce and assemble nanoscale materials to form CNT yarn in a low-energy, automated high rate manufacturing system. The setup will be relatively inexpensive and the yarn properties can be tailored for 3D printer filaments.

![Figure 1. Floating Catalyst CNT reactor](image)

A syringe injector with a needle bent upward is used as the fuel injection system. It contains several 10-50 micron-sized holes drilled on the vertical part using the laser machining system. This design
generates a spray of vapor into the reactor. The temperature and flow rates are computer controlled. Experiments were conducted with different fuel recipes and temperature profiles. An example profile would contain the carrier gas as Argon at 500 sccm, the carbon precursor comprises of 10 ml Hexane and methanol, with a ferrocene-thiophene solution being injected into the reactor at 1,200 C. Figure 1c shows the CNT web along with Fe and S particles found in the sample, drawn out of the furnace. An EDAX spectrum of the sample indicates that it consists of Carbon and a small amount of Iron and Oxygen. Once the process has been initiated, the reactor will continuously produce high quality carbon nanotubes.

**Figure 2.** Manufacturing CNT yarn for printer filament: (a) Process of re-feeding yarn into the reactor to ply layers of sock on existing yarn to increase yarn thickness; (b) Hollow yarn can be formed by feeding a center wire mandrel that is later removed. The die is for extruding hollow nanotube yarn directly from the reactor [38].

To form yarn, a new approach was used where a die is used inside the reactor tube and the net is drawn through the die to align and densify the nanotubes and produce yarn. A roller and liquid bath may be installed outside the reactor chamber to further densify the yarn and increase the strength. Extruding yarn from a reactor will be done using dies similar to shown in Figure 2, which we believe has not been done before. A Multi-pass feeding system can be implemented to produce yarn of any desired thickness. A custom designed die system can be used to produce hollow yarn (as seen in Figure 2b). Hollow yarn will have biomedical applications and may also be used to contain the polymer material.
The advantage of this reactor is the low cost and high safety as no flammable gases are used. Hexane, methanol, ferrocene, thiophene, Argon used in this process are inexpensive. The reactor can be manufactured for less than USD 100K, and can further be scaled up easily for mass production. Nanotube yarn will be needed in very high quantity (thousands of miles) to supply the 3D filament manufacturing process. Future advancements will include a method of cleaning unused catalyst from the sock and levitating the sock to increase growth time. This will provide more purity and strength in the CNT yarn.

2.2 Carbon Nanotube Fiber Vs Carbon Fiber

In the introduction chapter, some of the major benefits of carbon nanotubes were discussed. The other carbon material which has been widely used as a reinforcement, especially in the automotive industry is the carbon fiber. The tensile strength, high strength to weight ratio makes it a popular choice of reinforcement in most applications. In the 3D Printing process, the reinforcement material will be mechanically fabricated in two stages (1) Filament manufacturing (2) additive manufacturing. In the first process, the reinforcement fiber will go through a wire coating extrusion process, where it will be subjected to a lot of tension and high temperatures. In addition, it will be coated by a matrix material, hence a good surface area for bonding is required. The second stage is 3D Printing, where the fiber in the form of a filament will again be subjected to tensile forces and high temperatures. But the most critical part is when it will be laid down on the bed. The toolhead will follow complex paths to deposit the material that includes cutting sharp corners, twisted and bend along the way. The filament should also have the ability to be trimmed easily when required. Based on these factors, we will compare CNT and carbon fibers to determine their suitability for 3D Printing.
Carbon fiber reinforcements consists of multiple long individual filaments about 5–10 μm in diameter [26]. The crystal alignment of carbon atoms, along the axis of the fiber provides a high strength-to-volume ratio. Multiple strands of loosely packed filaments form the fiber tow. They have high elastic modulus making them very stiff in addition to being strong. Therefore, carbon fiber cannot be twisted together to form yarns or braids. They are typically woven into fabric or mat form. As Carbon fibers are brittle, they fail by breaking abruptly on reaching critical load. This mode of failure may be unpredictable as the part can shatter into multiple pieces causing safety concerns. Carbon fibers have excellent thermal resistance and can withstand high temperatures of up to 1000 deg C [26]. The thermal expansion is basically zero which means they do not physically deform when subjected to high temperatures. This can be a very useful feature as the carbon fiber would be subjected to a wide range of temperatures depending on the matrix material being used.

On the other hand, CNT offers very high strength to weight ratio and excellent tensile strength close to 4.5 GPa, in certain cases [27]. On a macro scale the properties may not be so high due to the probability of a critical flaw, which increases with volume of CNT used in yarns. However, CNT yarn’s mechanical strength is well above the tensile stresses experienced during filament manufacturing and 3D Printing process. Additionally, CNT fibers are pliable and flexible and can even be tied in a knot without losing much strength. This allows the fibers to be twisted into yarns and braided into ropes like industrial fibers which will enormously boost the strength of the part. In addition, the high surface area of CNTs provides interfacial coupling [27] between individual threads. This will also help in functionalizing the CNT fiber with different nanomaterials/chemicals as it facilitates coating different types of polymers. During the 3D Printing process, the filament goes through tough physical environments and complex toolpaths. CNT yarn, being pliable, can successfully withstand these stresses without any physical damage.
Furthermore, the electrical and thermal conductivity of CNTs will make the printed parts multifunctional. CNTs also possess flame retardancy which makes the composite a safer material of choice in aerospace and military applications. Hence, the nanotube yarn will be the best filament material available for 3D printing.

2.3 CNT Reinforcements

Reinforcing the composite panels has always been one of the most critical design challenges. Although, polymer matrix laminated composites have displayed excellent mechanical properties, the lack of reinforcement through the thickness direction causes failure due to shear. This mode of failure is attributed to weak Interlaminar shear strength (ILSS) between the composite plies [27,28]. Over the years, several techniques have been developed to improve the ILSS. One such approach is by stitching the fiberglass plies together using a strong thread. Experiments were conducted with CNT yarn to be used as a reinforcement in laminated composites. CNT threads were used to stitch individual plies together in laminated composites. Sewing long CNT threads of small diameter along the composite prepreg or dry fabric can successfully reinforce composites along the Z direction. This fabrication process, once optimized, could be incorporated in mass production of laminated composites in a completely automated manufacturing line. These high strength nanocomposites could eventually replace metallic components on aircrafts. These tests were performed in collaboration with Dr. Yi Song, post-doctoral researcher at Nanoworld Laboratories.
Machine sewing will eliminate the difficulties faced during manual stitching and improve the process speed, accuracy and repeatability. The Sewing machine (as seen in Figure 3b) will be used to perform the stitching process. Below are some of the specifications of the sewing machine.

**Manufacturer:** Brother International Corporation

**Model Name:** LS-2125i;

**Needle size:** size 11 (lightweight fabrics)

**Yarn size:** 150um (2 plies)

**Speed:** Intermitted (15-20 stitches per sec)

Stitched fabric/thermoplastic resin composites are processed using vacuum bag resin transfer molding followed by hydraulic hot pressing.

**2.3.1 Analysis of 3D Stitching**

Stitching is a mechanical process that involves penetration of sharp needles through the dry fabric at a fast rate. This process primarily disturbs the orientation of the fibers at places where the needle breaches. Frictional forces are generated due to the rubbing action between the needle, thread and
the fiberglass. This causes localized heating and as a result, damages the glass fibers. Some of the factors that affect the mechanical properties are discussed below.

As the needle penetrates the fabric, fibers get misaligned in both in-plane and thickness directions. Strands of fiberglass get pushed away by the sewing needle to accommodate the thread. Further, the degree of misalignment is expected to increase with the stitching tension. This tension in the sewing thread deflects the fiberglass to create a wavy pattern as shown in Figure 4a. The waviness angle increases with the increase in diameter of the sewing thread and tension of the stitch. A significant change is observed in the microstructure of the composite at places near the sewing thread.

Furthermore, when the needle drops through the fiberglass layers, the fiber strands fold and causes fiber crimping. The crimped fibers are usually confined to a very small volume around each thread. However, the volume of fibers that are crimped by stitching tends to increase with the volume fraction of the sewing thread. Fiber crimp is a concern because it can reduce the compressive strength by promoting micro-buckling and kinking. One of the consequences of fiber distortion is the formation of fiber-depleted regions. These regions are filled with resin during impregnation.

**Figure 4.** Microscopic view of CNT stitched composite parts: (a) Close-up view of wavy fibers on dry fiberglass plies (b) Close-up view of CNT thread reinforced composite panel showing the resin rich zones.
and form resin-rich zones, as seen in Figure 4b. Microscopic study reveals that these zones are formed at places where the sewing thread goes through fiberglass. As the sewing thread tightens during the stitch, it forms an eyelet shape that is elongated in the fiber direction. The shape and dimensions of the resin zones are influenced by the diameter of the thread, needle size and tension of the stitch. These resin-rich zones cause unwanted residual stress. Although these areas are isolated from each other, the volume of these zones affects the structural integrity of the composite laminate. Fiber breakage is another defect that may arise due to stitching. Although the volume of fibers breaking are less, this can have a significant impact on larger parts like aircraft structures. When the needle tip contacts the fiber with a high force, frictional stresses are generated. This action damages the fiber and in some places the fibers are totally broken apart. The amount of fiber breakage is usually greater in the FRP prepreg because the fibers are not easily pushed aside by the needle and therefore are broken.

These defects are suggest that a better three dimensional reinforcement is required to incorporate CNT yarn in the composite parts. 3D Printing would be an ideal solution as damage to the fibers will be very less. In addition, the direction of the reinforcement can be controlled accurately. Custom toolpaths can help fill fibers in specific areas of the composite, depending on the loading conditions.
Chapter III

FILAMENT PRODUCTION SYSTEM

Filaments are one of the most important aspects of the 3D Printing process as it directly influences the properties of the printed parts. The plastic filament, in the form of a thin wire (about 1.75mm or 2.85mm) is basically melted and reformed into the final part. Enormous amounts of plastic pellets and filaments being produced around the world. Filaments even have their own market share in the 3D printing industry. Thus, it is important to understand the process involved in manufacturing the filaments.

3.1 Plastic Extrusion Technology

3D Printer filaments are produced by a method called extrusion, which has been used in the plastic industry for several decades and is very well established. Figure 5 illustrates a various stages of the filament production process.

![Figure 5. Illustration of Filament Production line, adapted from Eastman Chemical Company’s Extrusion Process. [31]](image-url)
In this process, raw plastic pellets and additives are fed into an enclosed chamber. Heaters are used throughout the chamber to melt the pellets into a homogenous blend in various stages. The giant screw or auger then drives the molten filament forward through a precisely designed die. The extrudate attains the final profile (shape of the filament) as it exits the die. The filament then passes through the several segments of a cooling system, each segment having its own water temperature. From the tank the cooled filament is then transferred to a precision motor driven Filament Winder or coiler. There is also a measuring gauge on the way that uses a laser system to measure the final diameter of the filament to ensure the output profile maintains the design standards. The gauge is connected to the cooling and winding systems using a feedback controller. Inaccuracies can be corrected by adjusting the winding and cooling parameters. The figure below illustrates the entire process.

