Manufacturing and evaluation of the tensile properties of 3D printed human hair reinforced composites

by

Gowtham Boyala

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Abstract

This thesis proposes a novel method to 3D print human hair-based polymer composites. Human hair is a biological fiber whose microstructure is well-defined. It possesses high tensile strength, thermal insulation, a unique chemical composition, and elastic recovery, among other qualities. However, its delayed breakdown causes numerous environmental issues. Although there are many viable applications for hair, it is still regarded as biological waste. In light of this, this study aims to investigate the feasibility of producing a class of polymer composites reinforced with short human hair fibers and continuous human hair fibers using SLA 3D printing technique. The first study used short human hair fibers to 3D print polymer composites as a proof of concept. Short human hair fiber-reinforced composites in the weight percentage of 1,5,10,15, and 20 were fabricated, and a tensile test was performed to determine the ultimate tensile strength of the composites. Although the concept of 3D printing natural fibers using SLA 3D printing was successfully proved, the strength of the fabricated composite specimens was substantially low compared to the neat polymer specimen due to the presence of voids and poor interfacial adhesion between the fiber and the matrix. Hence in the second study, the focus was to develop effective surface treatment techniques to improve the interfacial adhesion between the fiber and the matrix. The second study also investigates using continuous human hair fibers instead of short human hair fibers to fabricate composites using 3D printing. Human hair fibers were modified by grafted with MA-POSS and cold air plasma treatment. The effect of the surface treatment was investigated by performing single-hair pull-out tests. Post surface modification, human hair fibers were used to 3D print tensile specimens using SLA 3D printing to determine the effect of surface treatment of the fibers. SEM and an optical microscope were used to study the surface morphology of the modified fibers. XPS was performed to confirm the grafting of

MA-POSS on the human hair fibers. Voids, fiber volume, and fiber orientation were determined by performing Micro-CT.

Preface

A version of chapter 4 of this thesis is submitted for a peer-reviewed journal publication in the Additive Manufacturing journal (Elsevier) under the title “3D Printed Human Hair – Polymer Continuous Fiber Reinforced Composites through SLA Process.”

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CHAPTER 1

Introduction

1.1 Composites:

Composite materials started becoming popular a few decades ago due to the increase in demand from both consumers and industries for high-performance materials and structures [1]. Rapid growth in manufacturing industries has necessitated material advancements in terms of strength, stiffness, density, and cost-effectiveness with increased sustainability. Composite materials have emerged as materials with improved properties that enable them to be used in a wide variety of applications [2–5]. A composite material is a system of two or more materials with different physical/chemical properties combined on a macroscopic scale [2]. Composites can be fabricated to achieve tailored mechanical/physical/chemical or electrical properties of a material, which cannot be traditionally achieved with the base materials. In general, composites consist of a reinforcement (particles, flakes, fillers, fibers, etc.) embedded in a suitable matrix (Polymers, metals, ceramics, etc.), which holds the reinforcement to form the desired shape.

Humans have developed composites for thousands of years using naturally available materials like bones, animal skins, mud, plant fibers, etc. The Mesopotamians and early Egyptians in Iraq constructed the first man-made composites in approximately 1500 B.C. by mixing straw with mud to build strong and durable buildings [1]. During 1200 AD, the Mongols designed the first composite bow by gluing wood and bone together; the bows were highly accurate and robust, enabling Genghis khan's military to attain dominance. The composite bow was a dominant military weapon until the invention of gunpowder [1]. In 1869, John Wesley Hyatt invented the

first synthetic polymer-Celluloid derived from cotton fibers; this discovery was revolutionary [6]. The creation of new materials could free the dependence on natural resources and be inexpensive. This continued to be the start of the plastics revolution. During the early 1900s, many other synthetic polymers were invented, such as vinyl, polystyrene, polyester, etc. [7]. Although these new synthetic materials provided better performance than other existing materials in some applications, they were not alone enough for structural applications. In 1935, the American company Owens-Corning fibers mass produced fiber glass; this coincided with the rapid development of new polymers in the polymer industry [8]. This marked the beginning of the Glass Fiber Reinforced Polymers -The first generation of modern composites [9]. With the continued demand for lightweight and high-strength materials from the military and space for their vehicles, other fiber reinforcements like carbon, boron, and armind fibers were developed by industries. This led to the general notion of composites – A composite is now defined as a combination of two or more heterogeneous phases or materials [10]. Scientists and engineers focused on the interface between the phases since the structure's mechanical properties depended on the interface's quality and began the development of crucial additive substances which could favor the formation of chemical bonds between the two phases [5]. The rise of automobiles and other consumer goods further led to the development of other innovative reinforcements and polymers used in composites. By the 1990s, academic and industrial researchers focused on developing hybrid materials and nanocomposites by combining organic and inorganic materials.

1.2 Types of composite materials: [11]

Composites can be broadly classified into two distinct levels:

1. Based on the matrix material, the composites are divided into three types

- Organic Matrix Composites (OMCs) – Composites consist of a matrix of organic polymers. The matrix can be either thermoset or thermoplastic resin.
- Metal Matrix Composites (MMCs) – Composites manufactured with fibers or particles embedded in a metallic matrix such as steel, aluminum, etc.
- Ceramic Matrix Composites (CMCs) – Refers to composites with ceramic reinforcement in a ceramic matrix.

Organic Matrix Composites (OMCs) can generally be further classified into Polymer Matrix Composites (PMCs) and Carbon matrix composites, commonly referred to as carbon-carbon composites.

2. Based on the type of reinforcement used, composites can be classified into
    - Particulate composites – These consists of particles in the form of flakes or in powdered form distributed or embedded in a binding matrix.
    - Fiber-reinforced composites (FRCs) – Consist of fibers embedded in a matrix material.
    - Laminar composites – They consist of reinforcement materials stacked together by the matrix.

Fiber-reinforced composites (FRCs) can be classified into discontinuous fiber composites, short fiber composites, and continuous fiber composites.

1.3 Fiber- Reinforced composites (FRCs)

FRCs are made up of high-strength, high-modulus fibers incorporated in or attached to a matrix having different interfaces (boundaries). Even though the fibers and the matrix retain their physical and chemical identities, the two components work together to provide a unique

combination of qualities that could not be obtained by each of the parts functioning alone. Fibers are usually the load-carrying members, while the surrounding matrix keeps them in the appropriate placement and orientation. It serves as a load transfer medium and protects them from environmental damage. Therefore, in a fiber-reinforced composite, the matrix provides several useful functions in addition to providing reinforcement for the fibers [12].

The strength–weight and modulus–weight ratios of these composite materials are far superior to those of metallic materials due to their low density **(Figure 1).** Composite laminates also have excellent fatigue strength and fatigue damage torerance [13]. Therefore, FRCs make an excellent alternative to traditional manufacturing materials in applications such as aerospace, space, automobiles, and sports equipment. However, traditional metals are isotropic materials, i.e., their properties are consistent across all directions, but FRCs are non-isotropic, and hence their properties vary depending on the measurement direction. For example, the tensile strength of FRCs is highest when measured along the fiber orientation and is lower when measured perpendicular to the fiber orientation. Other mechanical and thermal parameters, such as impact strength, coefficient of thermal expansion (CTE), and thermal conductivity, all show isotropic behavior in FRCs. Reinforcement that is bi- or multidirectional produces a more balanced set of characteristics. Although their mechanical properties are generally less than those of a unidirectional composite, they still offer a significant advantage over common structural metals in terms of unit weight. Due to the differences in characteristics in multiple directions, designing a fiber-reinforced composite structure is far more complicated than designing a metal structure for any given application. On the other hand, the non-isotropic characteristics of a fiber-reinforced composite material provide a unique opportunity to customize its properties to the design needs. This design flexibility can be exploited to selectively reinforce a structure in the

directions of large stresses, improve its stiffness in a preferred direction, build curved panels without the need for secondary forming, and create structures with desired coefficients of thermal expansion.

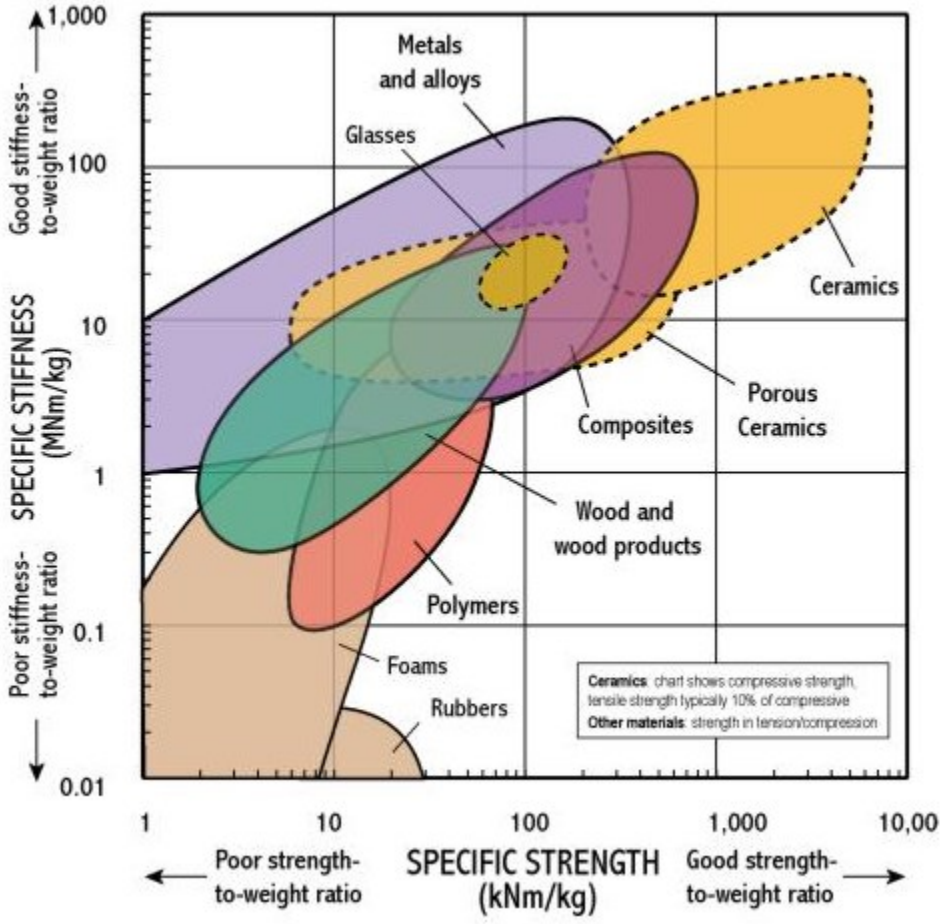


Figure 1: Composites specific weight ratio vs. specific stiffness [9]

The use of fiber-reinforced polymer as the skin layer with lightweight core materials, such as aluminum honeycomb, plastic foam, metal foam, and balsa wood, to construct a sandwich beam, plate, or shell allows for additional design flexibility not possible with metals. Recent aircraft like the Boeing 787 Dreamliner [2,14] and Airbus A350 XWB [15] use over 50% of composite laminates in their outer skin, as represented in **Figure 2** [16]. With such a sandwich structure, high rigidity can be achieved with little weight gain. Fiber-reinforced composites can be further

classified into synthetic and natural fiber composites. This dissertation mainly focuses on developing a method to manufacture and design natural fiber composites, although the process can be adapted to other fibers with some modifications.

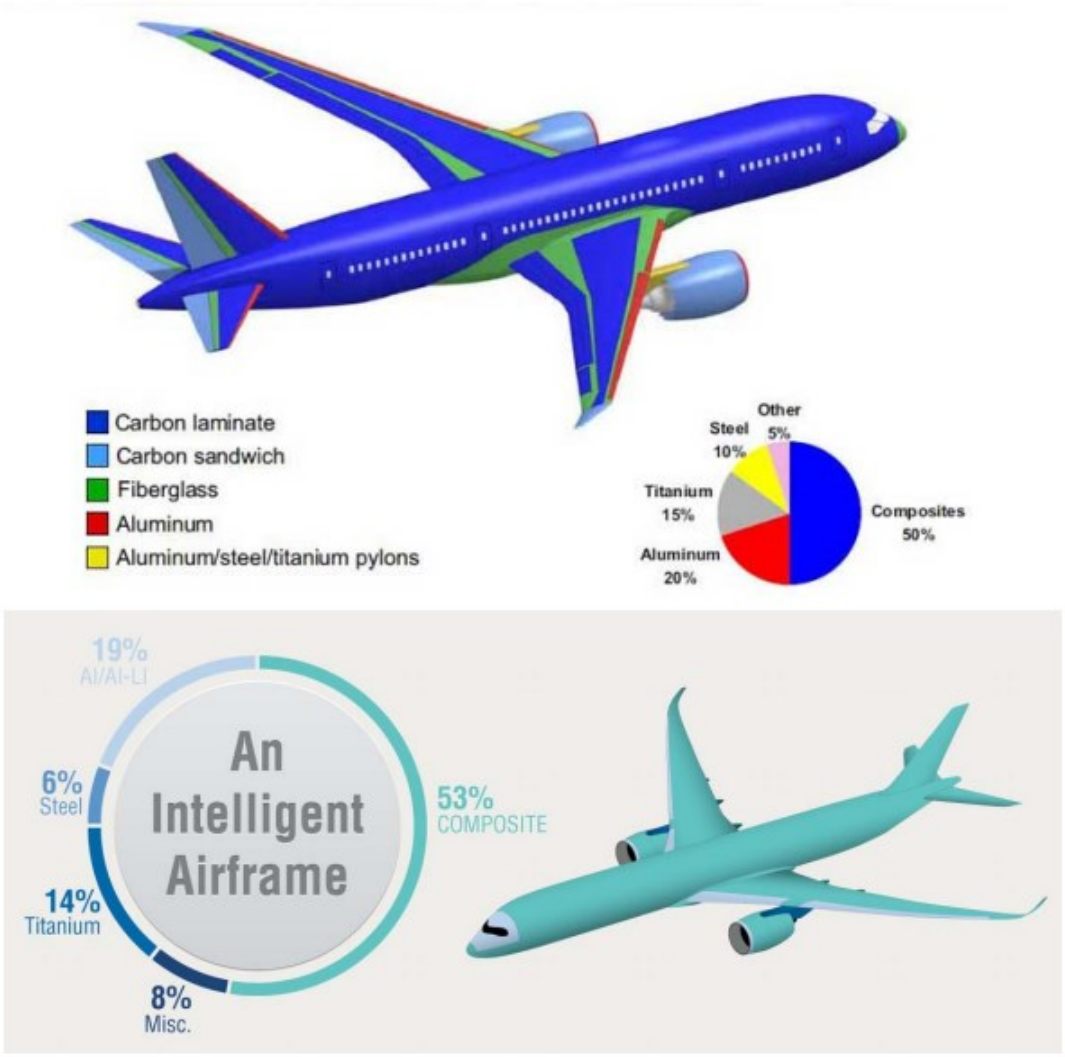


Figure 2:Materials used in the outer skin of a) Boeing 787 Dreamliner [10] b) Airbus A350 XWB [11]. Image obtained from [12]

1.4 Natural Fiber Composites:

Natural fibers are organic fibers produced or obtained from plants, animals, or minerals and are not synthetically made by humans [17]. Owing to the increased environmental awareness and need for sustainable materials, there is considerable and growing interest in natural fibers. Natural

fibers are one of the most environmentally friendly materials, with superior or comparable characteristics to synthetic fibers. Natural fiber composites can be classified into three categories: vegetable or cellulosic fibers, animal fibers, and mineral fibers. Animal fibers include fibers such as silk, wool, human hair, bird feathers, and other similar materials. They are the second most important natural fibers after plant fibers in terms of reinforcing materials in composites. It is also the most widely available natural fiber, second only to plant fibers in terms of availability [18]. Various options are available for each type of animal fiber; for example, wool can be sourced from sheep, alpaca, angora, bison, cashmere, muskox, and many other animals. Similarly, silk, hair, and feathers are harvested from various sources, including birds, insects, and humans. Natural fiber composites (NFCs) are well positioned to take advantage of the growing demand for innovative composites in manufacturing.