The filament manufacturing process can be divided into three stages where each stage is its own process that is designed to perform a specific role. The processes are listed below.

1. Extruder Assembly
2. Cooling System
3. Filament pulling mechanism

### 3.1.1 Extruder Assembly

The extruder comprises of a single screw extrusion setup, where the molten material is mixed and pushed forward by a single big screw called auger. The chamber is internally divided into several zones where each zone has its own heating element. These heating elements have to be maintained at specific temperatures to produce the best results.
Figure 6. Illustration of Single Screw Filament Extruders (a) Standard filament extruder with varying diameter Screw, adapted from “Troubleshooting the Extrusion Process” by Maria del Pilar Noriega E., Chris Rauwendaal, Chapter 1: Requirements for Efficient Troubleshooting, Hanser Publications, ISBN 978-1-56990-470-1 [30] (b) Concept design of Wire coating filament extruder.

Figure 6 shows the internal view of the extrusion unit. It can be divided into three zones based on the temperature. The first zone is called the Solid conveying zone. The main purpose of this zone is to preheat the plastic and move it to the following zones. The resin pellets are usually gravity-fed continuously from a hopper that is located at the beginning of this zone. The design of the hopper feed is particularly important as it determines the rate at which the raw material is supplied. The next zone is the plasticizing zone. Here, the pellet additive mixture is partially molten as it slides through the auger. The channel depth in this zone gradually decreases. This generates pressure inside the screw and helps pushes the material forward into the melt zone. The auger design also facilitates better heat transfer and squeezes out any trapped air bubbles from the plastic back into the feed zone. The final zone that leads to the output die or nozzle is called Melt Conveying and mixing zone. In this zone, the screw depth is constant but lesser than that of the previous zone maintaining the decreasing channel width in the entire extrusion unit. The uniform temperature and pressure helps in homogenizing the molten plastic. This zone is typically longer
which allows for complete mixing of plastic pellets and the additives. The molten plastic is then extruded through a well-engineered die or nozzle to produce the final filament profile.

The auger is designed in the shape of a screw so that the rotational motion of the shaft drives the mixture forward. The auger surface has a low co-efficient of friction and this allows the molten plastic to flow over easily with less sticking and dragging. The friction between the barrel and the pellets are high on the other hand. The screw drives the material forward and the barrel opposes the flow which in turn result in proper mixing of the molten plastic. The extruder works as a volumetric pump and hence it needs to be powered by high torque producing motors. Electric motors located at the far end drive the auger continuously to push the pellets forward. The thermoplastic pellets will soften and melt as they reach the melt zone. Squeezing the plastic melt through the die will produce a continuous extrusion of plastic with the outer profile similar to that of the cavity in the die.

Industrial filament production units have this entire sequence preconfigured. The process parameters are specific to each company or product and has been developed based on thorough research and testing. Some filament extrusion lines can simultaneously extrude multiple filament strands at a given time. As their production capacity is very high, they can typically output tons of filaments in an hour. They may also require larger chambers and heavier motors to drive the extruder.

### 3.1.2 Cooling system

The behavior of the molten plastic that flows out of the nozzle or die is not easy to predict. The ideal method is to control the output profile is by means of cooling. The molten extrudate is pulled and stretched as it exits the nozzle. During this process, the plastic can develop some internal
thermal and residual stresses. Hence, an effective cooling system is required to maintain the structural integrity of the product.

Depending on the application, different types of cooling techniques can be implemented to the extrusion line. Free extrusion cooling is one of the basic and most commonly used techniques. In this method, the filament coming out of the nozzle goes into an open water tank. Water is typically used as the main quenching medium as it is low cost and has a good rate of heat transfer. Although the heat transfer medium is maintained at an ambient room temperature, it is periodically recycled to ensure the temperature does not go past a recommended range. Other quenching media include controlled air streams, which can be used when the product is very sensitive to cooling, or needs to be cooled very slowly. In general, plastics have poor thermal conductivity, which means they absorb and relinquish heat fairly slowly. They spend a lot of time in the hot chamber absorbing heat which is difficult to give up. Hence the heat transfer rate cannot be improved by the water temperature beyond a limit.

The more sophisticated cooling techniques combine vacuum sizing and cooling system in one enclosed space. As the extruded product comes out, it is drawn through the air gap and into a water chamber where the very outer layer of the plastic is cooled and forms a thin solid surface. The extrudate then enters the vacuum sizing chamber, where a negative-pressure environment causes the diameter of the extruded plastic to increase marginally. The product then passes through a vacuum sizer tooling, which contains a series of rings to control the final output diameter. The filament then enters the actual cooling chamber where temperature of the water is precisely controlled. Depending on the size of the chamber, the filament may be allowed to make multiple passes before exiting. The main role of the cooling chamber is to uniformly cool the final product before going to the winder for spooling.
The cooling tank used can be adapted to immersion or spray cooling. In immersion cooling the extruded product is cooled by completely submerging it. The plastics also have a tendency to float in water. When the product is only partially submerged, the bottom of the product is being cooled well whereas the upper portion is just exposed to air or being cooled at a different rate. Hence, rollers or levelers are employed to keep the product well under the water surface. In most cases, the cooling effect will be limited by the laminar effect of the water in the tank [33]. The water that surrounds the extruded product tends to get heated by the energy dissipated by the hot plastic. Due to this effect, the layer of water that is in contact with the surface is warmer than the set water temperature in the tank, thereby affecting the Cooling efficiency. Hence, various wiping methods are used to disrupt the laminar flow of the water that surrounds the outer surface of the product.

The second type of cooling system is called the spray cooling, where a set of nozzles that will spray the cool water all around the surface of the extruded product. This method of cooling the product is 20-40% more efficient when compared with the immersion cooling method [33]. Continuous exchange of cooled water applied to the surface of the product directly influences the cooling efficiency.

At the end of the cooling tank, there is also an optional short tank that is used to clear the product surface of any water. Water droplets may interfere or distort the optical-based measurement in the next stage. Hence, water blow-off device is installed in the tank to completely wipe the water off the surface. The device also prevents water from dripping on the floorspace, thereby keeping the surrounding clean.
3.1.3 Winding Mechanism

The final section of the extrusion line contains the Winding equipment. This equipment typically consists of a measuring gauge, pulling device and a spooler. The first device in this line is a measurement system which is used to verify the final diameter of the product. A laser gauge such as an optical micrometer continuously monitors the diameter and ovality. They are electronically connected to the filament tensioner by means of a feedback controller to change the process parameters when required. This helps to compensate for errors if any and plays an important role in quality control. The filament then goes through a pulling device which is equipped with filament tensioners. They determine the rate at which the filament is being pulled, which largely affects the final dimensions of the part. A speed control device receives the feedback from the laser gauge and controls the pulling speed. A slower speed may cause the filament to droop and a faster speed may cause the filament to slip through the rollers. Hence, it is important to precisely control and maintain the rate of pulling.

The final section in this line is the Spooler. The spooler is the device that winds the incoming filament into small or large reels depending on the need and subsequent storage. Each spooler is equipped with a digital spooling motor control and filament positioning slide. The slide allows for consistent layer build up over the spool and to avoid crossing over. While it is important to spool the filament correctly, it is also imperative to set a large curvature on the filament as this may affect the usability of the filament when feeding into the 3D Printer.

3.2 Filament Production Setup

In our project, the filament being used is a polymer coated fiber. Hence, the filament production process is slightly different from the conventional extrusion process. The major change is seen in
the first stage of the filament production that contains the extrusion unit. Figure 7 displays the complete extrusion line built and assembled at the Nanoworld. This setup was then tested at the University of Cincinnati Research Institute, where production runs were carried out.

On the left most end, we have the fiber stored in a spool, which enters one of the nozzle inlets. The molten plastic from the extruder which is being continuously pushed into the nozzle on the other inlet. The fiber is coated uniformly in the heating chamber of the nozzle as it flows over the fiber. The coated fiber leaves the nozzle where it is being received by the Filament puller. A small DC fan is used to cool the filament as it exits the nozzle. The filament puller which is placed after the cooling fan is connected to a speed control drive that controls the rate of pulling. The final composite filament can then collected by an optional spooler.

![Image of filament production line](image)

**Figure 7.** Wire-coating Filament Extrusion Production line developed in this thesis.

The composite filament developed in this project, consists of CNT yarn coated with a thermoplastic Nylon. The core fiber is the most significant part of the filament, which directly contributes to the
strength of the part. Experiments were also performed using other fibers such as Nomex and polyester threads. Manufacturing a composite filament is carried out in two individual steps, (1) Fiber Pre-coating (2) Wire Coating Extrusion.

3.3 Fiber Pre-coating

Pre-coating is the process by which raw fibers are coated with a very fine layer of polymer. During the extrusion process, reinforcement fiber has to passes through different physical environments where it will be subjected to tension, heat and pressure. This may potentially damage the fiber surface and even break a few strands. Hence, it is imperative to pre-coat the fibers prior to extrusion coating. The CNT yarn is first preconditioned by chemical treatment. Acetone is sprayed on the multiply yarn to densify and hold all the fiber strands intact. This treatment prepares the yarn for the precoating process. The preconditioned CNT fiber is coated with nylon in a dispensed medium. The first coating is crucial as it determines the extent of polymer infiltration into the individual fiber strands. Uniform and complete coating is essential to obtain good mechanical bonding. The bonding strength influences the mode of fiber failure in the final 3D printed part.

A technique called Immersion coating or Dip coating will be employed to perform pre-coating. In this process, a thin coating of the polymer is applied on to the precursor by temporarily passing the fiber through a solvent bath, containing Nylon and formic acid. The figure below illustrates this process. The setup developed by Noe Alvarez et al [35] at Nanoworld was used to perform the immersion coating process.
The dipped yarn moves at a slow speed to facilitate proper infiltration of the nylon particles on the surface of the CNT yarn. With a multiple ply yarn, it is important to completely wet all the individual plies. The coated yarn is allowed to dry completely before it is being spooled. This is required to evaporate solvent particles from the fiber. The process can be repeated multiple times to allow a series of thin coatings until a desired thickness is obtained. The CNT yarn was allowed to pass through until the coating thickness reached approximately 100 microns. The final product consists of the nylon finely coated CNT yarn. The diameter of the pre-coated fiber does not have to be precise at this step as it will go through the extruder, which will determine the final diameter of the filament.

3.4 Fiber Coating Extrusion

The extruder used in this project is designed based on a wire coating extruder. One of the commonly known applications of this device is the production of electrical cables. The primary difference when compared to a standard extruder is at the nozzle. The nozzle may have one or two channels for
polymers to flow around a main core wire. The pre-coated is fed through a special channel and comes in contact with the polymer only at the melt zone. A coaxial nozzle was designed specifically to fit the extruder used in this setup. This nozzle is capable of producing a composite filament of 0.35mm final diameter, which has significance in the 3D printing process discussed in the following chapter.

### 3.4.1 Extruder Design

The design of this filament extruder is based on the single screw extrusion system. The main idea here is to design a system that can melt and continuously push the viscous plastic through a nozzle of a small orifice. Figure 9a shows the complete extruder setup that was built based on the proposed design. Figure 9b shows a close up view of the nozzle. Some of the components used in this designed were obtained from the company Filastruder [36]

![Figure 9. Wire coating filament extruder: (a) Complete setup of the wire coating extruder retrofitted with a coaxial nozzle (b) Nomex fiber being coated and pulled out.](image)

The main structure is built from milled Aluminum blocks. A 12V DC gear motor is mounted on one of the vertical struts to drive the auger. The drive shaft of the gearmotor is coupled with the auger using a standard hex coupler. The central axis on both shafts should be collinear in order to for the auger to function correctly in the extruder. Misalignments can result in auger shaving the
barrel surface. Although, the coupler might help to compensate for minor misalignment, it is still recommended to have these parts precisely machined. The auger is supported by 2 flanges and thrust bearing on the second vertical strut. When molten plastic flows out through the small orifice, it applies a back pressure on the auger. The thrust bearings pressed against a shaft collar, is used to withstand this force and keep the auger in position. The auger is the most important tool in this extruder. The surface is well machined and has a low coefficient of friction to aid the plastic flow minimizing the drag. A cast iron pipe of 1” inner diameter, performs the role of housing the extruder. The clearance between the auger and the inner surface of the barrel is about 4 mm overall. This determines the volumetric flow of molten plastic along the length of the chamber. The tapered end of auger lies in the melt zone, where plastic pellets are homogenized and pushed forward. A cylindrical heater band controls the temperature at the melt zone. The heater band is about 2 inches long and spans over the melt chamber in the nozzle. A novel wire coating nozzle was designed for this project to coat any type of continuous fiber. It comprises two inlets, one large converging into the mixing zone for the plastic to flow in and the other is narrow fit the thin needle which feeds the fiber. This nozzle is fitted to the far end of the barrel. The electronic components are placed at the bottom in a 3D Printed housing. The main function of the electronics unit is to regulate the temperature in the heated chamber. A PID controller continuously monitors the temperature and supplies current to the heater band. A thermocouple is mounted inside the nozzle to accurately measure the temperature at the extrusion chamber. The current flow to the heater band is regulated based on the feedback from the thermocouple. A stall protection board is also used in the circuit to detect when the motor is stalled. When the load on the motor increases due to a failed heater coil, the stall protection unit automatically limits the current and voltage supplied to the gear motor.
3.4.2 Nozzle

The most important component of this extruder is the nozzle which performs the role of the wire coating die. The nozzle design should allow the molten plastic and the coated fiber to interact well within a small space and yet obtain good coating. In our project, a prototype of the nozzle was first created by fabricating pipe fittings and basic hardware components.

Figure 10. CAD Models of Coaxial Wire Coating Nozzle: (a) Brass plug fitted with the syringe needle (b) Nozzle outlet (c) model of needle (d) molten plastic inlet into the coating chamber (e) Cross section view showing the molten plastic flow and yarn feeding through the nozzle.
Preliminary designs were made on Solidworks 2014 to understand the internal profiles and working mechanism. Figure 10 shows a CAD model of the brass plug and the syringe used in the prototype stage. A ½” NPT square head brass plug was fabricated to form the nozzle. The main channel that feeds the plastic into this nozzle is produced by drilling a hole of size 2mm. The hole is drilled along the horizontal axis of the brass plug until a point midway in the square head. A second hole is drilled perpendicular to the central axis. Both holes meet inside the square chamber to form the channel for plastic to flow through. A stainless steel syringe needle of gauge 22 is used to carry the fiber into the nozzle. The length of the nozzle is trimmed to let the fiber contact the incoming molten plastic at the mixing zone. The inner diameter of the syringe closely matches the size of the fiber used, just enough for the fiber to slide through without too much friction. The needles have a highly polished surface both inside and outside. The low friction surface helps to minimize the disruption in the plastic flow. The needle is press fitted on the brass plug and fastened by means of clamp to hold it under pressure. The same setup was created with few different types of pipe fittings as seen in Figure 11. Several tests were performed with these prototypes to study the design feasibility. A few main factors that were crucial for the design are (1) smooth transition of polymer from the melt zone into the mixing zone (2) Reduced back pressure build up at the needle entrance (3) tight tolerances to achieve good fit. An additive manufacturing technique called Direct Metal Laser Sintering was used to produce the final nozzle design. The EOS M280 machine available in the Additive Manufacturing Laboratory at UCRI prints parts using a power bed fusion technique. The part is produced layer by layer by localized heating of the power using a carbon dioxide laser. Direct Metal 20, an alloy made of Bronze based alloy containing Ni was used to produce this component. The final part was then sandblasted to get a smooth internal surface. This is adequate for the purposes of this project. The nozzle can also be annealed to minimize the thermal degradation and relieve internal stresses.
Figure 11. Prototypes of the Nozzle assembly: (a) square head brass plug inserted with syringe needle (b) Coupling fitted to the brass plug (c) and (d) 3D Printed bronze nozzle using DMLS process (e) Complete coaxial nozzle assembly with a fixture on the left holding the needle in place

The nozzle outlet diameter is just one of the factors influencing the dimensions of filament. The diameter of the filament is primarily controlled by adjusting the rate of pulling. In general, a faster pulling rate will reduce the thickness of the coating. This may be applicable only within a certain range of speeds. Extreme speeds will adversely affect the quality of the final filament. Cooling channels and sizing chambers determine the roundness and the final profile which will be discussed in the following sections.

3.4.3 Filament Puller

The backbone of the 3D Printing advancements has been the contributions from creative minds in the world. The Filament puller used in this section is based on a design that was available in the open source community. Thingiverse user Wingmaster’s design [37] was used as the base template.
to build the Filament pulling system. A few enhancements were made to this system to make it suitable for composite filaments.

![Figure 12. Filament Winding system: (a) and (b) 3D Printed filament puller system pulling PCL coated CNT yarn (c) Speed control drive (d) Cooling fan](image)

The Filament puller consists of two sections, top and bottom section each bearing a roller. The top roller is spring loaded on to the bottom roller. The bottom roller is mounted on the base. There is also a guider placed at the entrance to prevent the filament from getting pushed towards the far ends of rollers. We have upgraded this puller with a DC speed control drive and a cooling fan to control the output characteristics of the composite filament. The composite filament can be pulled
at a slow and constant speed by adjusting the knob on the control system. Fine tuning the speed is critical to obtain precise dimensions and complete cooling. The role of cooling fan is very minimal for composite filaments as the coating made is very thin. The filament needs to be cold and dry to be pulled by the rollers without sticking. Spraying cold water mist was also tried to quickly cool the filament in certain trials. Some hardware enhancements were made to improve the gripping strength and the tension applied to the filament. Compression springs with increased thickness helps to apply a greater pressure on the filament while pulling. In addition, soft rubber sleeves were added to the rollers to reduce slippage.

3.5 Characterization

In this section, we will analyze the overall quality of the composite filament and its suitability for 3D Printing. The machine capabilities also need to be studied to understand the filament’s ability to be printed well. The Mark One 3D Printer can currently print carbon fiber, fiberglass and Kevlar. Although the mechanical properties vary between the fibers, the general specifications of the filaments are mostly similar. The composite filament produced should be comparable or better than these filaments in order to be have good printability. Table 1 lists some of the physical parameters of the composite filaments produced using the Extrusion setup in the previous sections

<table>
<thead>
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<th>Table 1. Composite filament specifications</th>
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<td><strong>Type of Filament</strong></td>
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<td>CNT fiber-Nylon</td>
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<td>Nomex fiber-Nylon</td>
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To understand the composite filament’s capability they need to meet certain requirements. The following are four main requisites that determine the filament’s capabilities to be printed on the Mark One 3D Printer.

(1) Diameter of the filament (2) Tensile strength (3) Printability (4) Minimum length

The diameter of the filament should be in the range of 0.25 to 0.5mm. This is determined by the size of the nozzle and the Bowden tube that feeds the filament to the nozzle. Anything beyond this range might possibly block or get coiled around in the channel. The filament is subjected to tension at the fiber cutter which requires the filament to hold its structural integrity throughout its journey. This requirement has been met as we already know that the tensile strength of CNT fiber is more than 400MPa. When it comes to printability, there are several factors to be taken into consideration, the most important ones are pliability, adhesion and bonding. CNT fibers are one of the most pliable fibers, they can even be tied into a knot. The chances of kinking or breakage is close to zero while being deposited on the build platform. Since they are coated with the same Nylon material as the matrix, the bonding and adhesion between layers will be similar to that of the parts made with pure Nylon. The final requirement is the minimum length. In the Mark One printer, the distance between the fiber cutters to the nozzle outlet is about one meter. In addition, the distance from cutters to the spool holder is about half a meter. Hence, a minimum length of 1.5 to 2meters of filament is required to print at least one complete layer of reinforcement.

3.5.1 Filament Analysis

Two different types of filaments were produced in this project (1) CNT fiber filament (2) Nomex fiber filament. Nomex® Fibers (a trademark product of DuPont) possess excellent heat, flame-Resistant properties and increased durability. They are primarily used in protective fabrics and
uniforms to be used in high temperature environments. The properties of Nomex also makes it ideal to be 3D Printed and coated without breakage or any physical damage. This fiber was chosen to test the feasibility of a commercially available product in 3D printing and compare it to the CNT Fiber produced in Nanoworld.

![Figure 13](image)

**Figure 13.** Microscopic images of composite filaments: (a) CNT yarn wrapped on sewing thread to test the effectiveness of compact wrapping (b) ABS coated CNT yarn (c) Spool of CNT filament – about 6m (d) Nomex fiber composite filament (e) CNT fiber composite filament

The composite filaments produced at Nanoworld have met all the requirements stated in the previous section. Figure 13 shows microscopic images of the filament at different stages of production. The CNT and Nomex fibers were coated with Nylon, a proprietary material from Markforged. We will look into some of the finer details that affect the quality of 3D Printed parts.
1. **Impurities and Defects:** This is the most important factor that directly affects the 3D printer and the printed parts. The commonly found defects include air pockets, which can lead to bubbling in the hot end and result in poor prints. Air bubbles are likely to form when the plastic pellets are not dehumidified before the extrusion process. Figures 13d and 13e show the microscopic image of Nomex coated Nylon and CNT fiber coated Nylon. They have close to zero air bubbles which is a sign of a well-controlled process. Surface defects can also come from contaminants like dust or foreign particles in the extruder. This can happen when the plastic or the filament was not cleaned properly. Presence of coarser foreign particles can lead to a nozzle clog on the printer. A very few impurities can be found on the Nomex filament.