In 2016, the worldwide natural fiber composites market was worth USD 4.46 billion. From 2016 to 2024, it is projected to grow at a CAGR of 11.8 percent [19]. The market is driven by the growing demand for lightweight materials in the automotive industry and increased consumer environmental stewardship. Natural fiber composites help to reduce component weight, cutting total energy consumption. Furthermore, the NFC moulding technique uses less energy than the glass fiber moulding process, lowering production costs by up to 10%. On the other hand, the moisture sensitivity of these composites is expected to stifle market expansion [19].

1.5 Major natural fibers and types.

Plant-based and animal-based fibers are the two major types of natural fibers. Cellulose, hemicellulose, and lignin make up the majority of vegetable fibers, whereas proteins make up animal fibers [20]. Pure fibers must be removed and isolated from all cementing components

found in the natural plant or animal raw material before being used as reinforcement (hemicelluloses, lignin, wax, proteins, etc.).

Wood, flax, kenaf, cotton, and hemp are some of the most common raw materials. The market share based on the raw materials is shown in figure 3. In 2015, wood dominated the market, accounting for 59.3 percent of total revenue. The current trend is expected to last until 2024. Wood's advantages, such as its great strength and solidity, are expected to increase its use in the years ahead [19].

With a market share of 13.0 percent in 2015, flax was one of the most extensively utilized materials [19]. In comparison to carbon fibers, flax is CO_2 neutral, vibration dampening, and renewable. Flax's advantages, such as strong tensile strength, UV ray blocking characteristics, vibration absorbent properties, and high water retention, have made it one of the industry's most widely utilized raw materials.

Cotton is a seed fiber that is widely utilized in the textile industry around the world. Cotton's moisture absorption characteristic makes it weaker than other natural fibers. It can absorb up to 20% of its dry weight in moisture [21]. With the rise of the textile and sporting goods sectors, the market for this area is likely to expand [22].

Kenaf is increasingly being used in a variety of industries, including construction, oil, and chemical absorbents, food packaging, and automotive. The material is exceptionally long-lasting and entirely recyclable [23].

Hemp composites can be used to replace glass fiber in a variety of applications and are biodegradable. The growing demand for environmentally friendly and renewable materials in the automotive and construction industries is expected to propel the market forward.

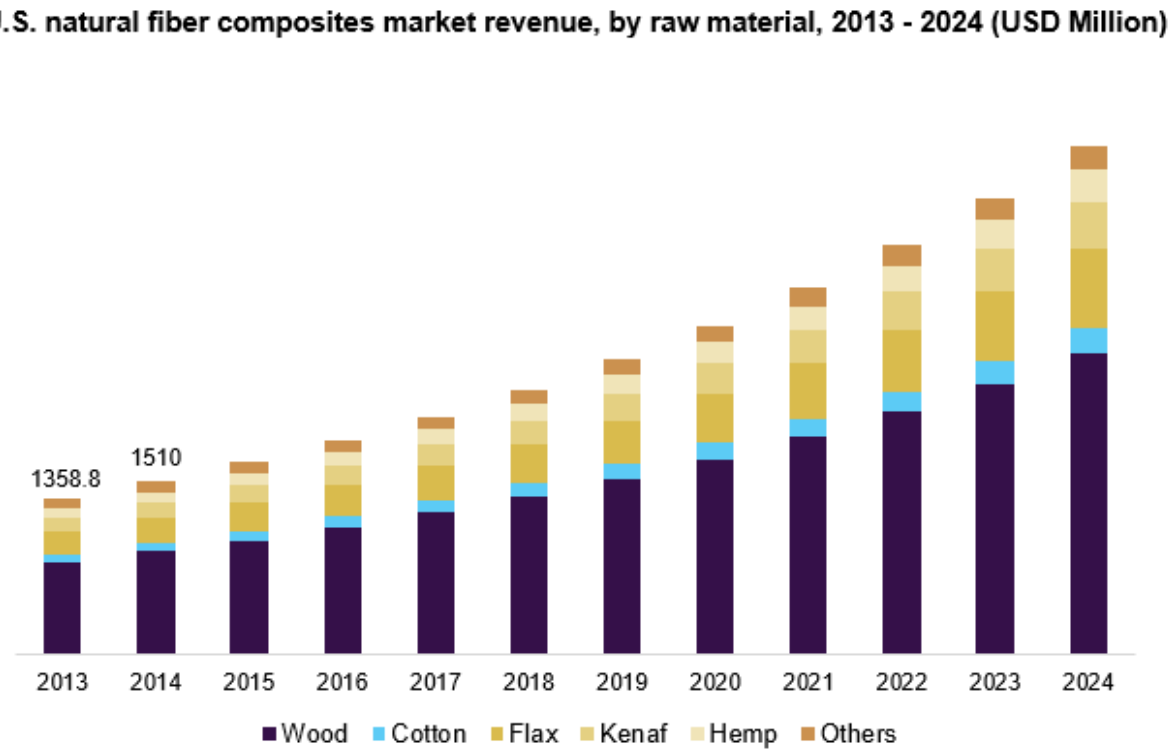


Figure 3: US natural fiber composites market size, by raw material, 2013-2014 (USD Million) Image obtained from [15].

The majority of research so far is concentrated on vegetable fibers, particularly bast fibers (flax, hemp, jute, and kenaf). This judgment is based on their better mechanical qualities and the ease with which clean fibers can be separated from the cementing ingredients in the bast. Vegetable fibers, on the other hand, have substantially more variability in their mechanical properties than synthetic fibers as a function of the plant's age, geographical and climatic growth conditions, harvesting methods, purifying technology, and so on. Furthermore, the availability of significant quantities of a given type of bast fiber depends on the location of cultivation: flax and hemp are dominant in temperate regions, whilst jute and kenaf are dominant in tropical regions [24].

Animal-based fibers have recently received great interest as prospective high-performance reinforcing fibers. Bio composites have been investigated using animal-based fibers like wool [25] and silk [26,27], commonly utilized for garment manufacturing. Surface hardness,

flexibility, and a high aspect ratio are all characteristics of wool keratin fibers, which are less hydrophilic than cellulose fibers. Feather keratin fibers have a hollow structure, which means that a given volume of fibers contains a substantial amount of air, resulting in a low density (0.9 g/cm3) and low dielectric constant (k1.7), which suggests that they could be used in electronic composites [28].

1.6 Human Hair

Human hair is a keratin-containing appendage that grows from follicles, which are large cavities or sacs. Hair follicles run from the skin's surface to the dermis. Protective, sensorial, and sexual appeal qualities are all provided by hair.

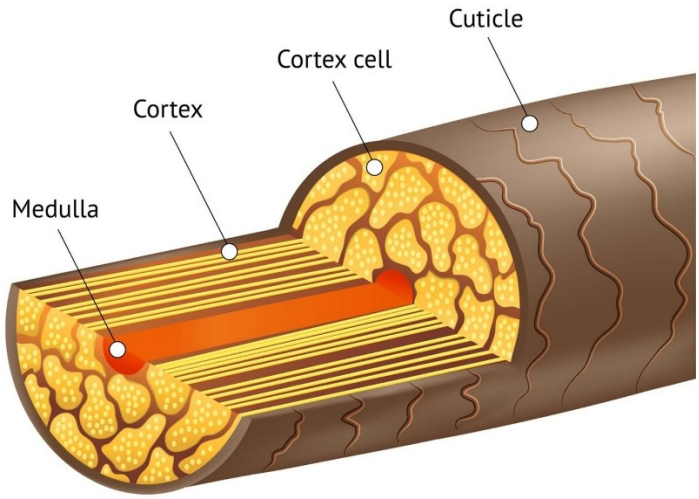


Figure 4: A sectional illustration of human hair and its parts. Image obtained from [29]

Hair is found in all mammals, and it covers a considerable portion of the body surface in humans. A fully developed hair fiber morphologically has three to four separate units or components. Hair has a thick protective coating at or near its surface, which is made up of one or more layers of flat overlapping scale-like structures called cuticles or scales, as shown in figure 4. Cuticle layers

surround the cortex; however, the cortex comprises the majority of the fiber mass. The cortex is made up of cells that are formed like spindles and run parallel to the fiber axis. Many fibrous proteins in the hair are found in cortical cells [29]. Most studies focus on hair growth, types, and hair care, but human hair is also an important biomaterial made of protein with many potential applications in composites [30].

Proteins, lipids, water, and trace elements make up the bulk of human hair. Human hair is composed of around 65 to 95 percent proteins, depending on its moisture level (up to 32 percent by weight) [29]. The remaining constituents are water, lipids (structural and free), pigment, and trace elements [31]. Trace elements are normally not free but are chemically coupled with sides of proteins or fatty acid groups of lipids that have been sorbed or bonded.

It is estimated that approximately 300,000 tons of human hair is thrown away globally every year [32] most of which will end up in landfills. Most saloons and hair dressers dispose human hair waste into landfills, although they are biodegradable, it takes about two to three years to entirely decompose [33]. Burning human hair or garbage piles that contain it, a practise that is common throughout the world, releases harmful gases like ammonia, carbonyl sulphides, hydrogen sulphides, sulphur dioxide, phenols, nitriles, pyrroles, and pyridines as well as an offensive odour [34]. The burning or dumping of large amounts of hair waste from the processing units at the banks of a river in Eluru district of Andhra Pradesh (India) caused pollution, health issues, and conflicts, but the authorities were unable to resolve the situation because they had no other option but to burn or dump the waste [35].

Human hairs have excellent mechanical properties and are highly durable. It is also resistant to environmental degradation and exhibits excellent tensile properties (Table 1). A handful of researchers have recently explored human hair as reinforcement in traditional composite

manufacturing techniques [36–41]. However, 3D printing of human hair-reinforced composites, as per our knowledge, has never been explored and is of great interest to us, given its potential to be used in many industries, including the space sector. In-situ resource utilization has recently attracted much interest in the space industry because of our desire to colonize mars and the moon. However, materials available on these extraterrestrial bodies must be extracted and processed, which is extremely difficult and expensive to achieve in a harsh environment. For Example, if colonizing mars. Human hair is one of the wastes produced by humans and could be used as a building material as a reinforcing material to build specific equipment like housing etc.

Table 1: Properties of a single human hair fiber [23].

Density, g/cm	Tensile Strength (MPa)	Young's Modulus (GPa)	Poisson's ratio
1.34	150-200	1.74 – 4.15	0.36 - 0.39

1.7 Summary:

From the above discussion, fiber-reinforced composites have drawn massive attention from the scientific and commercial community to develop next-generation composites. Due to the ease of availability and potential environmental impacts, natural fibers have received tremendous interest in developing reinforced composites. For various reasons outlined above, plant fibers have gained more popularity than animal fibers, such as human hairs. Although human hairs have excellent mechanical properties, they have not been fully explored as a reinforcement material in fiber-reinforced composites.

CHAPTER 2

Background and literature review

2.1 Natural fiber Polymeric composites (NFPC).

The number of NFPC applications is quickly expanding in a variety of technical domains. Many automotive businesses, including BMW, Audi Group, Ford, Opel, Volkswagen, Daimler Chrysler, Mercedes), Proton company (Malaysian national carmaker), and Cambridge industry, have emphasized the importance of natural fibers reinforced polymer composites in many automotive applications [42]. Natural fiber composites have been used in a variety of industries, including the building and construction sector, sports, aircraft, and others, for example, panels, window frames, decking, and bicycle frames [43]. Natural fiber composites have been known since the early 1900s, but not much attention was paid to them until the late 1980s. Boats, skis, agricultural machinery, and automobiles all use composites, which are primarily glass but also include natural reinforced composites [44–46]. Natural fiber composites aim to eliminate the need for costly glass fiber ($3.25/kg), which has a relatively high density (2.5 g/cm3) and is derived from nonrenewable sources [44,46].

Natural fibers are ones that already exist in nature and can be manufactured through a variety of mechanical and chemical methods. Nature has provided humanity with a vast number of natural fibers in a variety of colors, sizes, and shapes. These fibers can be divided into three categories based on their origin [47] :

1. Plant or vegetable fibers derived from natural cellulose/lignocellulose fibers consisting of macroscopic particles (millimeters) and obtained through specific technologies such as crushing the woody material extracted from filaments or long elements (meters) extracted

from the strong and dense leaves of tropical plants in the wild. A third method of obtaining plant fibers is to subject the vegetable matrix from which they are to be extracted to severe chemical treatments. Additionally, plant fibers can be classified as bast fibers, leaf fibers, fruit fibers, and seed-hair fibers. Oil palm, wood, rice straw, sisal, ramie, hemp, doum fruit, bagasse, pineapple leaf, cotton, flax, date palm, rice husk, wheat straw, coir, jowar, kenaf, bamboo, rapeseed waste, and jute are the most well-known plant fibers.

2. Animal fibers are natural fibers composed of specific proteins found in silk, hair, wool, and feathers, among other sources.
3. Mineral fibers (Example: Asbestos)

Although many mineral-based natural fibers are found in the asbestos group of minerals and were previously widely employed in composites, they are now avoided due to health concerns (carcinogenic when inhaled or consumed) and are banned in many countries [48]. Higher-performance plant fibers can typically achieve substantially higher strengths and stiffnesses than widely accessible animal fibers [20]. Silk is an exception which has shown significantly higher performance than jute fibers [20], as it can have extremely high strength but is also relatively costly and is less commonly available [49]

The early experiments concentrated on producing composites by replacing synthetic fibers with natural fibers in petroleum-based matrices. These composites were manufactured and characterized; their properties were significantly enhanced by surface modification techniques [42,50–55]. Because of the significant decrease of non-renewable resources used in composites and the replacement of mineral-inorganic elements with natural-organic materials, these composites have gained popularity [56]. Farmers now have a new alternative income

source thanks to the utilization of natural fibers in the composite sector. Using recycled plastics such as polyolefin successfully reduced the use of non-biodegradable polymers [20,57–60]. In addition, the biodegradable polymers were produced from renewable resources, such as polylactic acid thermoplastic polymer from maize starch and soybean-based thermoset matrix, using which composites were made entirely of renewable materials, earning them the moniker "green composites." [61–69].

As early as 1896, natural fiber composites were employed in airplane seats [70]. Due to the rise in the use of low-cost conventional plastics, the use of natural fibers has fallen dramatically and was on the verge of extinction until recently. Natural fibers have been used as reinforcements for composites in applications such as pipes, panels, and other uses in a few nations, such as India [71]. Natural fiber reinforced composites were pushed by the Indian government for constructions such as Madras House [72]. Natural fiber composites have regained popularity as a result of heated debates regarding environmentally friendly materials and the preservation of non-renewable resources [70]. Natural fiber composites account for a significant portion of the multibillion-dollar fiber-reinforced market. The global composites market size is projected to grow from USD 88.0 billion in 2021 to USD 126.3 billion by 2026, at a CAGR of 7.5% [73].

Meanwhile, the natural fiber composites market is expected to grow by 1.49 billion US dollars between 2020-2024 at a CAGR of 5 %, according to Technavio [74]. The report also concluded that the North American region led the natural fiber composites market in 2020, followed by APAC, Europe, South America, and MEA (Middle East and Africa). During the forecast period, North America is expected to register the highest incremental growth due to the increasing use of natural fiber composites in the production of particle boards, fiber boards, and composite panels in the region [74].

The expanding interest and importance of natural fibers, bio-based matrix, and biocomposites are reflected in numerous articles, including reviews, conference proceedings, and monographs [42,50–53,56,70,75–79]. Until 1999, Bledzki and Gassan [70] reviewed cellulose-based composites, and from 2000 to 2010, Omar et al. reviewed biocomposites [77]. The above-mentioned two studies provide a comprehensive analysis of biocomposites, primarily made of bast and leaf fibers, and their qualities up to 2010. The most detailed review on natural fiber composites, however, was presented by Aliakbar et al. in 2020 [80]. They have reviewed over 300 papers published since 1978 and have presented a detailed overview of the natural fibers available, their production and fiber modification techniques, etc. From all these literatures, it is clear that plant-based natural fibers are popular due to their availability and higher performance. Furthermore, plant fibers can be grown in many countries and harvested after short periods. However, animal fibers such as wool, hair, and feathers have recently gained popularity. Animal fibers contain proteins and can potentially be good candidates for reinforcement.