2. **Dimensional tolerance:** Having a filament of consistent diameter is important for achieving a good flow rate during the printing process. A filament of uniform diameter is required to keep the amount of plastic extruded closer to the predicted flow rate (from Slicer calculations). A good dimensional tolerance is obtained when the rate of pulling and extruder coating is kept at the right values. Both the filaments maintained a strict dimensional tolerance of +/- 50 microns. Uniform filament dimensions also prevents issues like extruder jams, under-extrusion and over-extrusion.

3. **Surface Roughness:** The surface of the filament being fed can have some minor impact on the mechanical components of the printer. In general, a smoother filament is preferred. The friction between the filament surface and the Bowden tube (through which the filament passes) should be kept very minimal. Rougher surfaces can abrade the inner walls of the tube. This can lead to localized heating on certain sections of the filament. The nozzle outlet design and quality has a significant impact on this parameter. Additionally, the blades in the fiber cutter may also be damaged over a period of time. The composite filaments produced have a very smooth surface as seen in the Figure 13d and 13e.
Minor quality improvements can also be achieved by water cooling instead of an air cooling system. A filament guide can also be placed at the fiber inlet to feed the filament at a correct height and angle. Fiber abrasion and misalignment at the mixing zone can be prevented by using a guided feed. The process can also further be optimized by tuning the feed rate, temperatures, pulling rate, nozzle outlet diameter. Having an advanced control system will help in precisely controlling the process parameters.

3.5.2 Conclusion
A simple and scalable filament manufacturing apparatus used in this project produced high quality composite filament. Several test runs were performed to optimize the process parameters. Matching the fiber feed rate to the volumetric flow rate of the molten plastic produced consistent filament coating and final dimensions. 3D printing with this composite filament will provide a great increase in conductivity and strength. Parts can be printed with different fiber orientations in each layer to produce best overall mechanical properties.
Chapter IV

3D PRINTING PROCESS

Fused Filament Fabrication technique has been chosen in this project as it aligns with the final goal of incorporating Carbon Nanotube yarn in Printed parts. Several 3D Printing techniques have been invented over the last few decades. The successful ones, like FFF, were developed into commercial 3D Printers. FFF based 3D printers are basically low cost, easy to modify and most importantly use a continuous solid filament as the raw material. The core components of the machine include (1) a toolhead that can move in three dimensional space, (2) Motion control stage for the toolhead movements, (3) a flat platform to build the 3D product, (4) an electronics unit that controls the machine (4) a frame to hold all these components together. Majority of the printers follow the Cartesian design, having three principal linear axes perpendicular to each other. A gantry system carries the horizontal linear guides which typically controls the toolhead movement in X and Y direction. Lead screws host the build platform that move vertically in Z direction. The axis movements are driven by stepper motors using belt and pulley drives. The motors have high precision close to a fraction of a millimeter. The Second most common type of 3D printer kinematics is based on linear delta robots, called Delta printers. They are operated by three freely suspended arms connected to parallel and equally placed towers. These printers allow faster movements, offer larger build heights. Lastly, there are a few printers that operate in polar coordinates and printers that use robotic arms. However, these printers are outside the scope of this report.
Figure 14. Fused Filament Fabrication 3D Printers: (a) Illustration 3D Printer toolhead – liquefier (b) Craftbot Plus 3D Printer – standard FFF type (c) 3D Printer control board with the electronics components and wiring schematics (Adapted from diy-india.com [42])

Figure 14a illustrates a cross section of the toolhead depositing plastic on the build platform. Interesting, the working principle of these printers are very similar to the filament extruder discussed in the previous chapter. A gear drive system is used to drive the plastic filament into a
heated chamber called liquefier. Stepper motors or servo motors are used to precisely control the amount of raw plastic filament being pushed. The solid filament entering the liquefier is heated past its glass transition temperature, thereby allowing it to be molten and mixed in certain cases. The solid plastic filament acts as a plunger pushing the molten plastic through a nozzle of small diameter (approximately 0.4mm). The molten plastic is deposited as thin strings in predefined places on a build platform. After one layer is complete, bed moves down one layer height distance and the second layer starts depositing. The new layer fuses with the previous layer and solidifies as and when it is deposited.

Multiple extruder systems allows more than one material to be deposited either simultaneously or independently. Most common uses of dual extrusion system are to use support material in conjunction with the build material, which can later be mechanically or chemically removed from the build material. There is a huge scope for improvement in this area. It is also possible to combine different types of thermoplastic materials to form a heterogeneous mixture.

4.1 FFF 3D Printers

Two different types FFF 3D printers were used to run experiments with the CNT filaments. The first one is the Makerbot Replicator 2X, a standard FFF 3D printer with dual extrusion capability. The configuration of this printer is close to the RepRap open source machines. Hence, it is relatively easier to upgrade the hardware and also have a better control over the software features. The second printer is a completely proprietary and closed source printer called Mark One which runs its own CAM software. The Mark One is the first of its kind 3D Printer that is capable of printing continuous fibers using a patented technology called Continuous Filament Fabrication (CFF). This printer has the built in hardware to integrate strong and continuous fibers into
thermoplastics in a fluent manner. This machine would be ideal to print continuous CNT filament. The process parameters including the fiber pattern, layer resolution, and infill ratio can be controlled by the cloud slicer. We will discuss about the experiments conducted on both printers in the following sub-sections.

### 4.1.1 Makerbot Replicator 2X

The Replicator 2X is one of the first commercial desktop 3D Printers. The printer has a dual extrusion set up and it seemed an ideal test machine to run some experiments with carbon nanotube yarns. The Makerbot Replicator 2X as seen in Figure - has 100-micron layer resolution and is very much suitable for printing CNT yarn. The aim was to print plastic layer followed by a CNT fiber to ensure that the CNT fiber adheres well onto the printing surface. A couple of different approaches were tried to blend the CNT yarn into the polymer filament. The first approach used an in process blending technique, where a separate CNT yarn and the plastic filament will be fed through two different channels and allowing them to combine at the nozzle. This resulted in the filament coiling inside the liquefier more often than extruding out successfully.

![Figure 15. Makerbot Replicator 2X 3D Printer: (a) Photographic image of the Makerbot Replicator 2X used in this project (b) Nozzle extruding ABS plastic over a small area (c) Part showing traces of CNT yarn on ABS plastic, String of plastic with CNT yarn extruded on the build platform.](image)
The second method used a CNT yarn coated on a plastic filament. The yarn was temporarily bonded by either heat or chemically using acetone. Figure 1c also shows a microscopic image of the blended filament that was fed through the open extruder, allowing the filament to directly enter the heating chamber. It is observed that the CNT yarn maintains its integrity during the process and is not thermally abraded. Although this approach was partially successful, the introduction of CNT yarn leads to a change in the flow characteristics of the filament. The volumetric flow of the molten filament is altered and this causes swirling or clustering of filament around the yarn at places. These experiments suggest that a different hardware setup was required to extrude filaments having continuous fiber. In addition, the travel velocity of the extruder head, torque of the gear drive and temperature of the heater block need to be optimized to suit the printability of composite filaments.

### 4.1.2 Mark One 3D Printer

The goal of this project is to be able to print CNT yarn. The Mark One printer from Markforged is currently the only printer in the market that is capable of printing continuous fibers. The fiber requirements are very specific and it can only print a limited range of fiber materials. In this machine, one nozzle is dedicated to print continuous fiber and the other one for a thermoplastic filament. This innovative design allows the user to print composite parts that are up to five times stronger and twenty times stiffer than traditionally 3D printed parts made from ABS plastic [7]. Parts made from Mark one will have a high strength to weight ratio which can give a tough competition to steel and aluminum alloys. In addition, having the ability to selectively place continuous fiber reinforcement in specific layers of the models provides a variety of options for engineers to control the mechanical properties, material cost and eliminate post processing in some
cases. Some common examples in the Engineering field would be to print brackets, tooling and fixtures

Figure 16. Markforged Mark One Composite 3D Printer: (a) Front view of Mark One 3D Printer (b) Dual extruder head with CFF nozzle and FFF nozzle (c) Printing Nomex fiber composite part (d) Top view of the gantry with extruder motors and fiber cutter on the left side.

The printing process in Mark One is similar to the standard FFF based printers with one unique addition, the fiber layup. Figure 16b shows the patented dual toolhead system, one with a CFF print head and the second using the traditional an FFF toolhead. The latter extrudes plastic in the conventional way, by forcefully pushing a 1.75mm diameter filament into a hot chamber carrying the nozzle. The CFF head on the other hand, softens the incoming composite fiber filament and lays it down. The nylon coating helps the fiber to adhere on bed or to the previously extruder layers of nylon. Figure 16c shows the Nomex fiber being printed on the build platform. The Mark One has a Core XY type mechanical arrangement, where stationary X and Y stepper motors drive the toolhead by means of belts and pulleys. This system keeps the toolhead light and eliminates inertia
due to a moving stepper. Figure 16d shows the most important part of the CFF system on the front left side containing the fiber cutter. The role of the cutter is to ensure that the fiber is spliced at the right lengths precisely based on the toolpaths. The cutter also has a tensioning system to prevent kinking or coiling of fiber inside the channel.

### 4.2 Software Toolchain

The software system plays a significant role in translating a concept design into the final product. There is no one software that can handle all the requirements. To successfully transform a model design into a 3D Printed part, three different software tools are required, namely, (1) CAD package (2) CAM software (3) 3D Printer Firmware. The concept model is first created in a CAD environment and converted into a file format readable by the CAM tool. The CAM software generates toolpath instructions (in the form of machine code) that contains information about building the model on a specific 3D printer. The electronics unit of the 3D Printer has an on board firmware that interprets each line of code and translates into a specific machine function. The flow chart below explains the commonly used software toolchain in 3D Printing.
Product designers use the CAD environment to create their design files, which contains the geometric data of the model. This model is exported as a 3D Printing design file which is readable by the CAM software. The most common and popular file type is called the Stereolithography file or the STL was developed by 3D Systems in 1988 [43]. In this file type, the solid model is represented in the form of thousands of triangular faces in a file containing 32-bit floating-point
numbers, which specifies the normal and the \( x\text{-}y\text{-}z \) coordinates of each vertex of the triangle. A process called tessellation converts a solid geometry into a triangulated mesh using an accuracy or offset parameter. An accuracy parameter determines the acceptable chordal error between the plane of a triangle and the surface it is approximating. The accuracy factor may not be relevant for planes or flat geometry, but is most commonly encountered in curved surfaces. Furthermore, the STL file format contains information only about the surface geometry of the model. Information on other parameters such as color, texture are not included in the file. Having said that, it does provide a fairly simple method of representing the 3D model and has become the industry standard in Rapid Prototyping systems. On the downside, the STL file contains a high degree of redundancy since the data for each triangle is individually recorded. This means that the data for shared edges between triangles are essentially duplicates occupying file space [43]. Sometimes the geometric model data from an external source is imported into the CAD package. As the STL translators within individual CAD systems may vary, the chances of producing files with discrepancy is high. This might result in loss of data or errors in the mesh. Most of these errors occur when importing external 3D model data. The local CAD post-processors will oftentimes approximate the geometry using simple mathematical forms which could result in these errors. Some common mesh errors can be found below

1. Models not being Water-tight: The boundary surfaces must enclose a finite volume. The mesh is incomplete when adjacent faces do not combine completely, thereby exposing the interior of the model that is not defined in the geometry

2. Non manifold segments: The edges of multiple surfaces or meshes have more than two faces joined to a single edge. Complex meshes may sometime lead to producing multiple faces that rest on the same edge.
3. Self-intersecting surfaces: The faces intersect or pass through one another or one surface folds back to intersect itself. Ideally, the surfaces must meet only at the edges.

Hence, it is important to post-process STL files using a Mesh repair software such as Meshmixer or Netfabb. These programs automatically scan the file to identify errors in the mesh. Using the options in the program it is possible to rectify the issues with a single click. In most cases, these programs are available outside the CAD package. Hence, processing large and multiple models can get tedious and time consuming. Recently, a new and more efficient 3D Printing design file called the Additive Manufacturing File format (AMF) has been developed specifically to overcome some of the limitations of STL. AMF is an xml file that contains information about the shape and composition of the model and also has native support for color, materials, lattices, and constellations. This file type is slowly being adopted across different additive manufacturing technologies.

In order to print a 3D object, the STL file is imported into the CAM software, which converts the model into a stack of thin layers along the along. Each layer consists of toolpath instructions which are represented in the form of Gcodes. The G-code comprises of toolhead movements, machine commands like heating and fan controls that are specific for the 3D printer. The firmware translates these gcodes into machine level instructions that makes the toolhead to lay down successive layers of molten plastic. CAM software has several built-in modules. The core modules include generating toolpaths, communication with the printer and maintenance. Some programs also have features to manipulate the models. CAM software used in this project will be discussed in detail in the following sub-sections.
4.2.1 Simplify3D

Simplify3D is a CAM based 3D Printing software that is used to convert 3D Printing design to machine readable printing instructions. This software is packed with advanced features including multi-extruder and multi-material printing options. The primary function of this software is to perform a process called slicing, where a 3D model is sliced into several horizontal layers based on the process settings. Each layer contains the precise toolpath instructions to deposit the molten plastic strings in a direction and quantity specified. Individual strings of plastic deposited then fuse together when they come in contact. All the above information is condensed into a gcode file which is generated upon slicing. The Figure 17 shows images from the Simplify3D interface. Figure 17a shows the virtual build environment where the 3D Printing design file is loaded. The model can be manipulated by changing its orientation, scale and position on the build platform. After slicing the gcode file is presented in a visual form in Gcode visualizer. This is a very powerful feature as it helps to preview the way toolpaths used to build the model. The process settings window shown in Figure 17c contains all the parameters that the machine needs to perfectly execute the print job.
Figure 17. Simplify3D Software Demonstration: (a) Virtual Build Environment (b) Gcode Visualizer (c) Process Settings Window

The CAM software is also intended to perform several other functions including maintenance. The Machine Control Panel establishes an active communication with the printer over USB or Wifi. Customized Gcode commands and scripts can be run from this interface to perform tasks like bed calibration, changing filaments, Extruder and Bed PID tuning, nozzle purging etc. This is
particularly useful when printing with low cost machines which may not have a visual interface or inbuilt maintenance routines. Furthermore, the Gcodes generated by Simplify3D offer readability and maintainability. This is a highly useful feature as it allows adding custom scripts in the default Gcode file. For example, if a machine needs to turn on the LED lights or custom servo motors at certain points in the print, the Gcode file can be opened and the custom commands can be inserted at the required places.

4.2.2 Eiger

Eiger is a cloud based CAM software which is specifically developed to work with the Mark One 3D Printer. This CAM software is a completely closed source and proprietary which limits the users to the access only the settings offered by default. The code and the algorithms that are used to generate toolpaths will handle fiber placements and CFF laying in addition to the standard FFF process. The gcode file as it is encrypted and hence custom commands cannot be inserted.

![Figure 18](image)

**Figure 18.** Eiger Cloud Software Demonstration: (a) Model of pipe bushing (b) Blue circles indicate Carbon fiber placement in the composite part (c) Fiber selection bar based on the layer count, presently selected layers 2 and 3.

The design files are uploaded to the software’s library. As Eiger is hosted on the cloud, it can be accessed remotely without being present in a close proximity to the printer. This also reduces the chances of software piracy and saves the manufacturer from distributing the software setup file
physically or electronically. Figure 18 contains a series of screenshots demonstrating the steps involved in creating a composite fiber part. Although the slicing parameters are limited, the software gives very good control over the placement of the fiber in the part. Figure 18b shows the X-Ray view of the model highlighting (in blue) the area where the fiber needs to be placed. Users have the option to pick specific layers to insert the fiber (seen in Figure 18c). Two different types of fiber layups can be chosen: concentric (seen in the picture) and isotropic. The software calculates the length of the fiber that can be efficiently placed for each layer. Sharp edges, small area segments are usually ignored as the fiber layup may not be possible in those areas.

4.2.3 Gcode

G-code is a type of numerical control programming language used to control machine tools. The Gcode file is typically generated by the CAM software. In 3D Printing, a typical Gcode can contain information on running a startup routine to warm up the machine, toolpath instructions to deposit molten plastic followed by an end routine to turn off the machine. It also contains information about the toolpath movements, machine tool controls required to produce a final product. These gcodes follow the NIST RS274NGC G-code standard [44], which is commonly used by the CNC machines. A variety of Gcode flavors are available and the most common ones for 3D Printing include RepRap, Sailfish, Bits for Bytes and Smoothieware. The slicing engine runs the CAD model through complex algorithms and post processing modules to generate the final Gcode file. Table 2 shows a sample section of RepRap gcode file. The gcode is separated into different segments based on its functions.
Table 2. Gcode commands and functions

<table>
<thead>
<tr>
<th>Gcode File</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>G90</td>
<td>In red, the first two commands are common instructions preset for a specific firmware type. The define the Type of coordinate system to follow, absolute coordinates in this case</td>
</tr>
<tr>
<td>M82</td>
<td></td>
</tr>
<tr>
<td>M106 S0</td>
<td>The green segments contain the startup sequence for this particular print job. The instructions tell the printer to turn on the part cooling fan, heat the extruder and bed to set temperatures, home the axes and prepare to print</td>
</tr>
<tr>
<td>M190 S70</td>
<td></td>
</tr>
<tr>
<td>M109 S220 T0</td>
<td></td>
</tr>
<tr>
<td>G28 ; home all axes</td>
<td></td>
</tr>
<tr>
<td>G1 E-1.0000 F2400</td>
<td></td>
</tr>
<tr>
<td>G1 Z0.394 F1200</td>
<td></td>
</tr>
<tr>
<td>; layer 1, Z = 0.39375</td>
<td></td>
</tr>
<tr>
<td>G1 X79.436 Y99.963 E0.0132 F600</td>
<td></td>
</tr>
<tr>
<td>G1 X80.678 Y98.992 E0.1938</td>
<td></td>
</tr>
<tr>
<td>G1 X80.763 Y98.929 E0.2059</td>
<td></td>
</tr>
</tbody>
</table>

In general, the Gcode commands having G as the prefix are used to perform toolhead movements in X, Y and Z direction. This includes extrusion, rapid movements and dwells. The MCode commands perform machine controls like heating, fan controls, motor controls etc. The most commonly used Gcode syntax is given below

```
G1 XaaYbb Ecc Fdd ; Comments
```

Here, \textit{aa} and \textit{bb} represent the X and Y coordinates. \textit{E} represents the movements by extruder stepper motor where \textit{cc} defines the length of plastic filament extruded (in terms of raw plastic). \textit{F} defines the Feed rate for any of the steppers, X Y Z or E. Comments can contain alpha numeric characters that
verbally define the task that a specific Gcode line performs. The comments usually follow the commands, separated by a semi-colon.

4.2.4 Firmware

Firmware is a type of software program that is embedded on the hardware device. 3D Printer firmware translates the Gcode commands into direct mechanical actions on the hardware like operating a motor, powering a heater, controlling a fan etc. It is typically stored in the non-volatile memory of the electronics board like the EEPROM (Electrically Erasable Programmable Read-Only Memory) or flash memory. EEPROMs can be programmed and erased in-circuit, by applying special programming signals [45]. Open source and non-proprietary 3D printers offer an option to upgrade the firmware on the memory. In most cases, the stock firmware can be replaced with a custom and self-configured version. This may require flash memory to be reprogrammed through a special procedure. The active involvement in the open source community has given rise to numerous firmware types each written in their own flavor. Hence, the CAM software should be capable of generating gcodes that can be interpreted by all these firmware files. The firmware is capable of performing a variety of tasks, mainly, controlling the input/output voltage states, motion control, path planning, stepper control, handling usb communication and buffering. In addition they should also be able to support peripheral attachments or upgrades like sensors and LCD control panels. One of the most common open source firmware is Marlin [46] that works with boards based on AVR microcontrollers. Marlin is developed with an aim to be highly configurable and adaptable to many different boards.
4.3 Composite Prototypes

The extrusion system developed in the earlier chapter produced some high quality CNT filaments. Building a prototype will help to establish a proof of concept for 3D printing CNT yarn. Commercializing the nanotube other proprietary fiber based filaments will depend on the printability of these filaments. Spools of composite filaments made of CNT fiber and Nomex fiber were stocked before running the experiments. Eiger automatically selects the material profile with optimized toolpaths, speeds and extrusion settings for the standard filaments that come with the printer. Based on observing similarities in material properties, the process parameters to run the composite filaments were chosen.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CNT fiber-Nylon</th>
<th>Nomex fiber-Nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Material type (input</td>
<td>Kevlar</td>
<td>Fiberglass</td>
</tr>
<tr>
<td>setting in software</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber Fill Type</td>
<td>Concentric</td>
<td>Concentric</td>
</tr>
<tr>
<td>Nylon Fill pattern</td>
<td>Triangular</td>
<td>Triangular</td>
</tr>
<tr>
<td>Nylon Fill density</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>No. of fiber layers</td>
<td>1 (Layer 3)</td>
<td>2 (Layer 3 and 4)</td>
</tr>
</tbody>
</table>

One of the initial challenges encountered in 3D printing CNT filament was in filament loading. The stock filaments come with a small plastic spool that can be mounted on the back wall of the machine. The absence of a well-designed filament spool left the filament hanging and coiling around. A classic approach of using 3D printing to resolve an issue in 3D Printing was adopted for this case. A custom filament spool was quickly designed and printed on the Makerbot Replicator 2X printer to hold the filament roll in place. A small filament guide was clipped to the spool to
more reliably feed the filament while still maintaining the tension. Furthermore, on loading each fiber spool, nearly a meter of filament was lost in feeding owing to the complexity of tensioning system. After running a few trials, CNT and Nomex filaments were successfully loaded and printed using the Mark One printer. A tensile test specimen (user jumpmobile in thingiverse [47]) was selected to print the Nomex fiber filament. The model was printed with 2 nylon base layers and 2 consecutive fiber layers. Figure 19 shows 3D Printed parts made of Nomex filament.