The form, size, crystallite content, orientation, and thickness of the cell walls determine the properties of a single fiber [81]. Natural fibers are known for their low energy consumption, low density, non-abrasive nature, low cost, renewability, biodegradability, ease of availability, and global abundance. Unlike brittle synthetic fibers, plant fibers are generally stiff and do not fracture during processing [82]. Plant fibers have unique strength and stiffness qualities comparable to glass fibers [83]. A retting procedure is used to separate bast fibers from the stem ribbon. This fiber has a moderately high tensile strength and stiffness, is affordable, performs well, and is readily available [81]. When strength, lightweight, and noise absorption are needed, such as in the automotive and construction industries, this fiber is more appropriate. Except for those grown in temperate zones with substantial use of agrochemicals (e.g., flax), most plant

fibers are classified as eco-friendly fibers since they are biodegradable and have no detrimental impact on the environment [81]. Animal fibers, on the other hand, have a low stiffness that is offset by their high elongation and elastic recovery [81]. They are also less hydrophilic than plant fibers, more robust with moderate resistance, poor heat conductors, susceptible to some alkalis, and capable of multi-axial reinforcement [81]. Table 2 summarizes some of the literature available on natural fiber composites.

Table 2: Shows some of the most used natural fibers and their mechanical properties when used in composites

Reference	Matrix	Fiber	Manufacturing method	Observations
Zampaloni et al. [84]	Polypropylene	Random-oriented flax, hemp, kenaf, sisal, coir fibers	Compression molding	40% weight-loaded flax fiber in Polypropylene shows the highest strength(75 MPa) compared to other natural fibers.
Joseph et al. [85]	Phenol formaldehyde	Banana fibers	Hand lay-up followed by compression molding	The interfacial shear stress for banana fibers is better than the glass fiber in Phenol formaldehyde. 30 mm banana fibers produced the highest tensile, flexure, and impact strength.
Biswas et al. [86]	Epoxy	Coir fibers	Hand lay-up	30mm fiber length of coir fibers produced the highest tensile, flexural, hardness, and impact strength. Pure epoxy strength was not reported. The effect of fiber loading was not studied, but the effect of fiber length was studied.
Gao and Mader [87]	Polypropylene	Jute fibers	Injection molding	The addition of 2% MAHgPP to polypropylene significantly improves fiber-matrix adhesion. The fiber length of 5mm produced the highest tensile strength.

Karmaker and Schneider [88]	Polypropylene	Jute fiber		2mm fiber length was used throughout the study while different weight loading was studied. 50% weight loading of jute with 3wt% maleic anhydride was used as coupling agents.
Shibata et al. [89]	Biodegradable resin CP-300	Random Kenaf and bagasse	Press forming	Effect of fiber lengths on the composites was studied. The flexural modulus of the natural fiber composite specimen formed from kenaf and bagasse increased as the fiber volume percentage increased, reaching 60% for kenaf and 66% for bagasse. However, the flexural modulus decreased above 60% and 66 percent due to insufficient resin.
Sharma and kumar [90]	Thermoplastic Polyurethane	Banana fibers	Compression molding	15 wt% banana fibers produced the highest tensile strength and tensile modulus.
Liu and Hughes [91]	Epoxy	Woven Flax fiber	Resin infusion	The addition of woven flax fibers improved the fracture toughness, which mostly depends on the fiber volume fraction.
Zhang et al. [92]	Phenolic resin	Flax/glass fiber hybrid	Compression molding	Tensile strength increased with the increase in the glass fiber content. The addition of the flax fibers improved the interlaminar shear strength and the interlaminar fracture toughness.

Li et al. [93]	Epoxy resin	Flax fibers coated with carbon nanotubes	Vacuum Assisted Resin Transfer Molding	Enhanced interfacial shear stress and enhanced fracture toughness.
Kafi et al. [94]	Polyester resin	Jute fabrics	Compression moulding	Fiber volume and fiber/matrix interfacial strength have a greater influence on the flexural strength of the composites. The degree of cure does not always play a major role in flexural strength.
Kinloch et al. [95]	Epoxy resin	Flax and cellulose	Resin infusion	The Natural fiber reinforced composites exhibited 75% higher interlaminar fracture energy than glass fiber reinforced composites.
Agunsoye and Aigbodion [96]	Polyethylene	Bagasse	Compression molding	The tensile strength of the composites increased with the increase in bagasse wt%. Impact and fracture toughness decreased with the increase in the bagasse wt%
Wong et al. [97]	Polyester	Bamboo	Hand lay-up	10mm bamboo fiber length and 40 vol.% produced the highest tensile strength. The composites were 25% stronger than neat polyester.
Alamri and Low [98]	Epoxy	Cellulose fiber	Compression molding	The mechanical properties increased with the increase in fiber content.

Muralidhar [99]	Epoxy	Flax-rib knitted	Hand lay-up	The elastic modulus changes with the number of preform layers and stacking sequence, although there are no consistent patterns. This pattern indicates that the effective elastic modulus of the composite is affected by the specimen's thickness and the number of preform layers.
Bledzki et al. [100]	Epoxy	Jute, Flax	Compression molding	Falx fibers exhibit better impact strength compared to jute fibers. Higher the void content, the lower the impact strength.

From the literature and as mentioned in the previous section, it is clear that most studies have concentrated on plant-based fibers among natural fibers due to their strength and ease of availability. Animal fibers, such as silk, wool, hair, and feathers, are the second most important source of natural fiber for reinforcement in composites after plant fibers. It is also the second most abundant natural fiber after plant fibers in terms of availability. Wool comes from sheep, alpaca, angora, bison, cashmere, muskox, and other animals, and there are various sources for each type of animal fiber. Silk, hair, and feathers are also gathered from various sources [69].

Animal fibers are often more expensive than plant fibers, and their availability is limited, making them expensive for most applications. These composites have the potential to be utilized in more advanced applications, such as in tissue engineering as biomaterial scaffolds and wound healing hydrogels [101]. Silk and wool are utilized in the textile industry for a variety of applications, and using them as reinforcement in composites could be costly. However, chicken feathers and human hairs are waste obtained from slaughterhouses and saloons and could be used as reinforcement. The chemical composition of these fibers, as well as their mechanical and thermal properties, are critical for their usage as reinforcement. Animal fibers, like plant fibers, have a variety of compositions and qualities that could be problematic. There are a few journal studies on each of the fibers described above as reinforcement, but no review study on animal fibers as composite reinforcement has been published yet as of the writing of this report.

Chicken feathers were used directly as a reinforcement fiber in many studies. In contrast, others processed the chicken feathers to extract keratin from them which were then used as reinforcement fibers or fillers [102]. The tensile strength, E-modulus, and flexural strength of whole chicken feather-reinforced polypropylene composites were higher than processed feather composites [102]. Cheng et al. [103] investigated the mechanical and thermal

characteristics of PLA composites reinforced with chicken feathers. Huda et al. [104] studied the acoustic properties of chicken feather reinforced composites, and the electrical properties of chicken feather reinforced epoxy composites were studied by Zhan et al. [105]. It was found that these composites can be used to produce printed circuit boards.

Hence it is clear that animal fibers can also be used in many applications. There is a significant gap in the literature in understanding the properties of several animal fibers and their reinforcing properties and applications.

2.2 Surface modification of natural fibers

The mechanical properties of the composites are primarily controlled by the interface between the fiber and the matrix. For the fabrication of natural fiber-reinforced composites, it is required to understand the interfacial bonding between the fiber and matrix. The hydrophilic nature of most of the natural fibers results in incompatibility and weak interfacial bonding with hydrophobic polymeric matrices leading to weak mechanical properties of the composites. Hence, it is required to modify these fibers using surface-modifying treatments to achieve better interfacial bonding with matrices. Surface modification techniques can be physical, chemical, or biological.

2.2.1 Physical treatment methods

Physical treatments are mainly performed for two reasons. First, to separate the fiber bundles into individual filaments to avoid any agglomeration problems in the composites due to stress concentration. Second, to change the surface properties of the fiber to increase the interfacial adhesion between the fiber and the matrix. Numerous types of physical treatments are available to modify the fibers' surface, like plasma, corona, ultrasound, and ultraviolet treatment.

Banana fibers treated with atmospheric plasma treatment have been shown to have effectively modified the surface of the fibers, which led to increased tensile strength and elastic modulus of the fibers [106]. Ebru Bozaci et al. [107] studied the effect of atmospheric plasma on jute fibers. Jute fibers were first pretreated with alkali NaOH treatment and then by plasma, leading to increased surface roughness. They also performed pull-out tests to characterize the interfacial shear stress between the fiber and the matrix. They concluded that the plasma treatment increased the interfacial shear stress due to the increased fiber roughness. The effect of plasma treatment on jute fibers and PLA composites was investigated by Gibeop et al. [108]. To study the interfacial shear stress, they performed a microdroplet study and showed that plasma-treated fibers performed better than alkali-treated fibers due to the increase in fiber roughness. They have also concluded that composites manufactured with plasma-treated fibers exhibited increased tensile, modulus, and flexural strengths. Ragoubi et al. [109] have shown that corona treatment on hemp fibers in polypropylene matrix has improved the composites' mechanical properties. The corona treatment also made the composites manufactured with treated fibers superior in their young modulus, stiffness, and elastic density energy. Also, modifying the surface with corona made it possible for the surface to produce better surface contact with the polymeric matrix. Pizzi et al. [110] manufactured nonwoven hemp, and flax fiber reinforced composites with natural resin and have found that corona treatment on the fibers has improved the modulus of elasticity and the tensile strength of the composites. Simultaneous ultrasound and alkali-treated Palm fibers reinforced with PLA have shown improved tensile strength, tensile modulus, and impact strength [111]. In a study by Gassan and Gutowski [112], ultraviolet treatment was used to treat jute fibers. This made the surface of the fibers more polarised. So, both the wettability of the fibers and the strength of the composite improved.

2.2.2 Chemical treatments methods

Natural fibers can also be treated chemically instead of physically. These methods include alkali treatment (mercerization), silane treatment, maleated coupling, acetylation, permanganate treatment, and peroxide treatment. Natural fibers are altered with these chemical processes to improve their surface and mechanical properties. These chemical change occurs when reactive parts of the natural fibers, like hydroxyl groups, react with a chemical reagent to form a covalent bond with the chemical reagent [113]. Several researchers have investigated different chemical modification techniques to improve interfacial adhesion in fiber-reinforced composites [114–117]. In a study by Annie Paul et al. [118], banana fibers were treated with alkali, benzoylation, $KMnO_4$, and triethoxy octyl silane (TEOS). Several thermophysical properties of polypropylene composites were examined to determine how these chemical treatments affected them. These chemical methods enhanced the composite's thermal conductivity and diffusivity to varying degrees. Weyenberg et al. [119] have reported that flax fiber- epoxy composites treated with alkaline treatment showed a 30% increase in tensile properties. Several researchers have modified the surface of glass fiber composites by treating them with silane [120–123].

Silane coupling agents were found to be good at modifying the interface between natural fiber and polymer matrix and making it stronger. Datta and Kopczynska [124] used acetylation, isocyanate, maleic anhydride, and potassium permanganate treatments on kenaf fibers to improve the interfacial adhesion with the polyurethane matrix. It was reported that the tensile properties were highest for potassium permanganate treated fibers. Bamboo fibers were modified with alkali, maleic anhydride, permanganate, benzoyl chloride, and benzyl chloride treatments to reinforce epoxy and polyester by Kushwaha et al. It was reported that the tensile properties increased by 25% with maleic anhydride and 54% with permanganate treatment [125]. Mishra et al. [126] treated raw sisal fiber used in sisal-polystyrene bio composites in a sodium chlorite solution. The fiber was delignified by bleaching, due to

which it showed decreased tensile strength than other chemically treated fiber composites. But the flexural strength was better for the bleached fiber composite because delignification made the fibers less stiff and more flexible.

Finally, the type of treatment to be used on a particular fiber depends on several factors, including the type of matrix, surface chemical properties of the fiber, the type of composite being manufactured, and the manufacturing setup.

2.3 Human fiber composites.

Human hair is a fibrous substance by nature. Keratin, which is made up of proteins and long chains of amino acids (polymers), is the most important component of the hair fiber. The tensile characteristics of human hair are principally determined by the cortex in the hair fiber [29]. Unlike other natural fibers, animal fibers are highly complex in nature, with qualities that change depending on various conditions. The area, age, and location of the fiber all influence the physical, chemical, and mechanical qualities of the fiber. Human hairs sourced from different ethic groups also vary in their tensile strength. I.P Seshadri and B.Bhushan studied the in-situ tensile response of Asian, African and Caucasian hair [127]. Based on ethnic origin, human hair is divided into three main, different groupings. Compared to Caucasian hair, Asian hair has a bigger diameter and a higher tensile tension. These two hair kinds behave extremely similarly when it comes to strain. African hair differs from Caucasian and Asian hair mostly by breaking earlier and requiring less stress to break [128]. M. Benzarti et al studied the mechanical properties of human hair from direct age groups and origin and have reported that the statistical difference in the stiffness of human hair of different ages were insignificant and have concluded that the stiffness in human hair is predominantly related to the origin and the relaxation time is related to the age [129]. Another study focused on the tensile properties of human hair based on diet, age and pigmentation and

have made the following conclusions. Elasticity of hair was statistically higher in children compared to adults, although tensile strength is higher in children compared to adults, the difference was statistically insignificant. The tensile strength was also higher in people who consume meat compared to those who identify as vegetarian, however the difference was insignificant [130].

Ganiron [131] looked into the effects of human hair additives on the compressive strength of asphalt cement mixtures and found that adding hair to the mixture considerably increases its capacity to endure higher loads. Choudhry and Pandey [132] investigated the mechanical properties of polypropylene matrix and human hair fiber and discovered that composites containing 3-5 wt. Percent human hair fiber has higher flexural strength, flexural modulus, and Izod impact strength than non-reinforced polymers, but composites containing 10-15 wt. Percent human hair fiber has lower flexural strength, flexural modulus, and Izod impact strength. Akarsh Verma et al. [30] looked at alpha-keratin fibers' mechanical properties and structure like wool, human hair, and other similar fibers. They found that human hair has the highest tensile strength of the group. He attributed this to the excellent properties of human hair, like its unique chemical composition, high tensile strength, thermal insulation, elastic recovery, and its unique interaction with waters and oils. Elanchezhian et al. [40] have concluded that composites made from human hair and epoxy resin showed higher tensile strength and highest breaking load when compared to Bombyx mori silk-based epoxy composites. However, silk-based composites showed better compressive, flexural, and impact strengths. V. Mittal and S. Sinha [133] have concluded that alkali treatment of human hair fibers improved the tensile strength of the composites compared to untreated human hair fiber composites. Table 3 shows studies published based on human hair composites.

Table 3:Summary of literature on human hair composites

Additives/ treatment	Manufacturing method	Observations	Reference
-	Hand-lay up	The addition of human hair fillers showed a substantial reduction in thermal conductivity of the composites	**Bishu and alok** [134]
-	Hand-lay up	Short fibers combined with other natural fibers produced better mechanical properties compared to continuous human hair fibers	**Balachander et al.** [135]
Alkali treatment	compression molding	Surface modification of fibers at 0.25 N alkali treatment improves mechanical properties (maximum tensile and flexural strength, modulus, and so on). If additional treatments (0.5 N alkali) are applied to Human hair, the characteristics of the fiber are reduced due to fiber surface fracturing.	**Prashant srivtava** [136]
Surface-Initiated atom transfer radical polymerization	-	Polystyrene brushes were grafted from natural horsehair	**Bin Mu** [137]

Table 3: Continued

Fiber	Matrix	Reference	Observations	Manufacturing method	Additives/ treatment
Short Human Hair	Epoxy	**Ravindra kumar** [138]	The addition of human hair-derived carbon fillers showed improved performance in static and dynamic mechanical tests over unfilled composites. 30 to 40 wt.% filler loading gives optimum performance.	Hand-lay up	-
Short Human Hair	Epoxy	**Ragul et al.** [139]	Three percent of human hair wt.% showed the maximum tensile strength. Over 100% increase in tensile strength compared to the non-reinforced specimen.	Compression molding	Alkali treatment
Short Human Hair	HDPE	**Sanjay Choudhry** [140]	Composites with 3 to 5 wt.% human hair loading showed higher flexural strength, flexural modulus, and impact strength than non-reinforced polymer. The tensile strength was always lower than neat polymer. The paper recommends using long fibers.	Compression molding	-
Short horsehair	Polystyrene	**Michael** [37]	The study compares the electrical breakdown strengths of several natural fiber composites with glass fiber-reinforced composites. Human hair composites performed better than other natural fiber composites at room and cryogenic temperatures and are second to glass fiber reinforced composites.	Compression molding	-

Matrix	Phenolic	HDPE	Polypropylene	Epoxy resin
Fiber	Carbon fabric as reinforcement and human hair-carbon as fillers	Human Hair	Short Human Hair	Short Human Hair

2.4 3D printed composites

Traditional polymeric composite materials manufacturing techniques mentioned below are primarily used in the fabrication of bio-composites. Machine presses, filament winding, pultrusion, compression moulding, resin transfer moulding, and sheet moulding are some of the standard techniques utilized to work with continuous bio fibers (All of those require a lot of physical labor or only work with a single or a few fiber strands, resulting in a long lead time). Extrusion and injection moulding are two methods for dealing with discontinuous bio-fibers.