![Figure 19. 3D Printed Nomex fiber composite part: (a) and (b) Microscopic images of Nomex fiber in the printer part demonstrating the quality of the print (c) The complete tensile test specimen printed on the Mark One](image)

The CNT fiber parts were printed using a custom model that would serve as a biomedical device. The aim was to have the CNT yarn make small loops around and in between those holes. However, the software limited the fiber layup quoting insufficient space available for fiber layup. This is one
of the limitations of the software at the moment as it is designed to minimize the risk in fiber cluttering. Figure 20 shows 3D Printed parts made from CNT fiber. The part was bent and flexed to see if there is any fiber damage, as seen in Figure 20d.

Figure 20. 3D Printed CNT fiber composite part: (a) and (b) Microscopic images of CNT fiber in the printer part demonstrating the quality of the print (c) The complete tensile test specimen printed on the Mark One (d) Manually flexing the printed part

4.3.1 Analysis

In this section, 3D Printed composite parts made from Nomex fiber and CNT fiber will be thoroughly studied. To analyze the fiber layup and bonding, some of these prototypes were stopped midway through the print. This gives ability to analyze minute details like layer defects using a
microscope. The main factors affecting quality of the 3D printed composite parts are listed below. The components will be assessed on their performance under each category.

1. **Layer Defects:** The regular 3D printed parts made of homogenous materials where the layer defects arise from improper and inconsistent extrusions. In composite parts containing fibers, the focus is more on the fiber layup. It is important to verify that the fiber followed the theoretically predicted toolpath. All the fiber layers must be properly aligned when a part is printed with multiple fiber layers. Discrepancies in this area can lead to dimensional inaccuracies. Figures 19a and b show the microscopic images of Nomex fiber layers. The fiber placements in each layer did not accurately follow the predicted path. The top fiber layer seems to be offset from the bottom fiber strand in the Y direction. This can happen due to the effect of fiber sliding over each other. When the layer height does not match the diameter of the fiber, the top fiber can force itself on the bottom fiber causing the one of them to slip away. The diameter of the Nomex fiber is about 480um whereas the stock fibers were more towards the 350um range. This implies that the nozzle was too close to the base layer and did not provide enough space for the fiber to be effectively laid down.

2. **Fiber-Matrix Bonding:** The ultimate test of quality for a composite material comes from the bonding strength between the fiber and matrix. This parameter directly influences the mechanical properties of the final part. Figure 20a and b show two different locations on the top layer of the part that had fiber reinforcement. In Figure 20a, the bonding is fiber matrix interface looks a lot smoother and stronger without any defects. On the other hand, visible airgaps were spotted along the interface in Figure 20b. The fiber has partially lost its structural integrity exposing individual strands. A similar effect is also observed with the Nomex fiber parts. In Figure 19b, the fiber-matrix interface looks distorted along the curved. In addition,
surfaces of the fiber strands are also exposed. This suggests that the amount of nylon material coated on the filament maybe insufficient.

3. **Fiber Performance**: The primary strength for the composite material directly comes from the fibers. So it is imperative that the fiber does not get damaged during the 3D printing process. The Nomex fiber used in this project is a commercially available product developed by DuPont. Nomex fibers maintained their structural integrity throughout the print which is expected out of a material produced in a large scale industry. The fiber remained strong and intact even at the places of defects which is a good proof of the fiber durability. On the other hand, the CNT fiber yarn unraveled at several points along the print. While printing, the nozzle applies pressure on the filament against the base layer. The fibers may tend to loosen up and split due to this effect. The lack of proper weaving is clearly the reason for this behavior. On the positive side, the yarn printed well without any damage or breakage to the fibers. This is a measure of the outstanding properties of CNT yarn, being strong but yet pliable.

### 4.3.2 Conclusion

The CNT fiber and the Nomex performed incredibly well as fiber reinforcements for 3D Printed composites. The filament diameter plays a significant role in determining the quality of the printed parts. Layer height needs to be consistent with filament diameters to prevent defects. Using an incorrect layer height will also affect the mechanical properties of the printed part. Hence, the layer height should be equal or slightly more than the diameter of the filament. Due to this constraint, the choice of layer resolution is limited and parts will mostly have a coarse surface finish. On comparing the parts printed with Nomex fiber and CNT fiber, Nomex fiber seems to have performed better as a filament material owing to its good structural integrity. However, the CNT yarn is a far more superior filament in terms of its material properties. The coating thickness also
plays an important role in eliminating the defects in printed parts. Minor quality improvements can be made by controlling the amount of nylon coated for each fiber. The Nomex, due to a larger diameter and higher fiber density seems to require a thicker and slower coating when compared to the CNT which only contains seven individual plies. From the above experiments, the proof of concept has been established for printing any good fiber. It is evident that a lot of trials and experiments are required to completely understand the factors influencing the composite material printing. Eiger plays a crucial role in the testing the composites efficiently. A software offering much more control over process parameters like Simplify3D would be preferred for printing with fibers. Rigorous testing, evaluation and refinement are the best means to optimize the process parameters that yield perfect results.
Chapter V

APPLICATIONS

In the previous chapters, an innovative filament manufacturing process was developed, tested and analyzed. The ability to 3D print functional end products without assembly and post processing is still in its nascent stages. This research work has made some significant technical advances, namely, (1) development of hybrid nanotube yarn plastic filament for 3D printers that is strong, electrically and thermally conductive (ii) a 3D Printing process that will allow producing composite parts made of any custom fibers. Composite parts manufactured from these materials will create new products and solutions, particularly in the medical and aerospace industries. Medical applications can be found in (1) Biomedical implants, including customized prosthetics and organ tissues; (2) Pharmaceutical research on drug delivery. There is an enormous potential in both these areas as they require a very high quality, multifunctional material to fulfill the needs. Hybrid filaments developed in this project will be an ideal candidate for manufacturing composite aerospace parts, biomedical stents, functional body suit sensors, drug delivery systems, and devices that have built-in power conduction and communication (electronics built-in to plastic and composite materials to reduce size, cost and weight). 3D Printing can also improve the production efficiency, cycle time and reduce manufacturing costs.

5.1 Bio Removable wire

The concept of biodegradable devices for use inside the body has been in use for several years. Some of the most commonly devices include bioremovable sensors, drug delivery capsules, fragility fracture fixation devices etc. A Bio-removable wire (BRW) is biodegradable device containing a drug
delivery capsule. Part of the device can be removed from the body after injecting the drug while the rest of the device slowly degrades in the body. An ideal BRW design may consist of thin and complex features that can pack the sensors, drugs and electronics into one compact device. 3D Printing is the most effective way to manufacture a device like BRW as it is can produce complex devices in a cost effective way. Additionally, efficient usage of the polymer material reduces the burden on degradation. Smart implant technology adds complexity, but will provide a least invasive way to remove the device post usage.

5.1.1 Material of Choice – Polycaprolactone

Polycaprolactone is one of the few synthetic polymers that could be degraded by microorganisms. Some interesting properties like high solubility, low melting point (59–64 °C) and exceptional blend-compatibility has made this polymer a great candidate for biomedical applications [49, 50]. In the past, PCL and its copolymers were used in a number of drug-delivery devices due to its slow degradation rate and tailorable kinetics. In addition, they also possess many desirable characteristics from a manufacturing standpoint like ease of shaping and simple fabrication methods. Although PCL does not have any high strength and load bearing characteristics, it is biocompatible and proven to be conducive for in-tissue implementation. This makes PCL an ideal choice for soft implants. PCL’s superior rheological and viscoelastic properties allows the material to be formed into a wide variety of scaffolds [49]. In addition, numerous drug-delivery devices made of PCL already have FDA approval and CE Mark registration [50]. Despite having these accreditations, it is surprising that PCL composites have still not been extensively tested as biomedical implants.
5.1.2 Fabrication process

The fabrication process for bioremovable wire is a typical use case for testing the effectiveness of the extrusion setup developed. A Bare bone model of this device was produced by the wire-coating extrusion process. A thin copper wire (AWG 30) was used as a test model in place of a CNT wire. The copper wire was fed through the needle inlet at the nozzle. The glass transition temperature of PCL is below 0 °C. Hence, a few experimental trials were required to determine the extrusion temperature. A temperature of 52 °C (8 °C below the melting point of PCL) yielded best results. The temperature set point was decided to ensure that the PCL coming out of the nozzle does not droop down.

In ideal conditions, the molten PCL wraps around the Copper wire and maintains its external profile. Water-Cooling method can be used to cool outer surface rapidly and maintain the cylindrical profile. Figure 21 shows the prototype of the Bioremovable wire being set up in a silicone cast to mimic testing in a tissue environment. The PCL sleeve is stripped off at the ends of the extruded copper wire before placing in silicone casts. The silicone was allowed to cure for 24-48 hours before being tested. The copper wire ends were sanded to remove protective coating.
5.1.3 Testing

BRW is implanted into the body where it is in close contact with live cell tissues. Once the drug is delivered the device will be removed in the least invasive way. In order to remove the device, BRW need to be heated by supplying a small value of current through the wire. The temperature should lie within a safe range of 27 °C to 35 °C in order to prevent any damage to the tissues. At the same time, the wire should also slide through the easily. To demonstrate this process, a benchtop test apparatus was setup (as shown in Figure 22).