3D printing of composite materials has been employed in a variety of industrial and sociocultural areas, including manufacturing, medicine, and the military, allowing 3D printing to become a successful commercial technology [141].

Three-dimensional (3D) printing technologies are now classified in many ways. This paper's classification method is based on the form of the process's beginning material:

- Powder-based (Selective Laser Sintering (SLS))
- Material extrusion
- Liquid-based

2.4.1 Powder based systems

The fact that powder-based 3D printing starts with powdered ingredients distinguishes it. Because it is difficult to establish a flat layer of powder-fiber combination, powder-based technologies are not suited for making fiber-reinforced composites [142]. Researchers have tried to homogeneously blend composite powder to improve 3D printed item resolution and smoothness [143]. Mechanical [144,145] and melt mixing [146] methods, as well as dissolution-precipitation [147,148] and surfactant-facilitated latex [149] methods, have all been tested using bio-fibers. As a result, the types of fibers employed in such systems are currently limited, and they all employ the selective laser sintering (SLS) procedure.

SLS was founded in the mid-1980s by Dr. Carl Deckard of the University of Texas at Austin. One layer of powdered material is melted together by a moving laser beam, which is directed towards locations conforming to a computer-aided design model, resulting in the formation of a solid item [150]. It is necessary to perform numerous cycles of rapid melting, cooling, and solidification to sinter fine powder material on a powder bed [151,152]using a 25-50W YAG or CO2 laser [153,154]. Heating the loose powder material just below its melting point helps to improve bonding and reduce the deformation of the finished product. Consequently, less power is required from the laser [150]. The powder remains loose in portions of the part not sintered by the laser beam, but it supports the hardened sections of the component [150]. These granules may be easily separated and removed from the finished product after completing the fabrication.

Wood powder, often known as wood flour, is one of the most commonly used loose powders in biocomposite SLS and is one of the most widely utilized in the industry. Biocomposite parts were printed using SLS by Xin et al. [155] using wood powder from aspen trees that was 80-100 microns in size, 120-180 microns hot-melt glue powder, and 100-180 microns polypropylene (PP) powder. In order to create the basic material, a 1:2.50 mixture of polypropylene and hotmelt glue was used with no combining agent [155]. The percentage of

wood powder in the sample ranged from 10 percent to 40 percent, with 10 percent increments between the two extremes of the distribution. The effect of varying the amount of wood powder in a biocomposite on its mechanical properties was investigated using 3D printing technology. The scientists discovered that increasing the amount of wood powder in the composite material decreased both tensile and flexural strengths, which they ascribe to poor interfacial bonding between the wood and the plastic material. On the other hand, the tensile and flexural moduli of the biocomposites increased gradually as the amount of wood powder in the composites increased, demonstrating the reinforcing effects of the biofiber.

2.4.2 Material extrusion systems

It is a common 3D printing technology that uses material extrusion to create biocomposites made up of fibers infused with molten polymers. Material extrusion can be used to create both discontinuous (short) and continuous (long) fibers. As of today, this is by far the most widely used additive manufacturing technique [156–158] and the most advanced technology in the biofiber-reinforced polymer 3D printing field. Traditional material extrusion technologies generate parts by depositing molten filament materials consisting of polymers such as polylactic acid (PLA) [159] and acrylonitrile butadiene styrene (ABS) [160,161]. In order to be extruded, the solid filament must be heated to a temperature of between 210 degrees Celsius and 250 degrees Celsius [162,163], which is higher than its melting point. The extrudate is cold-fused to the part surface in less than 0.1 seconds, despite the fact that the part surface is at a substantially lower temperature [150]. Separately extruded support materials [164,165] are utilized to fabricate overhang support structures and flat base supports to stabilize the part during the production process.

Biofiber-reinforced biocomposites are created by combining polymer pellets with chopped short fibers in a blender, which are then transferred to an extruder for further processing into

filaments [166]. A second extrusion procedure could be done to ensure that the fibers are dispersed uniformly throughout the product. It is also possible to use long continuous bio-fibers infused or coated with polymer paste to create pre-preg composite filaments that can be extruded straight into 3D printed parts. Both technologies are referred to as fused filament fabrication (FFF) in the literature [143]. Fiber content typically can currently reach up to 40% by weight, and composites with higher fiber content are unable to be manufactured because of issues with print head nozzle clogging. Furthermore, due to the loss of toughness, composites with increased fiber loading are more challenging to convert into continuous filaments for FFF [166]. As a result, the low fiber content of the composites produced has a negative impact on their quality. Another stumbling block for FFF is the difficulty in incorporating continuous fibers. In most studies to date, the addition of short fibers to a polymer matrix has been the only topic of discussion [166].

2.4.3 Liquid-based systems

SLA (Stereolithography) and Digital Light Processing (DLP) are both classified as liquid-based technologies since they both begin with a liquid polymer or resin as their starting point. When 3D printing at high speed, high-resolution layers are pulled out of the resin to make room for the uncured resin at the bottom of the container, which is then used to build up the next layer of the object, or they are pushed down and out of the tank with the next layer of the object being cured on top [167]. SLA was the first material addition rapid prototyping technology, launched by 3D Systems Inc. in 1988 and based on Charles Hull's research [150]. It was developed by 3D Systems Inc. and introduced to the public in 1989. Originally, SLA was a technology for fabricating solid plastic components from photosensitive liquid polymers by using a focused laser beam to solidify the layers [150]. Each layer has its own two-dimensional geometry, and the solid part shape is created by adding layers one after another. There have been few investigations into bio fiber-reinforced SLA polymer

composites, despite the fact that the low strength of the cured photosensitive resin has always been a major concern in the development of photocuring SLA polymer materials. More research and analysis are needed to advance the development of 3D printing with bio-fibers using SLA technology, which is currently in its early phases of development. It has been demonstrated by certain researchers that the mechanical properties of the components are superior to those of their plain resin counterparts. However, despite the fact that they only used advanced fibers in their research, their efforts have piqued the interest of those who are interested in combining bio-fibers with normal and/or biodegradable photosensitive resins to make bio composite parts utilising SLA technology.

The limited choice of materials available in current 3D printing procedures, as well as the poor mechanical performance of 3D printed items, are two major issues with 3D printing natural fiber-reinforced composites. Table 4 summarises some of the 3D printing research done thus far on the bio-fiber reinforced composites mentioned above, including the technique used, as well as the biofiber, matrix, and any necessary post-processing.

Table 4: Summary of 3D printing of natural fiber reinforced composites. Compiled from [126,127]

3D printing technology	Reinforcement fiber	Matrix	Post-processing	Reference
DLP	Wood pulp-derived CNC	PEGDA	UV cured	Quan et al. [168]
SLA	Micro-scale bamboo	Palm-based resin	SLA	Wu et al. [169]
SLS	Wood powder	PP	N/A	Xin et al. [155]
SLS	Alkalized wood powder	Co-PES	Wax infiltration	Guo et al. [170]
SLS	Rice husk powder	Co-PES	Wax infiltration	Zeng et al. [171]

FFF/FDM	Sugarcane bagasse	PE,PP,ABS, PLA	N/A	Montalvo and Hidalgo [172]
FFF/FDM	Microwood fibers	Co-PES	N/A	Correa et al. [173]
FFF/FDM	hemp, Harakeke	PLA	N/A	Stoof et al [174]
FFF/FDM	Wood flour	PP and PLA	N/A	Montalvo et al. [172]
FFF/FDM	Hemp fiber	Recycled PP	N/A	Milosevic et al. [175]
FFF/FDM	Continuous flax fiber	PLA	N/A	Duigou et al. [176]
FFF/FDM	Continuous Twisted Jute fiber	PLA	N/A	Matsuzaki et al. [177]

2.5 Conclusions from the literature review.

All the literature reviewed well establishes that natural fibers are an attractive option for fiber reinforcement. Although there are many papers reviewing plant fibers and their use as reinforcement, to date, there is no literature reviewing animal fibers as reinforcement in composites. Plant fibers are the most studied natural fibers as reinforcement, and just a hand full of researchers have studied animal fibers, leading to a huge gap in the literature. Plant fibers are attractive because of their availability. However, the steps involved in extracting, isolating, and processing these fibers are expensive and time-consuming, which will add to the cost of the composite produced.

On the other hand, human hairs are readily available and have excellent properties to be used as reinforcements. Most studies concentrate on traditional composite manufacturing techniques like the hand-lay-up method to manufacture natural fiber (Plant and Animal

fibers) composites. These traditional manufacturing techniques are expensive and can only be economically in large-scale production. The results outlined in all these literature also contradict each other in terms of the effect of fiber loading on the composites, the effect of fiber length on the composite strength, etc.

Recently 3D printing technology has been used to manufacture natural fiber composites. Most research in 3D printing composites is again concentrated around the fused filament deposition technique. It is limited to short fiber reinforced composites, and we have not found any literature on manufacturing human hair composites using the SLA 3D printing technique. There are many unknowns, like the critical fiber length for reinforcement, the effect of fiber loading, and fiber-matrix interfacial interaction. Finally, the following points sum up the conclusion from the literature review. Human hair can be used as a reinforcing fiber in composites due to its excellent mechanical and chemical properties. SLA 3D printing is still an emerging technology in manufacturing fiber-reinforced composites, and parts can be fabricated at higher speeds compared to other technologies with minimum pre-processing.

To address some of the gaps in the literature, this work aims at manufacturing human hair reinforced composites using SLA technique; the flowing section describes the objectives and hypothesis of this work.

2.6 Hypothesis and thesis Objectives

2.6.1 Hypothesis

A novel method to manufacture natural fiber reinforced composites using 3D printing is believed to be achievable by modifying the vat photopolymerization process. It is believed that 3D printing composites with human hairs as reinforcement will improve the tensile properties of the composites, given that there is sufficient interaction between the fiber and the matrix. Hence, it is hypothesized that one may be able to enhance the stiffness/tensile

strength of the material and reduce the cost by reinforcing the UV curable resin with human hairs; however, since human hair and the resin do not interact well and results in poor reinforcing properties, it may be required to modify the human hair fibers or the polymer to improve the strength of the composites.

2.6.2 Objectives

General and specific objectives can be extracted from answering the following research questions:

- "Can human hairs be used as reinforcements in 3D printed composites"?
- "What sort of reinforcement (short or continuous) fibers will produce better tensile properties of the composites."?
- Does human hair need any modifications, and If the fibers are modified using surface modification techniques, will the performance be improved"?

Based on these three research questions, the general objective of this work can be articulated as follows.

General Objective

This research aims to demonstrate a repeatable and accurate method to 3D print human hair-reinforced composites. Study the tensile properties and understand the failure modes in both random short fiber reinforced composites and continuous fiber reinforced composites. And finally, determine what surface modification technique should be used to improve the interaction between the fiber and the matrix to improve the overall tensile strength of the composite.

Specific objectives

The specific objectives and their organization in this thesis are outlined below.

1. Study the effect of short human hair reinforcement on the tensile properties of the composites 3D printed and determine the failure cause.
2. Study the effect of fiber modification techniques on the interfacial shear stress between the fiber and the matrix
3. 3D print continuous human hair reinforced composites with surface modified human hair fibers and characterize their tensile properties.

2.7 Thesis outline and methodology

The experimental methodology and various characterization tests to support the objectives of this work are summarized in figure 5 below.

The thesis structure and organization of chapters are discussed here. Based on the objectives outlined above, the first step was to prove that human hair-based composites can be 3D printed.

Chapter 3, presents the proof of concept for 3D printing random short fiber human hair composites. Short human hair fiber and resin mixture were created with varying fiber loading, and 3D printing parameters were optimized to 3D print composites. To determine the tensile behaviour of the composites, tensile tests were performed on all samples, and the results were compared with pure resin samples.

Chapter 4: Based on the preliminary proof of concept study, it was understood that human hair fibers and the resin used had poor interfacial adhesion. Also, short human hair fibers did not contribute to the load transfer between the fiber and the matrix resulting in inferior composites. Therefore, In chapter 3, we have used a chemical and a physical surface

modification technique to modify the surface of the fiber to improve fiber-matrix interaction. Human hairs were modified with cold plasma, and MA-POSS grafting and the effect of surface modification on the interfacial shear stresses were studied by performing single fiber pull-out tests. The fiber changes in the surface morphology and surface chemical composition were analyzed using SEM and XPS, respectively. Finally, continuous human hair reinforced composites were fabricated using SLA 3D printing with two different fiber loading, and the tensile behavior of these samples was studied and compared with pure resin samples. The void content, fiber volume fraction, and fiber orientation were analyzed using micro-CT analysis.

The final chapter provides a conclusion for the whole thesis and describes potential future opportunities to extend this work.

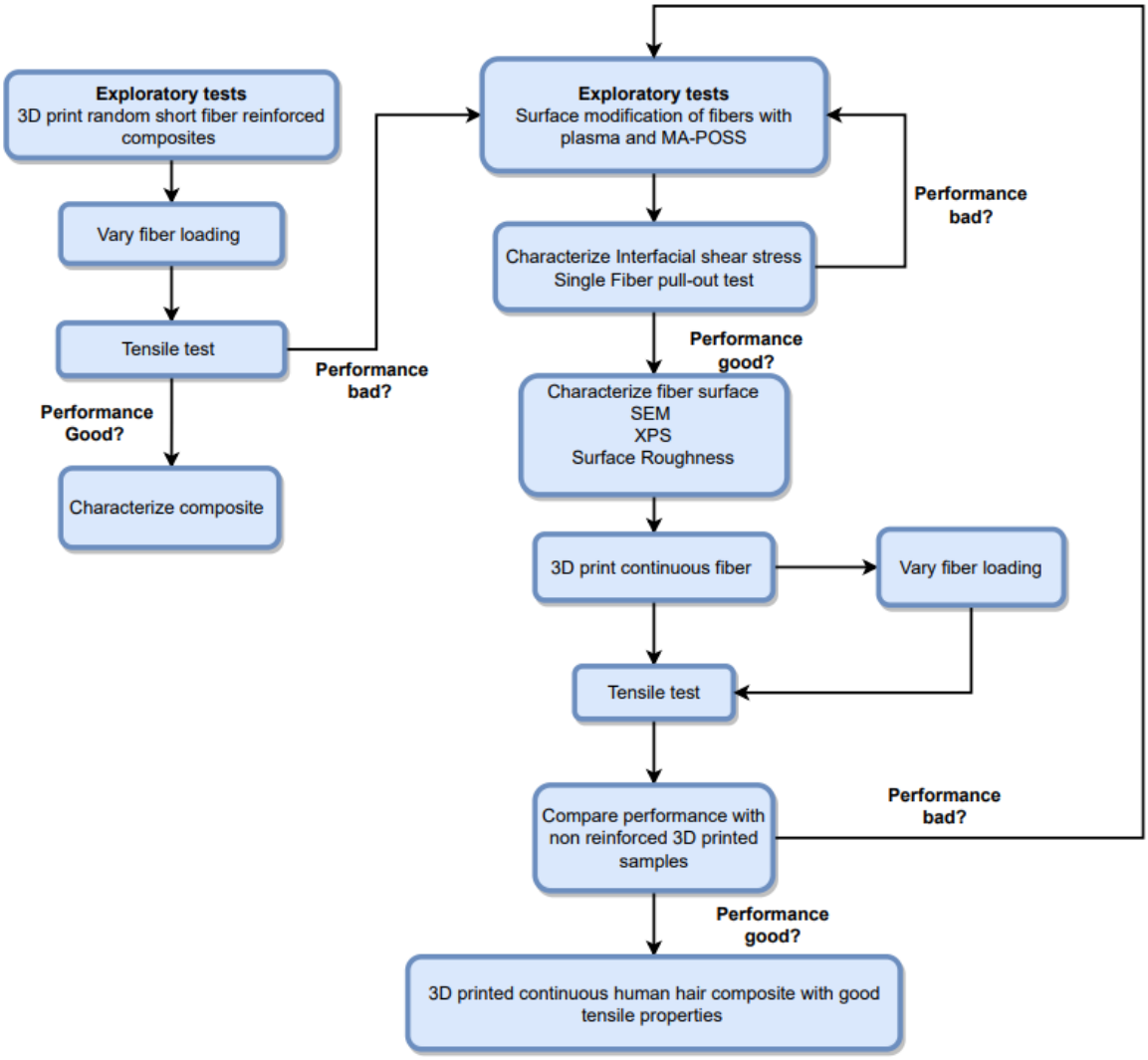


Figure 5: Flowchart describing the methodology adapted in this thesis.

CHAPTER 3

Short Human hair composite

3.1 Objective

To understand the feasibility of 3D printing composites with human hair, A preliminary study was performed to 3D print short fiber-reinforced composites. The main objective of this chapter is to present a proof of concept for 3D printing human hair composites and to study the reinforcing behavior of short random oriented human hair fibers in 3D printed composites. The effect of fiber loading on the composites was also studied to determine the optimum fiber loading in 3D printed composites.

This chapter describes the methods used for the preparation of short human hair fibers, preparation of the resin-fiber mixture and 3D printing of short human hair composite, their mechanical behavior, and failure analysis.

3.2 Methodology

Human hairs were first processed to remove any impurities and then chopped into the required size. The chopped fibers were mixed with the resin in weight percentages of 1%, 5%, 10%, 15%, and 20% to obtain resin formulation with different fiber loading. Settling time tests were conducted to determine if the resin required any additives to prevent particle settling during the printing process. The tensile samples were 3D printed after the printing parameters were optimized by the trial-and-error method. Five samples for each fiber loading were 3D printed and were post-processed under a broad-spectrum UV light. The tensile tests were conducted, and the composites were compared with pure resin 3D printed samples.

3.3 Material preparation

3.2.1 Human hair processing

Human hairs were purchased from a local wholesaler. For better adhesion between the matrix and the hair, it is necessary to prepare the surface. The hairs were washed first using hot water to remove lipids, and other impurities, then washed with ethanol to remove any organic impurities. After this process, the hairs were then washed several times with distilled water to remove any alcohol residue. Finally, they were dried in a hot oven for over 48 hours to remove the water [178]. Treated human hair was chopped into 2 -5 micrometers lengths using a cutting mill.

3.2.2 Polymer composite resin preparation

Chopped human hair fibers in weight percentages of 1, 5, 10, 15, and 20% were then mixed with a UV curable Autodesk Clear polymer (PR-48) using a mechanical stirrer for 10 min and was then degassed to remove any trapped air. Human Hair particles dispersed in the UV curable pre-polymer tend to settle down due to gravity. This sedimentation, in turn, affects the printability in terms of light penetration required for the curing process and affects the particle distribution in the printed samples. The time required to print the standard tensile samples as per ISO 527-2 (1BB) was 8 minutes. A simple settling time experiment was performed to determine the hair fibers' settling time. Prepared human hair fibers were suspended in a graduated beaker filled with the UV curable resin PR-48, and the settling times for the first fiber to settle at the bottom of the container were captured using a digital camera. Figure 6 shows an example of the experiment performed, and table 5 shows the results of the experiments.

It should be noted that as the weight percentage increased, the settling time decreased. It was determined that for printing the tensile test samples, a rheological additive for controlling the particle settling was not necessary since the settling time for all the suspensions was greater (20min) than the print time for the tensile samples, and also the Ember printer moves the

polymer vat essentially mixing the polymer after each layer. However, if printing times were longer, a suitable additive must be used to control the settling of the fiber.

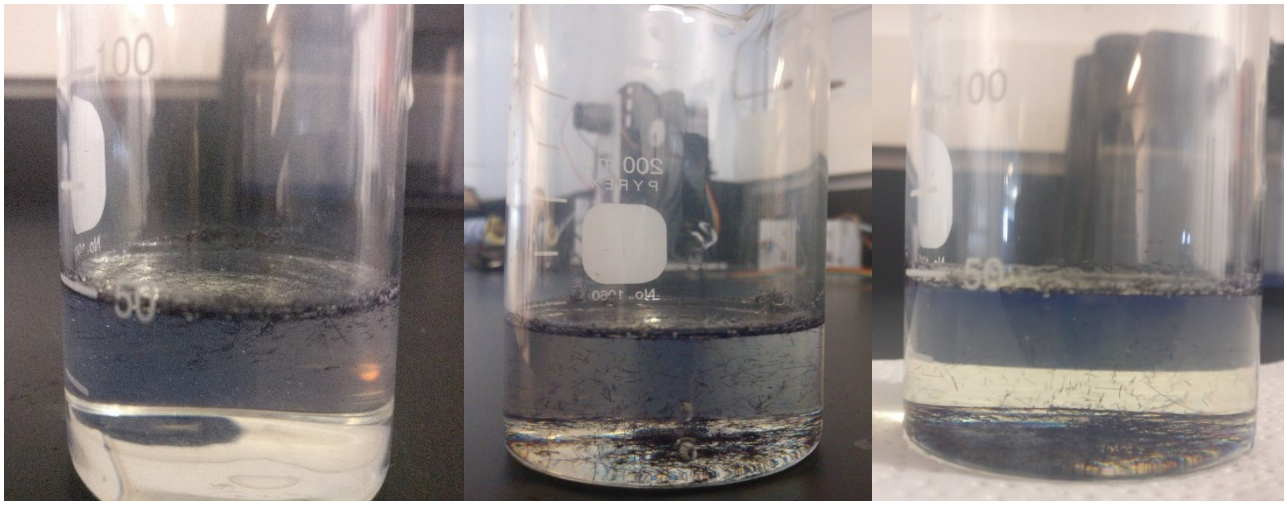


Figure 6: Human hair suspensions in PR-48 resin after a) 1 min of suspension b) 10 minutes of suspension c) 20 min of suspension.

Table 5: Settling time for different weight percentage of human hair

Human hair weight percentage	Settling time
1%	1 hour 18 min
5%	45 min
10%	35 min
15%	30 min
20%	20 min

3.4 3D printing and characterization

Printer: An Autodesk Ember 3D printer shown in figure 7 was used for this study due to the open-source nature of the product. Ember is a digital light processing printer capable of high-resolution prints with a print volume of 64mm x 40mm x 134mm. In this process, a 3D model is sliced into cross-sectional layers that are then transferred to the printer. These images are projected at a series of micro mirrors, which reflect onto a vat of photosensitive resin, curing the material one layer at a time. Ember, in particular, projects a 405-nm UV LED using a

DLP 0.45-in WXGA Digital Micro mirror Device (DMD) projector from below the resin vat. The first layer adheres to the build head, while each layer following sticks to the previous layer. With each layer, the resin tray is rotated back and forth by 60 degrees, ensuring that the printed part does not stick to the resin vat. CAD software: All CAD models were created using SOLIDWORKS® 2015 by Dassault Systems. Slicing software: Autodesk Print Studio v1.6.5 software was used to process the CAD models.

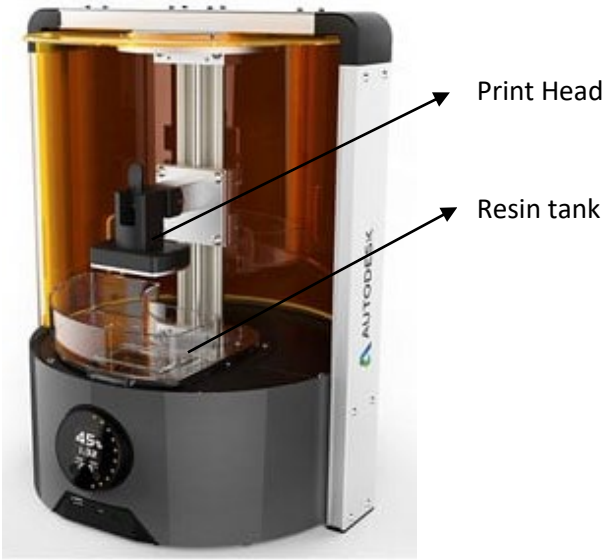


Figure 7: Autodesk Ember 3D printer.

3.3.1 Test Specimen

The tensile test specimen used for this work were printed in accordance with the ISO-527-1/2:2012 standards. Test specimen type 1BB was selected due to the restriction of the print volume of the printer. A schematic view and the dimensions of the specimens are shown in figure 8. Instron 5966 testing machine (Instron, Norwood, MA, US) with a 10kN load cell was used for performing the tensile test, and the deformation rate was set at 5mm/min. Five samples were tested for each specimen to ensure the reliability of the results.

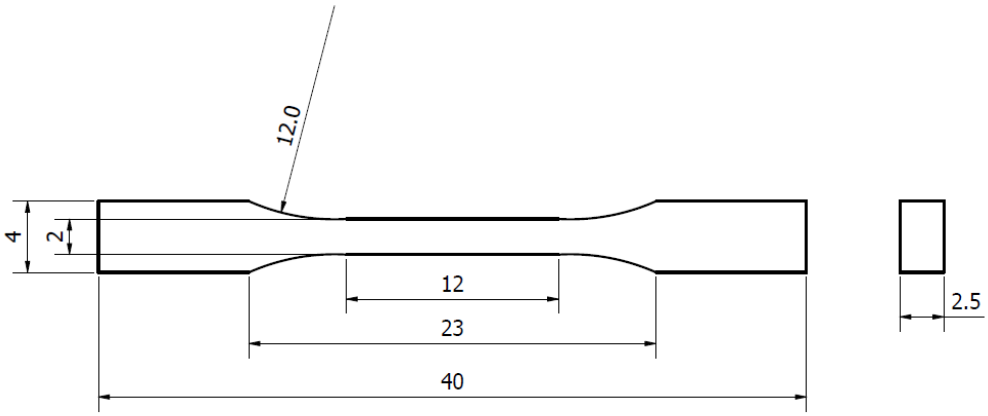


Figure 8: ISO 527 specimen type 1BB and measurements (mm)

3.3.2 Additive manufacturing RP48-human hair composites

Once the test specimen was modelled in Solidworks, the STL format of the files was imported into the Autodesk print studio software, and the print parameters, such as layer height, 1st layer exposure etc., were adjusted by trial and error to obtain a good quality print. The layer height for all the samples was fixed at 50 microns. All the final print parameter settings used for each sample are shown in table 6. All other print settings were maintained as default (Recommended settings) for PR-48 resin. Five samples for each type were printed.

Table 6: 3D printing process parameters for each sample type

Parameter	1%	5%	10%	15%	20%
Layer Thickness	50 µm	50 µm	50 µm	50 µm	50 µm
First layer exposure time (s)	9	9	10	12	13
Burin-in layer exposure time (s)	4	4	5	7	8
Model layer exposure time (s)	2.3	2.5	3.2	3.4	3.8

The printed samples were treated in a bath of 98 percent isopropyl alcohol bath for 3 min as per the manufacturer's recommendations to dissolve any uncured resin that may have remained on the part. The parts were then exposed to a broad-spectrum UV light for 1 hour for post-curing. The printed samples after UV post-processing are shown in figure 9. As seen in the figure, excess hairs not part of the samples are extending out of the sample. This was removed using an electric shaver, ensuring that clean external surfaces were obtained. Figure

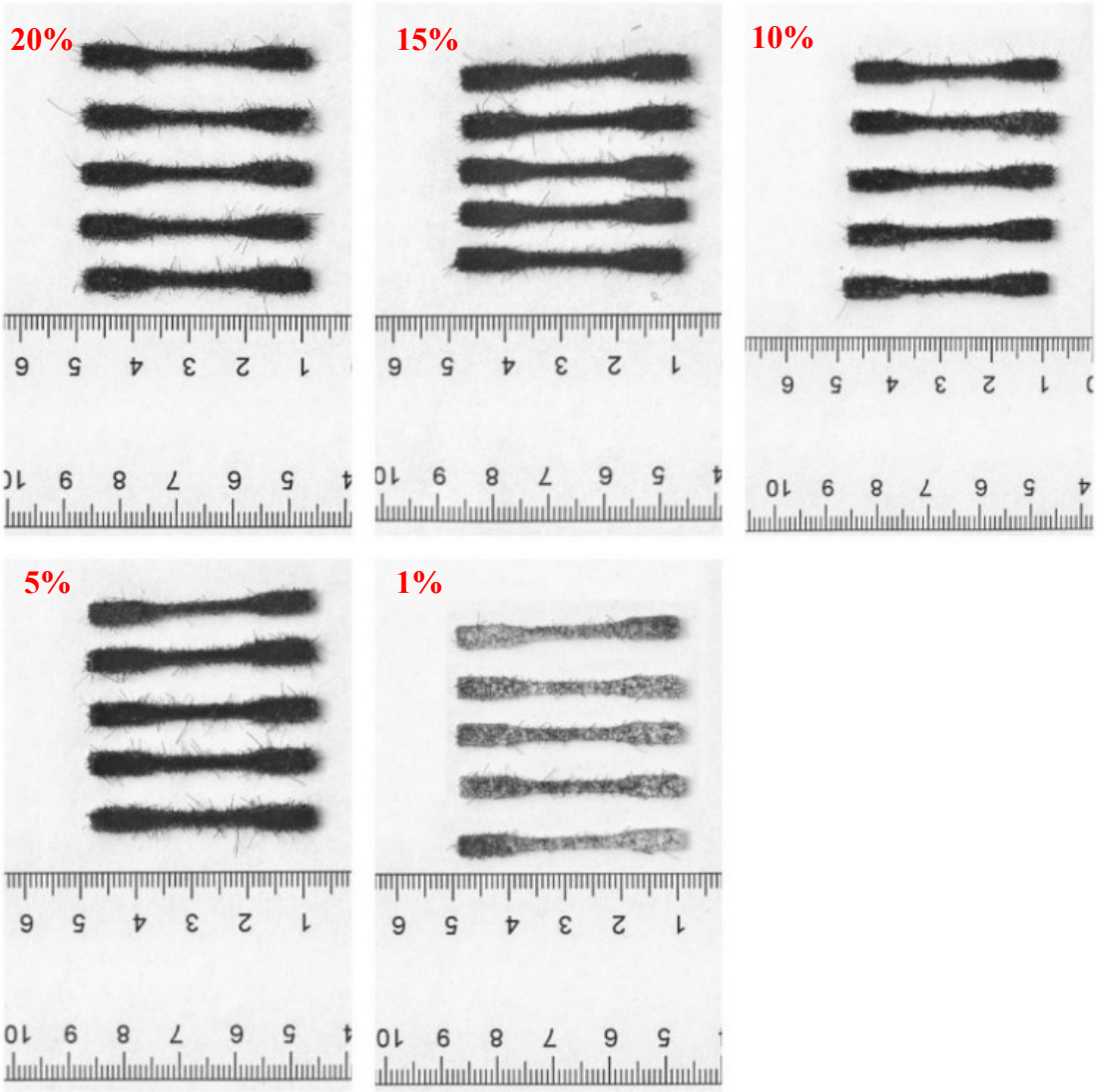


Figure 9: Printed Samples for 1%, 5%, 10%, 15% and 20% weight concentration of human hair –polymer composite resin before removing excess hair.

10 shows the samples after removing excess hair.