![Figure 22](image)

Figure 22. Benchtop test setup for Bio-removable wire (a) Bio-removable wire silicone mold set up on a wooden block and copper wire ends are connected to power terminals (b) and (c) Thermal images of the setup when power is supplied through the wire (d) Bio-removable wire being pulled out of the mold where ambient conditions do not cross 35 °C. (Courtesy: Seyram Gbordzoe)
The wire leads are connected to an external power supply unit to provide a controlled power input. Power input directly influences the heat generated in the copper wire. A thermal imaging system was used to determine the temperature at various points in the BRW. The outer surface of PCL is in direct contact with the silicone and must be maintained at temperature less than 35 °C. This is the bearable heat the tissues can take without getting damaged. Figure 22c shows the state of device when it is prepared for removal. The temperature at external surface (point 1) is 25.9 °C and point 2 where the wire is in direct contact with the silicone is not exceeding 32 °C, which ensures the safety of the tissues. At this point, the wire was successfully pulled off using tweezers (as shown in Figure 22d), leaving the PCL to stay inside the cast. In the real world, PCL will slowly degrade in the bloodstream over time after the drug has been delivered. Thus the proof of concept has been established for the BRW. The ability to custom 3D print and extruder devices will make this a much more suitable option in clinical research. Polymer implants that controllably degrade and disappear will be a great asset in the modern drug delivery system.

5.2 Winding Apparatus

The CNT Reactor in Nanoworld produces large quantities of yarn and sheet during the production run. The raw CNT sock coming out of the reactor needs to be sprayed with acetone and collected in a drum. Having a device to automatically spool the yarn or sheet would be a valuable addition to the reactor setup. 3D Printing can help translating the idea of customizable winding equipment into a real life solution. A customized design for the in-process winding apparatus can be 3D printed in shortest time and lowest cost.

The Winding system can be split into two modules. The first module is a height adjustable platform with spool holders that can hold CNT spools. This will also be a part of the feeding system to produce
multi-ply yarns. To be more efficient, a 3D Printed screw jack model (designed by a user Intentional3D on thingiverse.com [53]) was used as a template. The platform of the jack was modified to attach a separately designed bobbin stand. The Screw jack was printed with a black Polycarbonate (PC) filament. PC is commonly used in making functional parts that offers excellent structural strength and durability such as plastic gears and bearings. Figure 23b shows the 3D Printed screw jack with bobbin holder mounted on top. The bobbin holder tray is printed with Markforged Nylon material which is chemically resistant to solvents like Acetone. The tray can carry up to six bobbins at a time.

![Figure 23. Design for Winding Apparatus (a) CAD models for a concept winding apparatus that can be 3D printed using functional CNT composite parts (b) Bobbin holder mounted on top of a screw jack assembly (Courtesy: Guangfeng Hou)](image)

The second module comprises of an entire winding set up that was conceptualized and designed specifically to suit the needs of the CNT reactor. Figure 23a shows some initial designs of the winding equipment modelled on Solidworks. The system will be driven by two DC motors (motor 1 and 2) one to drive the main shaft rotating the yoke and the second one to rotate only the inner shaft that drives the barrel. Belt and drive system will drive both the shafts. Angular bevel gears will transmit
power to the barrel through the inner shaft. The Yoke can hold a Spool barrel of up to six inches in length. This will make it easy to collect both sheets and yarns. By adding speed controllers to the setup, winding speeds can be varied to the desired amounts providing greater control over the quality of the spun yarns. Some of the important parts like the bevel gears and pulleys will be printed using premium plastic filaments like PC or PEEK. The cost estimate for a similar setup produced commercially would be close $5000 including the labor. 3D Printing this system will reduce the cost by more than 60%. In house manufacture will also provide the flexibility to do multiple design iterations in a shorter duration. The cost estimate for the project completed in house would be close to $1000 including the cost of materials and fabrication for multiple iterations. Lastly, lead time in procurement can be shortened and majority of the supply chain issues can be avoided.

5.3 Commercialization of Nano-filled Composites

Throughout the report, many different technical applications were discussed. The outstanding properties of CNT and composite filaments have secured a very high place in the materials market. Nanoworld at the University of Cincinnati is one of the very few laboratories in the world to produce high quality Carbon Nanotube yarn. With the technical expertise and state of the art equipment, it is possible to start a business venture from this research. Some of the important industry trends and market potential for 3D Printing premium composite parts has been discussed. The application will lay the foundation to kick-start a 3D Printing Company that offers premium and customizable 3D Printing material and printing services.

5.3.1 Operating Model

The name of this venture will be PN3D, which stands for Print Nano in 3D. PN3D will be a product and service based company. CNT and other custom filaments will be available as products for
purchase. 3D Printing services will be offered for customers, particularly composite and filaments with custom blend. The flow chart below illustrates the basic operating model.

![Flowchart describing the operating model of PN3D.]

**Figure 24.** Flowchart describing the operating model of PN3D.

The Production Facility consists of three units: Nanomaterials synthesis unit, Filament Production Unit and a 3D Printing Unit. The raw data, in the form of digital files or sketches will be acquired from the customers. For direct printing requests, the design team would communicate with the clients regarding print feasibility. Processed files are sent to online repository, which can then be accessed by the printing unit. The requests for filaments will be sent to the Filament production Unit. An inventory check will per formed in case the order needs CNT filaments. Depending on the need for nanomaterials, the filament production unit will plan production runs and update the inventory.
Once the product is completed, it will be sent for packaging and then to the work-in-progress inventory. The 3D Printing unit checks print estimates and schedules a print job with the machines that are available. Printed parts will go through a quality control process to determine if post processing is required. The final part is sent for packaging and the engineering team works with the customers to ensure that product quality is satisfactory.

### 5.3.2 Products and Services

PN3D will offer two types of 3D Printer filaments. The flagship product will be the CNT yarn for which the dimensions and composition are preset. The Nanoworld labs and PN3D have engineered this filament to exhibit outstanding mechanical strength and electrical properties. The second type of product will be the custom filament. Customers can choose from a set of fibers available from the catalog or present their own fibers to check if it qualifies for 3D Printing. The table below shows the list of items in the product catalog.

<table>
<thead>
<tr>
<th>Table 4. Product Catalog – 3D Printer Composite Filaments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product Name</strong></td>
</tr>
<tr>
<td>PN-CNT</td>
</tr>
<tr>
<td>PN-Custom</td>
</tr>
</tbody>
</table>
Rapid prototyping of composite plastic parts will be the main service offered in the company. To get the best value for product, requests will be taken only for short production runs of 1000 items or less. This is to ensure both the customers and the company find this solution to be economically viable and time efficient. The Engineering team at PN3D are pioneers in 3D Printing. In addition to printing, PN3D will also offer Design for 3D Printing. Manufacturing components that specifically suit 3D printing is one of the key requirements in product development phase. CAD models will be designed to meet client’s final product requirements. The table below summarizes the list of services offered.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Description</th>
<th>Price</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-Print</td>
<td>Customers can request print jobs. Choice of material: Composite and standard thermoplastic</td>
<td>Varies</td>
<td>Small batches of 1000 parts of lesser are usually preferred</td>
</tr>
<tr>
<td>PN-Comp</td>
<td>A complete package from design to 3D Printing. This is ideal for customers who need complete solutions.</td>
<td>Varies</td>
<td>Includes free Engineering consultation.</td>
</tr>
<tr>
<td>PN-Subs</td>
<td>Subscription service for clients who need 3D printing parts round the clock. Up to 100 parts per month*. Additional parts will be charged at half the regular price</td>
<td>$50/ item for standard 3D Printed parts. $100 onwards for premium composite parts</td>
<td>Includes free Engineering consultation.</td>
</tr>
</tbody>
</table>

*Part quantity is determined by the size. Each part should completely fit in a 4” cube. If dimensions exceed the given value, it will be counted as the second part.
5.3.3 Market Analysis

3D Printing industry has been growing consistently well since the entry of low-cost desktop machines back in 2012. Market trends and predicted based on analyzing the current developments in the market across different segments such as application, material and demographics. Wohlers Associates Inc. have reported that the global 3D printing industry has grown to a total of $5.165 billion in 2016 [18]. The consistent growth is a direct result of latest innovations in 3D Printing, especially in electronics and materials. The analysis from ReportsnReports predicts the 3D Printing market to reach USD 30.19 billion by 2022, at a CAGR of 28.5% between 2016 and 2022 [55]. This estimated growth takes into account various 3D Printing technologies, printer manufacturers, materials, education and other businesses. The explosive growth of 3D Printing in the various fields like aerospace, medical, automotive sectors and consumer goods also positively influenced the 3D Printing materials market. An overview of the material trends in 3D Printing presented by Markets and Markets shows that the materials market is expected to grow from USD 530.1 Million in 2016 to USD 1,409.5 Million by 2021, at a CAGR of 21.60% during this period [57]. The market for materials alone has grown to the size of the entire industry 5 years back. This is a clear indicator of the humongous demand for new and innovative materials in the aerospace and biomedical industries. In the last couple of years, biomedical industry has invested heavily in 3D Printing research related to organ transplantations, dentistry and cosmetic implants. In addition to new materials, numerous other materials from traditional manufacturing methods have been tailored to work across different 3D printing technologies. It also suggests that people have been 3D printing a lot, from business use to hobbyist or recreational use. At this point, it is important to understand the size of market for FFF 3D Printing materials. The market for thermoplastic filament is expected to reach over $6.6 billion by 2026 [56]. This growth has been fueled by the need for high performance and functional materials that can be
used on desktop 3D Printers. In the upcoming years, new filament manufacturers and present market leaders are expected to delve into specialty filament materials.

5.3.4 Competitors and Customers

The materials industry is slowly moving towards specialty and engineering grade for high performance applications. PN3D targets a niche segment in 3D Printing materials market. The competition is very stiff considering the fact that 3D Printing materials market alone is close to a billion dollars worldwide. The competitors to this business would more likely be thermoplastic filament manufacturers. The product offerings of numerous of 3D Printer manufacturers and filament makers were taken into consideration to determine the availability of exotic filaments. There were only a handful of key players in the market who are direct competitors. Based on the data acquired from companies producing 3D Printer filaments around the world, the current and potential competitors for PN3D has been listed in Table 6.
<table>
<thead>
<tr>
<th>Name of the Filament</th>
<th>Nanomaterial</th>
<th>Volume resistivity (ohm-cm)</th>
<th>Price</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN3D filaments</td>
<td>CNT yarn</td>
<td>0.005</td>
<td>$600 per Kilogram</td>
<td>Continuous fiber. Highly customizable</td>
</tr>
<tr>
<td>Onyx from Markforged</td>
<td>Chopped carbon fiber</td>
<td>NA</td>
<td>$80 per 250 grams</td>
<td>Also produce continuous Carbon, Kevlar and Fiber glass</td>
</tr>
<tr>
<td>Black Magic 3D Conductive Graphene Filament</td>
<td>Graphene powder</td>
<td>0.6</td>
<td>$550 per Kilogram</td>
<td>Filament designed only for low current applications Nozzle size of min 0.5mm (std size is 0.4mm)</td>
</tr>
<tr>
<td>Tiamet3D (Netherlands based)</td>
<td>Carbon nanofiber</td>
<td>No info</td>
<td>No info</td>
<td>Not launched yet</td>
</tr>
<tr>
<td>3DX Tech’s 3DX Nano</td>
<td>Carbon nanotubes</td>
<td>No Info</td>
<td>$30 per 200 grams</td>
<td>Available in combination with ABS and PETG</td>
</tr>
<tr>
<td>FilaOne™ GRAY</td>
<td>Carbon nanotubes</td>
<td>No info</td>
<td>$99.50 per 250grams</td>
<td></td>
</tr>
</tbody>
</table>

Having the advantage of producing some high quality CNT yarn, PN3D has a great advantage over its present and upcoming competitors. The recent trends have shown that many industries have started implementing 3D Printing technologies in their businesses. As the only player in the market producing multifunctional CNT yarns, it is easier to build strong business relationships with companies from diverse backgrounds. Majority of the customers for PN3D are expected from education, aerospace, defense and military and medical research laboratories. The increase in demand
for multifunctional CNT filaments will attract a lot of clients especially from Research and Development in the medical and aerospace industries. Bioremovable wire that was discussed earlier in this chapter has received great interest from University of Cincinnati Medical Sciences Department. Furthermore, architectural and product design companies have made heavy investments in integrating 3D Printers in their production processes.