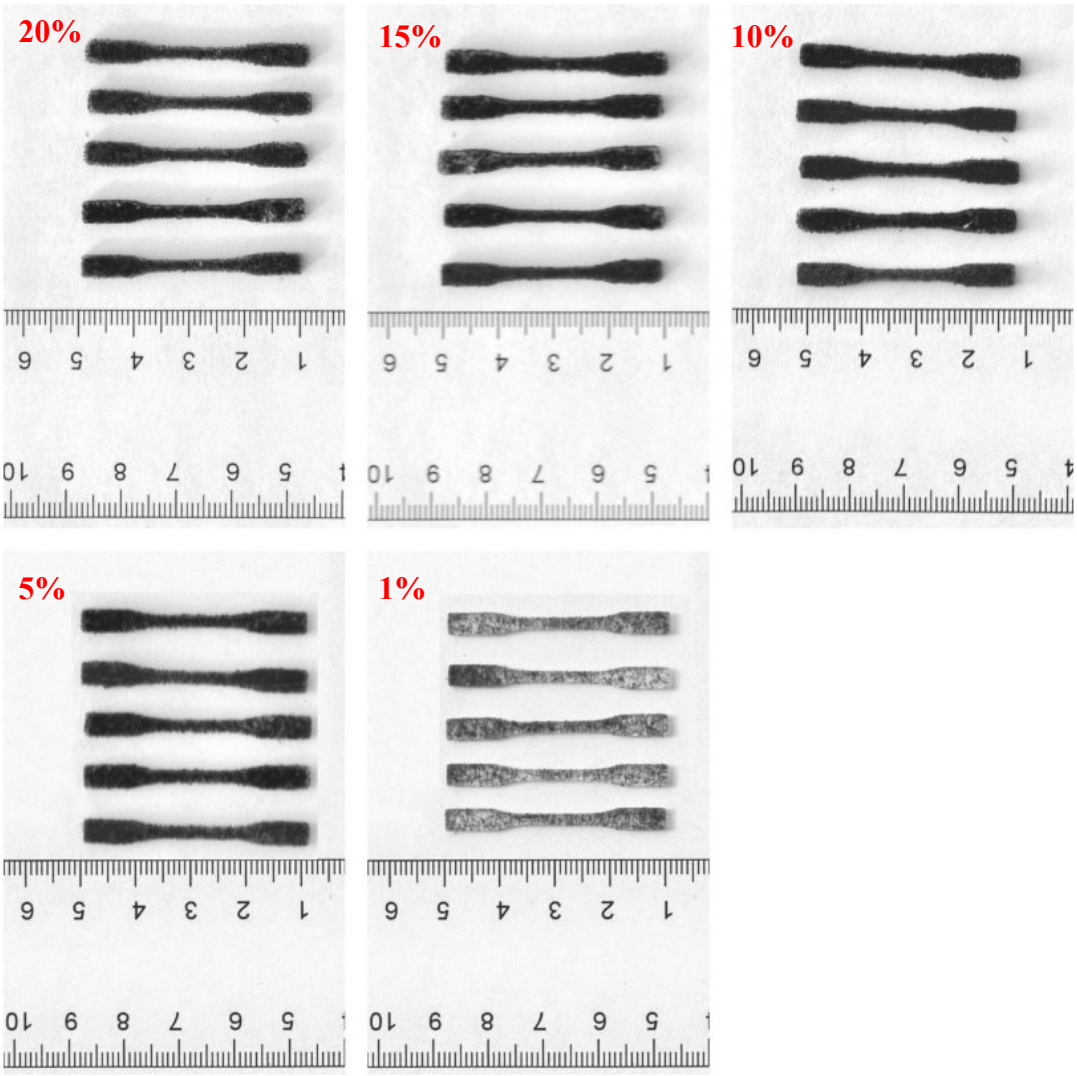


Figure 10: Printed Samples for 1%, 5%, 10%, 15% and 20% weight concentration of human hair –polymer composite resin after removing excess hair.

3.5 Tensile test results

The Tensile test results are shown in figure 11. It can be seen from the figure that the Ultimate Tensile Strength (UTS) of the composite was significantly lower than that of the sample with no reinforcement. The samples with no human hair reinforcements exhibited a mean ultimate tensile strength of 18.835 MPa with a standard deviation of 1.695 MPa. The

mean UTS of the composite sample with 1% weight of human hair was 15 MPa, and that with 5% percent, human hair was 16.12 MPa. After which, increasing the fiber loading saw a decrease in the mean UTS due to the lack of resin availability in the composite. Although the concept of 3D printing human hair fiber-reinforced composite was successfully established in this study. The decrease in the tensile strength was significant, and this could be explained due to the presence of a high number of voids and weak fiber-matrix interaction. Further characterizations and studies were not continued since this study was a proof of concept, and it was established that to study the fiber matrix interaction and to improve the tensile strength of the composite surface, modification of fibers was required.

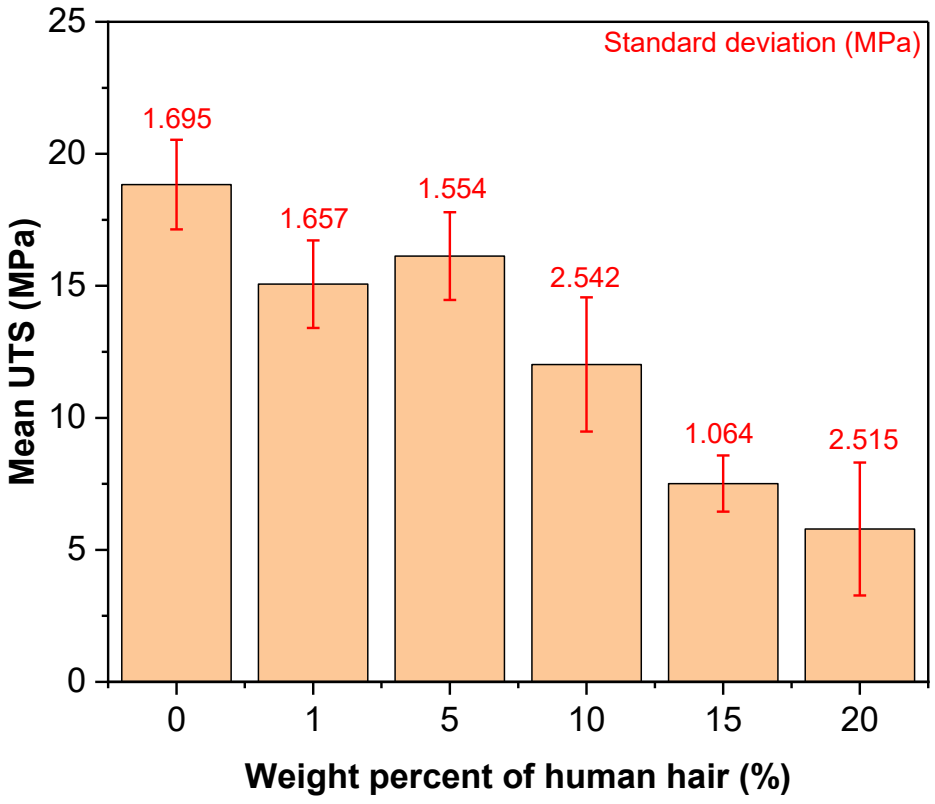


Figure 11: Ultimate tensile strength of 3D printed random short fiber reinforced composites

3.6 Conclusion

From this study, it was understood that 3D printing natural fiber composites using SLA 3D printing method were relatively easy and cost-effective compared to traditional composite

manufacturing techniques. However, the composites fabricated performed inferior compared to samples with no reinforcements. From the tensile test coupons, it was identified that the samples had a significant number of large voids as can be seen from figure 12. It was also noticed that the fibers embedded in the samples could be easily pulled out of the specimen due to poor interfacial adhesion between the resin and the matrix. Further, from this study, we also concluded that a critical fiber length exists below which the fibers would not contribute to the load transfer mechanism in the composite. To continue optimizing the fabrication process of random short fiber reinforced composites, it was essential to first determine the critical fiber length for human hair fibers. This posed two significant challenges. Firstly, it was required to perform single fiber fragmentation tests to determine the critical fiber length, which is very challenging on elastic fibers like human hairs. Secondly, we noticed that it was challenging to chop the human hair fibers into smaller fragments to manufacture short fibers, and it would be very difficult and time-consuming to identify a process to chop these fibers into precisely the required length. Finally, we also believe that the tensile coupons printed as per the ISO 527 – 1BB were too small to perform further studies on the critical fiber length because the samples were only 2 mm wide and 2.5 mm thick at the gage length, which means that the fibers had to be smaller than this size.

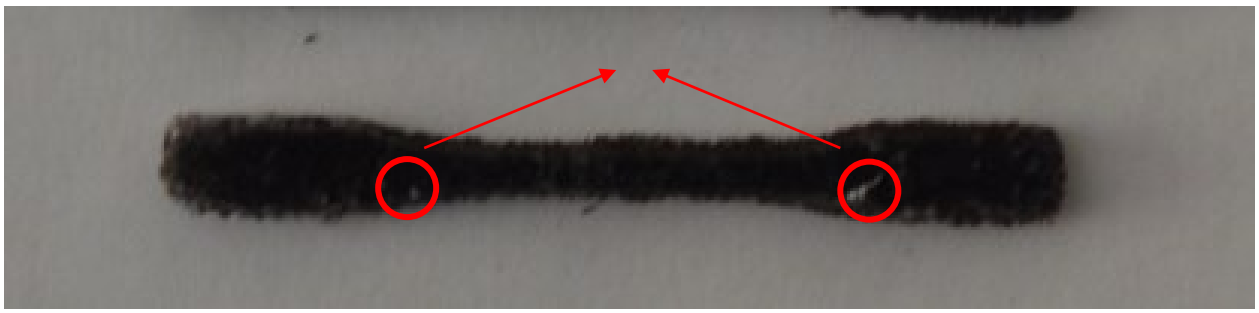


Figure 12: Example of voids in the 3D printed random short fiber reinforced human hair composite.

CHAPTER 4

Continuous Human Hair Reinforced Composite

4.1 Objective

Based on the observations and conclusions made from the previous study, It was required to modify the fibers to improve the performance of the 3D printed human hair composites. It was also concluded from the previous chapter that short human hair fiber reinforced composites were inferior compared to pure resin samples and that there were significant challenges to optimize/improve them. Hence it was decided to work with continuous human hair reinforced composites.

The main objective of this chapter is to discuss the process of 3D printing continuous human hair-reinforced composite with surface-modified human hair fibers. Surface modifications on the human hair fiber to improve fiber-matrix interfacial adhesion using cold plasma treatment and MA-POSS grafting are also discussed in detail in this chapter and to quantify the interfacial shear stress using single fiber pull-out tests. The 3D printed composites were subjected to tensile tests and then were compared with samples with no reinforcements. Fiber morphology was also analyzed in this chapter using SEM, XPS, and surface roughness to determine the effect of surface modification on the fiber-matrix interaction.

4.2 Introduction

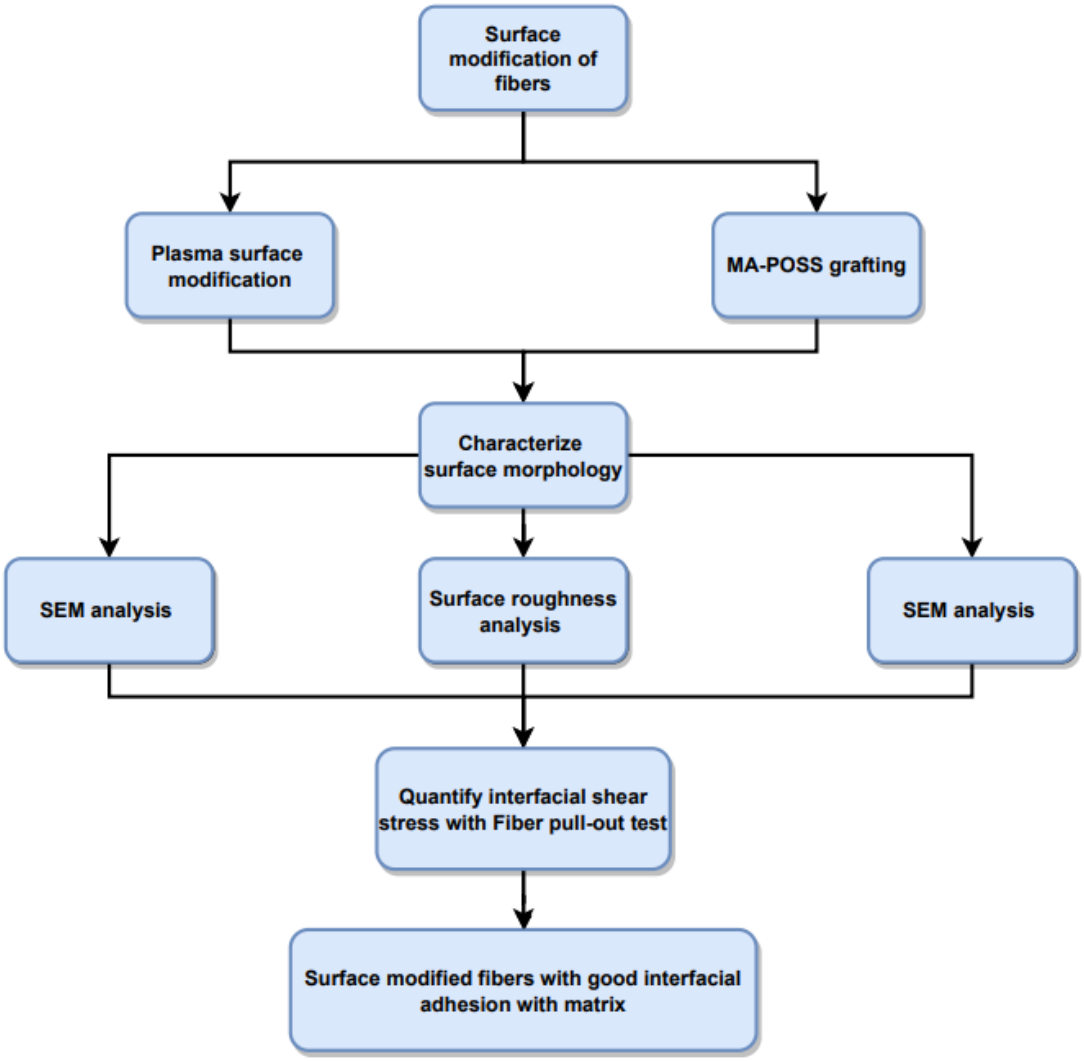
Many authors indeed investigated surface treatments (both physical and chemical) to improve fiber-matrix adhesion to improve the mechanical properties of the composites [111,179–184]. Alkali treatment of fibers has been shown to improve the strength of human hair/HDPE polymer composites [133,178]. J. Morales showed that plasma treatment of cellulose fibers improved the interfacial adhesion with polystyrene, and micro bond tests were performed to quantify the average interfacial shear strength. The results showed that two minutes of continuous glow discharge plasma treatment improved interfacial strength [185]. Plasma treatment introduces polar groups on the fiber surface and increases fiber roughness, which helps in improving interfacial adhesion [185].

Cordeiro investigated the effects of various plasma treatments on the fiber-matrix interaction and showed that low-pressure plasma coupled with sulfur hexafluoride (SF6) had been shown to improve the interaction between softwood fibers and polypropylene matrix [186]. Other types of plasma treatment, like air and oxygen, have been shown to improve the surface roughness of coir fibers. They have been shown to have improved the tensile strength of the composites by up to 375% and the elastic modulus of composites by 2022% when compared to composites with untreated fibers [186]. Jute fibers subjected to low-temperature oxygen plasma have shown an improvement in both tensile and flexural strength of the jute/HDPE composites [187]. Monofunctional (methacrylolsobutyl) and multifunctional (methacryl) polyhedral oligomeric silsesquioxane (POSS) grafted on carbon fibers have shown to have improved interfacial adhesion with unsaturated polyester resin [188]. Keratin extracted from chicken feathers grafted with polyhedral oligomeric silsesquioxanes (POSS) nanocages have been shown to have improved the mechanical properties of keratin/styrene and 2-(acryloyloxy)ethyl stearate composites [189].

In this study, for the first time, we report the use of SLA 3D printing to manufacture continuous human hair polymer composite laminates. To deal with the problem of poor interfacial adhesion between the fiber and the matrix, two different types of surface treatments were investigated, Air plasma treatment and MA-POSS grafting. The interfacial shear stresses for untreated, plasma-treated, and chemically treated fibers and matrix were quantified using a simple fiber pull-out test. Besides, tensile coupons were 3D printed by SLA 3D printing, and the mechanical behavior of the 3D printed human hair composites with different treatments is evaluated through tensile tests. In addition, the effect of different fiber loading on the composite strength is evaluated.

4.3 Methodology

The experimental methodology and the characterizations used in this chapter are summarized in figure 13. First the human hair fibers were processed to remove any impurities and then were surface modified using cold plasma and MA-POSS grafting. Two different plasma exposure times were used to identify the optimum exposure time. The surface modified fibers were then characterized using SEM and surface roughness. XPS analysis was used to study the surface chemical composition of MA-POSS grafted fibers. Custom-made single fiber pull-out test coupons were fabricated to quantify the interfacial shear stress, and fiber pull-out tests were performed. Once the fibers were modified and characterized, continuous human hair fiber reinforced composite tensile test coupons were fabricated using SLA 3D printing with three different fibers (Virgin, Plasma modified, and MA-POSS grafted). The effect of fiber loading was also analyzed using two different fiber loading. The printed composite coupons were subjected to micro-CT analysis to determine the void percentage, fiber volume fraction, and fiber orientation in the printed coupons. Finally, tensile tests were performed on all the types of samples and were compared with samples with no reinforcement.


Surface modification of fibers
Plasma surface modification
MA-POSS grafting
Characterize surface morphology
SEM analysis
Surface roughness analysis
SEM analysis
Quantify interfacial shear stress with Fiber pull-out test
Surface modified fibers with good interfacial adhesion with matrix

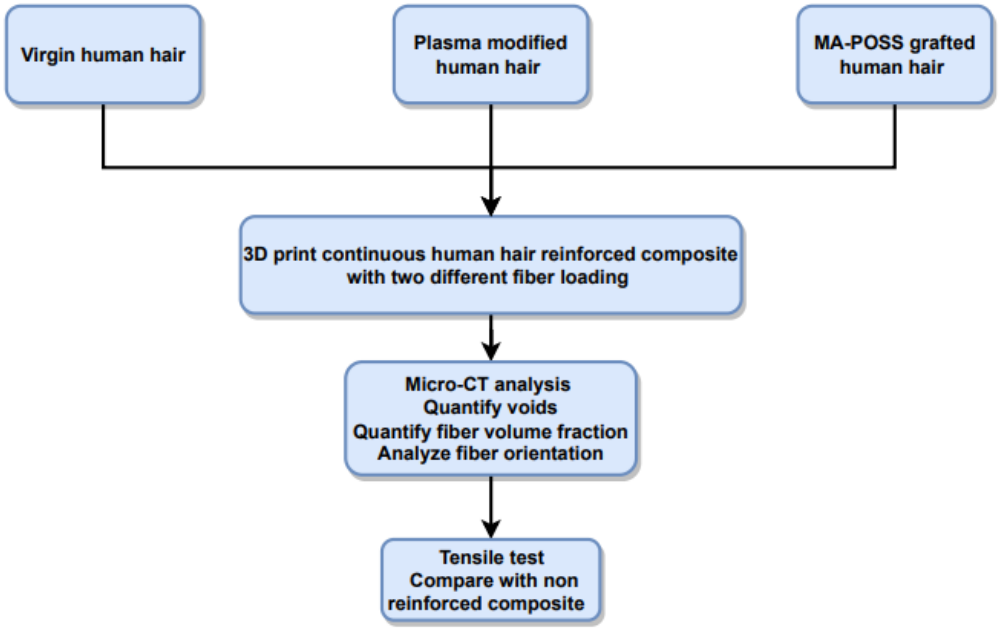


Figure 13: Summary of the experimental methodology adapted in this chapter

4.4 Material preparation

4.2.1 Materials

Human hair was bought from a local wholesale store and washed twice with distilled water before being dried for 24 hours under atmospheric circumstances. To ensure that all moisture was eliminated, the fibers were then heated for 2 hours in a hot air oven set to 40C. Fisher Scientific supplied 99 % hydrochloric acid, 99 % potassium persulfate, and 99 % sodium thiosulphate, while Hybrid Plastics supplied Methacryl POSS (MA0735). Unless otherwise noted, all chemicals were used as received. The Autodesk Standard Clear Prototyping resin (PR-48) was sourced from CPS polymers, a division of the Sartomer Arkema company headquartered in Boulder, Colorado, USA.

4.2.2 Plasma Surface modification

A room temperature (Cold plasma) atmospheric pressure Dielectric barrier discharge plasma system (PG 100-3D, Advanced Plasma Solutions, Malvern, PA) was used. The plasma pulse

is created by applying an alternating current and pulsed, high voltage of 0 to 30 kV with 0-2mA of output current. The frequency was set at 3.5 kHz between the electrodes with a duty cycle of 70%. Approximately 5 grams of fibers of length of approximately 300 mm were placed in the sample holder, and the distance between the electrode and the surface of the fibers was maintained at 2mm. Two different exposure times (15s and 25s) were chosen to understand the effect of plasma on the surface of the fiber. Once the fibers were exposed to plasma, the sample container was sealed airtight and was then immediately dipped in the photopolymer used in the 3D printing (PR-48), which adheres to the surface of fibers due to the presence of free radicles and reactive sites.

4.2.3 Surface Modification of Human hair with MA-POSS (Methacryl silsesquioxanes)

First, a mixture consisting of 100 mL of deionized water with 5 mL of 1 M HCl solution (to maintain pH ~ 5−6) in a three-neck round bottom flask is prepared. 5g of washed and dried human hair fibers were added to the mixture, and the mixture was stirred and purged with nitrogen gas for 30 min. Potassium persulfate (27mg) and sodium thiosulfate (15 mg), which act as initiators and reducing agents, respectively, were added to the mixture. 1g of Methacryl POSS (MA-POSS) was then added to the reaction mixture under inert conditions. The reaction mixture was stirred for 24 h at 80 °C. After this, the flask was opened and exposed to air, and placed under cold water to quench the reaction. Figure 14 shows the schematic of the grafting. The reaction mixture was filtered, and the fibers were thoroughly washed with distilled water to remove salts. In addition, hexane was used to remove unreacted MA-POSS. The modified fibers were dried in an oven for 24 h at a temperature of 80 °C and then were characterized.

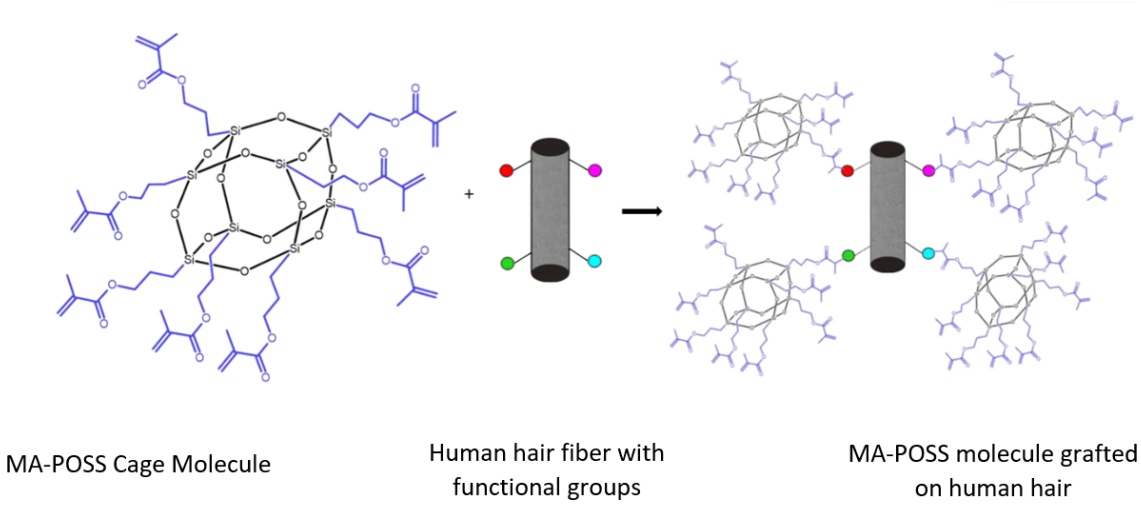


Figure 14: Schematic of MA-POSS grafting on Human hair

4.2.4 Single fiber pull test/Adhesion evaluation

Single fiber pull-out tests were performed to evaluate the interfacial shear strengths and the effect of plasma treatment and MA-POSS on the interfacial shear strengths. Figure 15a shows the test setup of the pull-out tests, which were performed on an Instron 5966 testing machine (Instron, Norwood, MA, US) with a 5N load cell. Figure 15b and 15c show the test coupons and the fiber grips mounted on the Instron test machine. To prepare a pull-out test coupon, a 3D printed mould was created using the same PR48 resin. The mould cavity was 25mm in length and 15 mm in width, and 2.5 mm in depth, as shown in figure 15d. The distance between each fiber was maintained at 5mm, and fibers were embedded in the mould at a depth of 1mm from the bottom surface of the mould cavity. The mould was also provided with a grip section to enable easy griping in the tensile testing machine. The single fiber pull-out test coupons were prepared as shown in figure 15e with four individual fibers embedded in the mould, and the mould cavity was filled with PR 48 resin after placing single hair fibers in the cavities and was cured under UV light with 405 nm wavelength. During the tensile tests, each hair fiber was pulled out of the matrix individually using a fiber grip on the loading size and a regular wedge grip on the bottom to secure the matrix rigidly. The

embedded length of the fiber was constant at 15mm for all the specimens. The free end of each fiber was attached to a teflon tape to allow for each mounting on the grips and will further prevent any slippage of the fiber during testing. All the tests were performed with a deformation rate of 0.005mm/s. Due to the high variations intrinsic to the hair fiber itself, a total of 10 single fiber pull-out tests were performed for each type of specimen (Untreated, Plasma treated, and MA-POSS grafted) to ensure reliability and repeatability of the tests. The load vs. displacement curves for all the single fiber pull-out tests were recorded.

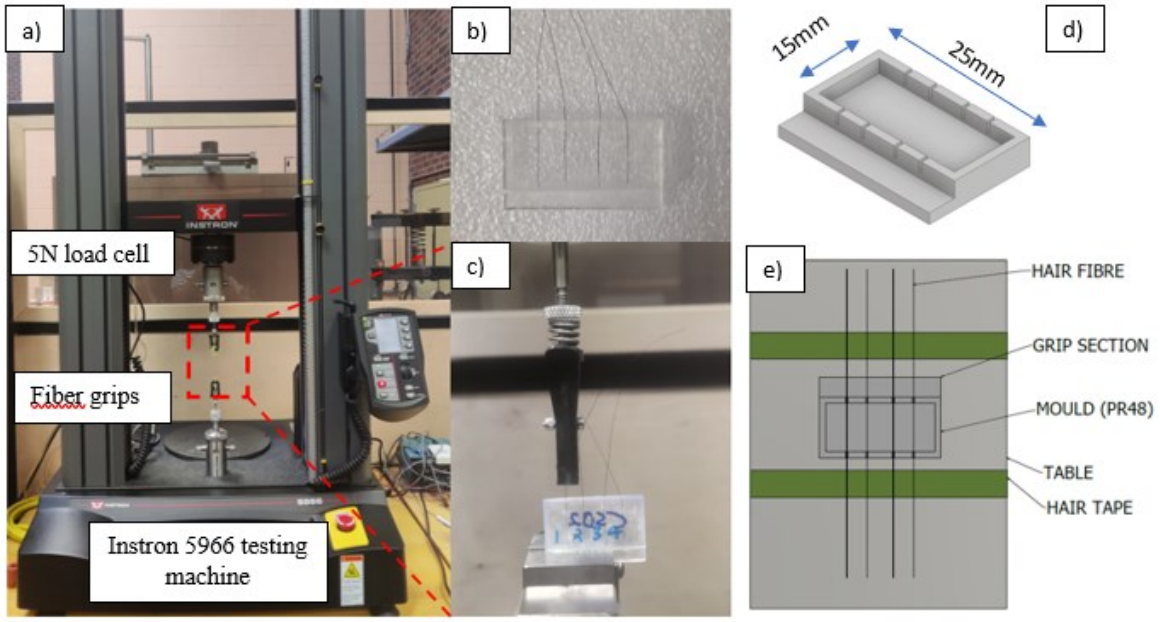


Figure 15:a) Single fiber pull-out test setup b) Single fiber pull-out test specimen prepared c) Put-out specimen mounted between the grips d) Mould used in the process of fabricating pull-out test coupons, e) Schematic of the process of fabricating pull-out test coupon.

4.2.5 3D printing human hair fibers with PR 48.

From the single fiber pull-out test, it was decided that 15s plasma treated fibers have similar behavior to MA-POSS grafter fibers. Therefore, only 25s plasma treated fibers, MA-POSS modified fibers, and virgin hair fibers were used to 3D print composite tensile coupons. An Elgoo Mars 2 Pro LCD 3D printer (ELGOO Inc, China) was used for the 3D printing of

composite hairs. The printer has a light source of 405 nm. Figure 16a shows the schematic of the 3D printing process developed for the fabrication of the composite laminates. The printer has a build volume of 130 x 80 x 160 mm. First, to calculate the exposure times for PR 48 resin for 100 micros layer height, a single layer was printed with different exposure times, and the layer was measured with a gauge. The Exposure time required for 100 microns layer height was determined to be 20 seconds with bottom layer exposure time set at 30s to ensure good layer adhesion with the build plate. Pre-cut length of the fibers of length 300mm was arranged in the shape of a single layer fiber mat and was dipped in the resin to make sure the fibers were sufficiently wetted. The following order was used to 3D print laminates. 1) Print layers of clear resin. 2) Pause the print when it is time to add a fiber layer 3) When the build platform raises, place the fiber layer on the build head and rigidly place clamps to hold fibers in place and change exposure time to 30s. 4) Resume printing and once the fiber layer is printed, change the exposure time back to 20s. 5) Remove the clamps and pause the print, cut excess hair from the edges and resume printing polymer layers. Repeat steps 2,3 and 4 for as many layers of fibers that need to be added. The exposure time was increased to 10s while printing the fiber layer to ensure any loss in the intensity due to the presence of fibers. Two types of composite laminates, one with a single layer and the other with two layers of fibers, were printed for all the different hair types. Since the tensile coupons had a thickness of 4 mm and consisted of a total of 40 layers, for single-layer laminates, the fibers were placed at layer number 20, and for double-layer laminates, the fibers were placed at layer numbers 10 and 30. Once 3D printing was complete, the tensile coupons were removed and washed twice for 5 minutes with Isopropyl alcohol and were then post-cured under UV light of 405nm wavelength for 10 minutes on each side.

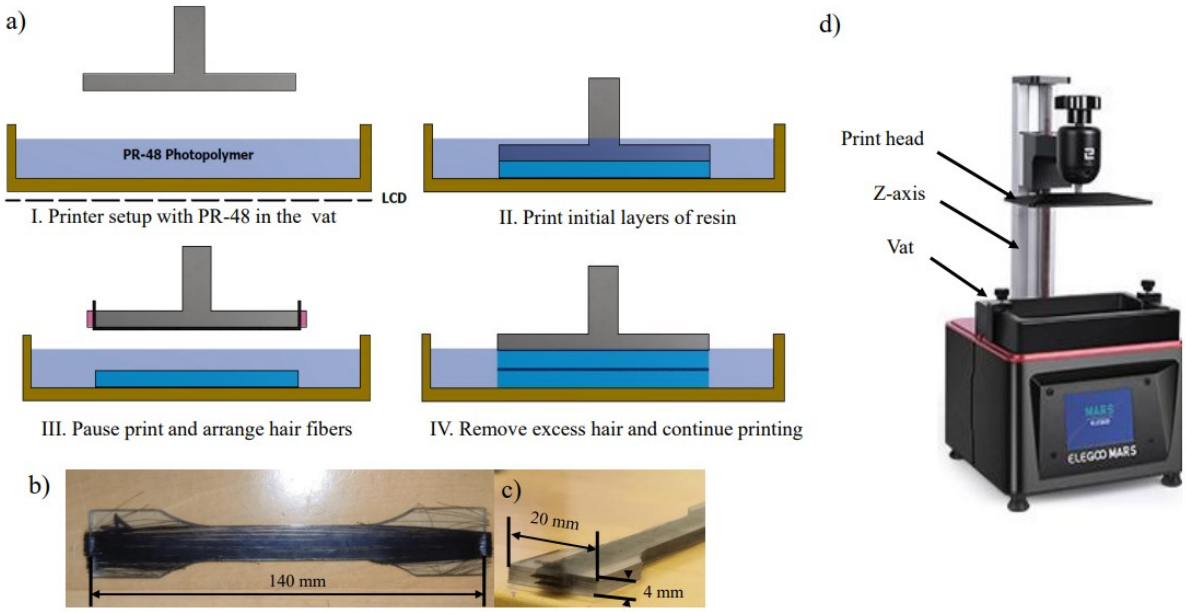


Figure 16:a) 3D printing set up and schematic b) Top view of the 3D printed composite laminate c) Iso view of the laminates printed with two layers of human hair fibers d) Elgoo Mars 2 Pro 3D printer

4.2.6 Tensile tests and Characterisations

The tensile tests were performed as per the ASTM D638-14 [190] with a modified type IV size specimen. The type IV specimen must be modified due to the limitations of the build volume of the 3D printer machine. The modified dimensions of the specimen are shown in Figures 16b and 16c. The width of the gauge length was maintained at 10 mm. Five tensile coupons were printed for each type. Therefore, a total of 30 samples were printed. The tensile tests were conducted on an Instron 5966 testing machine (Instron, Norwood, MA, US) equipped with a 10 kN load cell. The displacement rate was set at 5 mm/min as directed by the standards. For each tensile coupon, the thickness and the width were measured at three separate locations along the gauge length, and the average width and thickness were used in all the calculations.