5.3.5 Business Strategy

The Unique Selling Proposition of this business would be the CNT filament which is not sold commercially anywhere else in the world at present. The capital required to launch the company is close to USD 300,000, which on the smaller side for a manufacturing firm. Investments can be sought from partnerships with existing companies, investments from outside investors, venture capitalists and business loans. Collaboration with Universities and research institutions is another avenue which has kickstarted many small and innovative companies in this space. Majority of initial investments will go towards purchase of equipment and supplies required to start operation. Table 7 lists the equipment and asset the company would need to acquire at the startup stage.
Table 7. List of equipment and personnel required for business operation

<table>
<thead>
<tr>
<th>Name of the Machine</th>
<th>Description</th>
<th>Price</th>
<th>Personnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floating Catalyst Reactor</td>
<td>CNT yarn Synthesis</td>
<td>$130000</td>
<td>Engineer and Technician</td>
</tr>
<tr>
<td>Filament Extruder</td>
<td>Producing high quality 3D printer filaments</td>
<td>$15000</td>
<td>Technicians</td>
</tr>
<tr>
<td></td>
<td>Plastic pellets and filaments</td>
<td>$2500</td>
<td></td>
</tr>
<tr>
<td>Spooling equipment</td>
<td>Winding 3D printer filaments at the right tension</td>
<td>$12000</td>
<td></td>
</tr>
<tr>
<td>Mark Two printer</td>
<td>Printing composite parts</td>
<td>$18000</td>
<td>Engineer and Technician</td>
</tr>
<tr>
<td>Ultimaker 3D Printer</td>
<td>Printing plastic parts</td>
<td>$6000</td>
<td></td>
</tr>
<tr>
<td>Raise3D Printers</td>
<td>Printing plastic parts of larger dimensions</td>
<td>$2500</td>
<td></td>
</tr>
<tr>
<td>Computer Systems</td>
<td>5 Desktop computers, 2 Laptop computers And peripheral devices</td>
<td>$3000</td>
<td>Engineers</td>
</tr>
<tr>
<td>Software Packages</td>
<td>Solidworks</td>
<td>$7500/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Simplify3D</td>
<td>$150</td>
<td></td>
</tr>
</tbody>
</table>

The second round of investments can be used to cover operating costs including payroll, taxes, utilities and marketing campaigns. The business is expected to generate revenue from both the
product and services side. Having a constant revenue stream from subscription models is a great way of keeping the ball moving. Several other business strategies like Cash flow, income statements, and balance sheets are beyond the scope of this report and hence will not be discussed in detail. Although, it is good to develop and understand the financial plan before approaching investors.

Prices for 3D printers have been continuously dropping due to the availability of cheaper hardware and lower manufacturing costs. On the other hand, the filament prices did not really follow the same path. They costs have reduced only marginally. At present, the filament prices still hover around 25-30$ per 1kg spool for standard PLA or ABS. With new types of filaments coming in the market, a rise in competition between industrial filament producers can be observed. In long term, this should create a drop in prices. A particular segment of filaments called the exotic or premium filaments have seen a constant increase in price. Exotic filaments include special materials like metal filler, nanomaterial etc. The prices for these filaments start from $50/kg and go all the way up to $500/kg. The competition for premium filaments is very less and selling these packages can be a lucrative business. There is always a huge demand for these filaments as end users and professionals in different field are willing to experiment with new materials.

One of the key aspects of any business venture is the localized production. The CNT synthesis unit and the filament production unit need to be at a closer proximity to have a higher production efficiency. The 3D Printers can be stacked in movable shelves and do not need too much floor space. Producing nanomaterials in house will shorten the supply chain. The company needs a maximum of 10,000sq floor space to accommodate the equipment and office space. The floor space can be rented in location close to clients or in a central business location. Inventory planning plays a major role in any businesses. Table 8 lists the materials and supplies needed during operation.
Table 8. Inventory and stock management at PN3D

<table>
<thead>
<tr>
<th>Type</th>
<th>Items</th>
<th>Lead time to order</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Materials</td>
<td>Plastic Filaments and raw pellets</td>
<td>2-3 Business Days</td>
<td>Microcenter, Rapid Direction Inc</td>
</tr>
<tr>
<td></td>
<td>CNT synthesis chemical ingredients</td>
<td>Varies</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Work-In-Progress</td>
<td>Custom filaments, Nanomaterial</td>
<td>N/A</td>
<td>In-house</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Hand and power tools, electrical wiring, tapes,</td>
<td>3-5 Business Days</td>
<td>McMaster Carr, Grainger</td>
</tr>
<tr>
<td>Repair Operation</td>
<td>lubrication</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finished Goods</td>
<td>3D printed parts ready to be shipped</td>
<td>Varies</td>
<td>In-house</td>
</tr>
<tr>
<td>Digital Repository</td>
<td>In-house data management system will be required to</td>
<td>N/A</td>
<td>Best-buy, Amazon</td>
</tr>
<tr>
<td></td>
<td>store production and customer files</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The inventory planning is primarily focused on filament production and nanomaterial synthesis unit where there will be constant demand for materials. Having the ability to produce most of the components in house allows having a smart inventory which is small in size. The growing ecommerce industry has immensely reduced the lead time on supplies. Anticipation and buffer inventory items can be maintained to handle unexpected needs.
The demand for the 3D printing materials among professionals in aerospace & defense and medical & dental is slowly increasing. This is a great sign for a new business offering a high end niche product. The CNT fiber filaments and will continue to have a growing demands owing to its outstanding properties. In addition they also offer other advantages such as quality and durability. With a lot of innovation happening in the industry, the focus is slowly shifting from hobbyist printing towards the production of functional parts. This trend is in line with PN3D’s business strategy which will make them leaders in the premium composite filaments market.
Chapter VI

SUMMARY

The expectations from 3D Printing have drastically changed over the last few years. This demand has sparked innovation in materials and led to the production of state-of-the-art machines. Multifunctional Composite materials like CNT yarn will create new applications that demand high performance. Many research groups and industries have already started experimenting with CNT in biomedical and aerospace applications. Commercialization of CNT filaments will create a new market place, jobs and improve the scope for 3D Printing. This project could provide a large return on investment in time and money by producing a new commercial filament.

Materials play a significant role in the 3D Printing process as they form the final part. The market for 3D Printing materials alone is more than half a billion dollars and is steadily increasing. There is good competition among the material manufacturers at present. New materials have always been well received in the 3D Printing industry. Introducing customized high performance materials like CNT yarn will create a new market place and could pay rich dividends in the next few years. The ability to 3D print CNT with almost any polymer blend will be a great asset for many industries. Investigating the methods proposed in this project to produce CNT filaments will be the key to commercialization. On the contrary, materials are facing challenges from the health and safety administration, particularly in the biomedical industry. For commercial use of products like sensors, sutures, implants, drug-delivery devices and bone transplants, several safety standards documents and research data needs to be produced. This makes materials like CNT-PCL composite to go through a tedious testing procedures before it can get approval. The government bodies like NIH, OSHA, FDA and similar agencies in other countries across the globe should work in parallel
to establish regulatory standards for new and upcoming materials. The biomedical industry in particular requires plenty of documentation on waste disposal, recycling, environmental impact and occupational safety standards. In addition, some materials may even require several years of testing before it can be approved for use. Hence, the industries and the government agencies should collaborate and make proactive efforts to expedite this process.

Rapid manufacturing is the direction towards which the industry is moving. End users do not see 3D Printing as a prototyping process anymore. Faster production cycle with lesser design iterations and reduced material usage will enhance the production efficiency. There is a huge demand from industries to simplify the software toolchain involved in 3D Printing. The present software toolchain complicates the process of translating the design into a 3D Printing job file. A company called 3DPrinterOS [58] is working on creating a dedicated operating system to integrate all the software tools in one place. In addition, the entire system will be hosted on the cloud platform which allows the users to remotely control print jobs. With the low-cost hardware, software developments already in place it is time for the materials to catch up in the race. Multifunctional composite materials are needed to keep up with the rapid advancements and rising demand of this revolutionary technology.

6.1 Future recommendations
The next step in this research would be work on improving certain limitations of this process, namely, yarn spinning process. A commercial industrial yarn spinning equipment should be used under controlled conditions to produce CNT yarns. This will increase the durability and toughness of the final fiber reinforcement. Secondly, the filaments need to be characterized to study the effectiveness of bonding between the fiber and the coating. Thermal Gravimetric Analysis (TGA) can be performed to study the effect of temperature on properties of different coating materials.
The cross section of the fiber may also have to be analyzed to determine the polymer infiltration into the individual fiber strands.

With respect to the printer hardware, a new 3D Printing head could be developed that is capable of printing with materials like thermoset resins and low melting point metals. Epoxies have been the widely accepted composite resin in aerospace and automotive industries. CNTs have demonstrated good performance in aircraft components, antiballistic jackets, wind turbine blades and bodysuits for soldiers. Hence it is easier to implement and test if the same materials are used in the 3D Printing process. CNT yarn can be coated with a viscous epoxy resin and allowed to partially cure to before feeding into the chamber. As the epoxy resin is tacky, the inner walls of the nozzle can be coated with a super dry material that will help the resin to slide through easily. Post processing can be done in a controlled heated chamber. This process will facilitate fabrication of Fiber reinforced laminated composite materials with current low cost 3D printers. Furthermore, CNTs can also be used with flexible thermoplastics. As 3D printing flexible polymers like TPU and TPE has been recently growing, it is important to experiment nanomaterial integration in flexible polymers. These materials can find applications in smart wearables and shock absorption products. A wide range of new 3D printing composite materials can be produced by introducing CNT yarn. 3D Printing CNT with epoxy and flexible parts will revolutionize the manufacturing process and create jobs in the biomedical aerospace and other high end applications.
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Appendix

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