The virgin human hair fibers and the modified fibers were characterized using a Zeiss EVO M10 SEM imaging system, using the accelerating voltage of 10 kV and the working distance of 7.5 mm. Prior to imaging, the fibers were coated with gold on a Denton sputtering machine with a deposition rate of 8nm/min for two minutes at 10 mA current. Once the samples were coated with gold, fibers were cut into small lengths and were mounted on a sample holder with carbon conductive tape.

The chemical composition of virgin human hairs and MA-POSS grafted human hair surface was studied by XPS (X-ray Photoelectron Spectroscopy). The XPS measurements were conducted on PHI Versa Probe III equipped with Al Kα (1,486.6 eV) monochromatic source. The analysis spot was 400 × 700 μm. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks.

To quantify the surface roughness of the fibers, the surface roughness of the fibers was measured using a three-dimensional Zygo optical profilometer with a 50x objective lens, a resolution of 0.11 microns, and a field of view of 0.07 x 0.05 mm. The fibers were rigidly mounted on the table with scotch tape. Measurements were taken at three separate locations for each hair fiber.

Micro-CT was performed on a Zeiss Xradia versa 620 X-Ray microscope (XRM) with a field view of 10 mm x 10 mm and a resolution of approximately 10 microns to quantify the voids and the fiber volume fraction in the samples. Dragonfly software (developed by object research systems) was used for the post-processing of XRM data. The OrientationJ plugin available on the ImageJ was used to study fiber orientation. Fiber orientation for each sample was obtained, and the mean fiber orientation was calculated for the samples with multiple layers of hair fibers.

4.5 Results and discussion

4.3.1 Interfacial shear strength

Many techniques, such as fragmentation tests, micro bond tests, and fiber pull-out tests, have been used to characterize the fiber-matrix interaction in polymer composites [191]. Amongst these, the single fiber pull-out test developed by Shiriajeva and Andreevskaya [192] has been used in this study due to its simple sample preparation and testing. Single fiber Pull-out tests were performed by embedding a single fiber in a matrix and performing a tensile test by fixing the matrix in the grips and pulling the single fiber out of the matrix, as shown in figure 15c. Figure 17 shows typical stress vs. displacement plot obtained during the fiber pull-out test, which generally consists of three zones - a linear elastic zone up to a critical force F_d after which crack initiation occurs and the fiber begins to pull out of the matrix by crack propagation, hence the decrease in the slope up to a maximum debonding forced F_{max} at which point all the fiber embedded in the matrix is completely debonded. The force recorded at this point is the friction forces between the fiber and the matrix. The quality of the interface can be determined using the interfacial strength (IFSS), which can be calculated from the maximum debonding load, $F_{max,}$ and fiber geometry. The apparent interfacial shear stress can be determined using the Kelly-Tyson equation, suggested by Greszczuk (Equation 1) [193].

$$\tau_{app} = \frac{F_{debond}}{\pi D_{fiber} L_{emb}} \qquad \text{(Equation 1)}$$

Where τ_{app} (MPa) is the apparent interfacial shear strength, F_{debond}(N) is the force required to debond the fiber from the matrix, D_{fiber} (mm) is the fiber diameter, and L_{emb} (mm) is the length of fiber embedded in the matrix.

The fiber diameter was obtained using a Leica INM-100 optical microscope, five different readings were taken along the length of the fiber, and the average fiber diameter was used in

the IFSS calculations. The apparent IFSS for all the plasma-treated, MA-POSS coated, and virgin human hair is shown in figure 18. The mean IFSS for virgin human hair samples was 0.0702 MPa, and the mean IFSS for 25s plasma-treated human hair samples was 0.230 MPa. From the single fiber pull-out test, it was observed that the IFSS for 25s Air plasma-treated sample significantly increased compared to the virgin human hair. The MA-POSS treatment was also effective in increasing the interfacial shear stress, which was comparable to 15s of air plasma treatment (the mean IFSS of MA-POSS treated and 15s of air plasma treated samples were 0.126 MPa and 0.146 MPa, respectively). The increase in the IFSS of plasma-treated samples can be attributed to the improvement in the surface roughness, which agrees well with the results presented by Yao and Chai [194,195]. In the case of the MA-POSS grafted fibers, the increase in the IFSS can be attributed to better fiber-matrix interaction due to the MA-POSS coating.

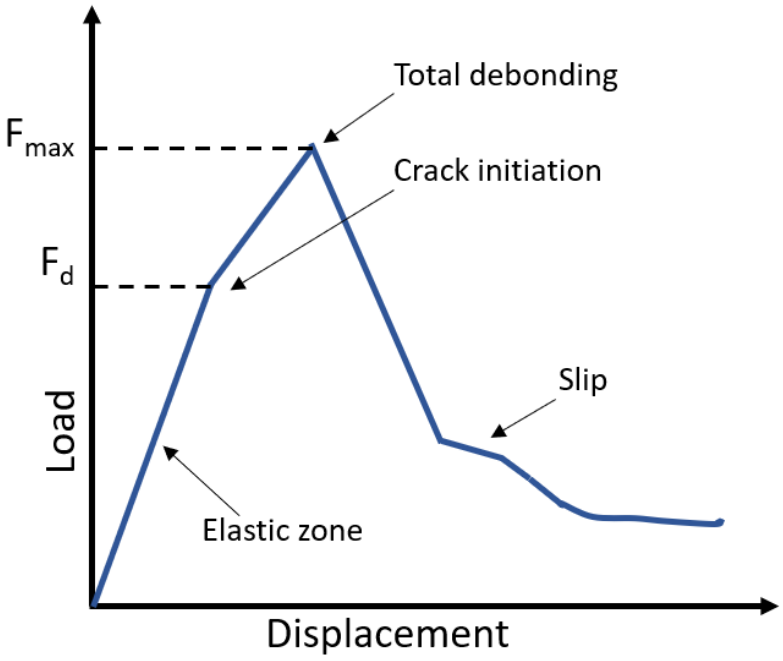


Figure 17:Typical load vs Displacement curve obtained during a single fiber pull out test

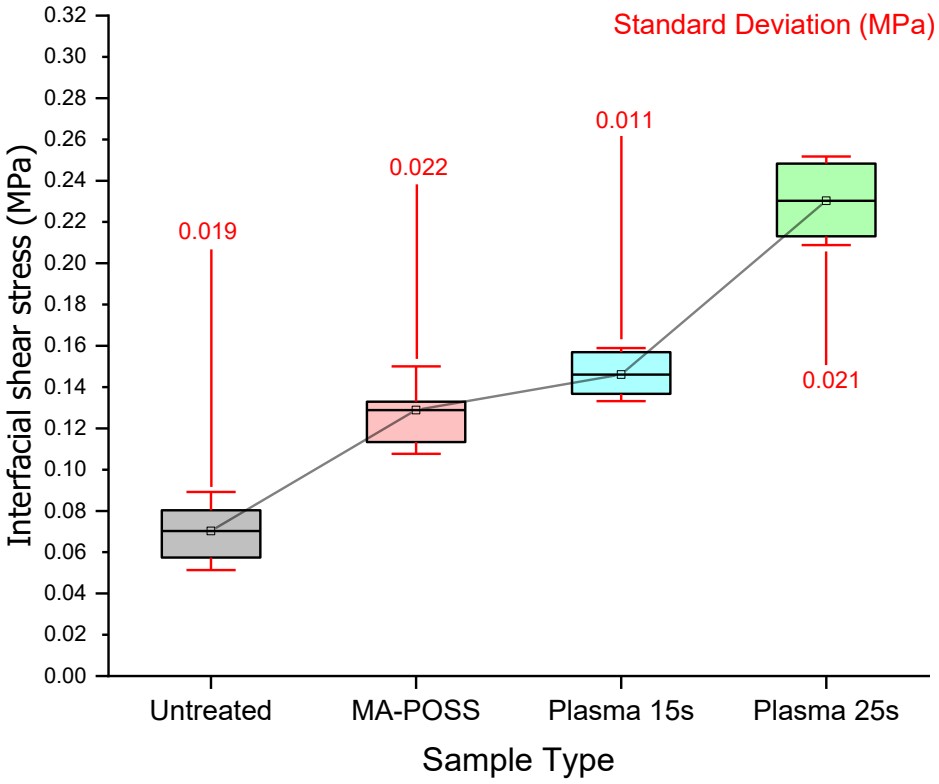


Figure 18: Plot of IFSS for virgin, plasma treatment and POSS treated sample.

4.3.2 Surface Chemical composition of human hair

The surface chemical composition and functional groups of MA-POSS grafted human hair samples and virgin human hair samples were analyzed using X-ray photon spectrometry (XPS), The peaks observed in the XPS spectrum at 103.3, 154, 284.8 402, and 532 eV correspond to Si 2p, Si 2s, C 1s, N 1s, and O 1s, respectively. Figure 19a shows the XPS survey spectra for both hair types. It can be noted from the plot that the virgin human hair sample is composed of oxygen, nitrogen, and carbon, while the MA-POSS grafted fibers have two additional peaks corresponding to Si 2s and Si 2p due to the presence of silicon from the addition of MA-POSS. This confirms the successful grafting of the MA-POSS on the human hair surface.

To analyze the functional groups on the surface of the fibers, a high-resolution C 1s scan was performed on the two hair samples, and figure 19b shows the high-resolution C 1s scan spectra. The neat fibers consist of only one peak with binding energy 284.9, which

corresponds to C-C/C-H functionalities. However, the MA-POSS grafted fibers show two additional peaks with binding energies 286 eV and 288.5 eV, which corresponds to C-O-C and O-C=O functionalities, which again confirms the grafting of MA-POSS on the surface of the fibers.

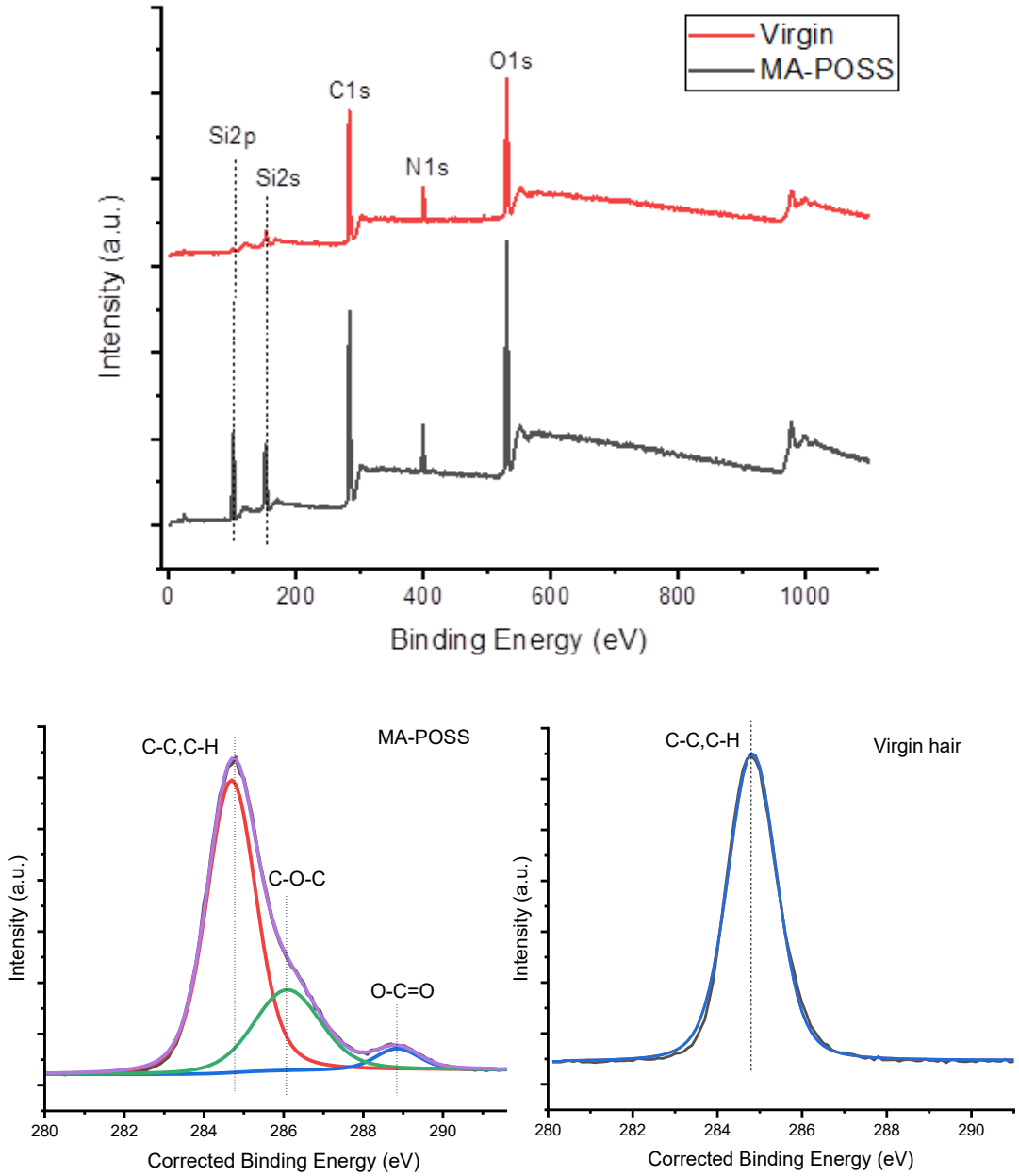


Figure 19: a) XPS survey spectra b) high-resolution C 1s spectra for MA-POSS treated fibers

4.3.3 Morphology of Human hair

Figure 20 (a,b,c,d) shows the SEM images of the virgin, MA-POSS treated, 15s, and 25s plasma-treated human hair fibers, respectively. It is also clearly visible from the SEM images the difference in the surface morphology of the fibers. Virgin human hair fibers show a film of lipids/oils, dirt, and other impurities on the surface of the human hair (as seen in Figure 20(a)). The process of air plasma treatment clears all the impurities without damaging the physical structure of the human hair (as shown in Figures 20(c) and 20(d)). The SEM images for plasma-treated fibers appear to be clean and exhibit improved fiber roughness compared to the surface morphology of other samples. The SEM images also confirm the MA-POSS nanoparticles were grafted on the human hair (as shown in Figure 20(b)). However, the surface morphology of the fibers appears to have changed, and the outermost layer of the hair, generally called the cuticles, is no longer visible. This may be due to the series of chemical reactions the fibers have undergone during the process of MA-POSS grafting on the human hair fibers. The fibers also were curly after the chemical treatment.

Figure 21 shows the mean Ra values for Virgin, MA-POSS treated, 15s Plasma, and 25s Plasma treated fibers. Roughness measurements were taken at three separate locations for a single hair fiber, and three different fibers for each type of hair were characterized to account for any uncertainties and challenges encountered in measuring the roughness of a curved surface using an optical imaging technique. The plasma-treated fibers showed improved surface roughness with a mean Ra value of 0.275μm and 0.484μm for 15s and 25s air plasma-treated fibers, respectively. The average Ra values for the virgin and MA-POSS treated fibers were similar at 0.13 microns. The RMS (Root Mean Square) value for surface roughness of the virgin fibers was 0.140 microns which agrees with the RMS values reported by H. You

and L.Yu [196] using atomic force microscopy. Hence the increase in the fiber roughness may have resulted in increased IFSS between the plasma-treated fibers and matrix.

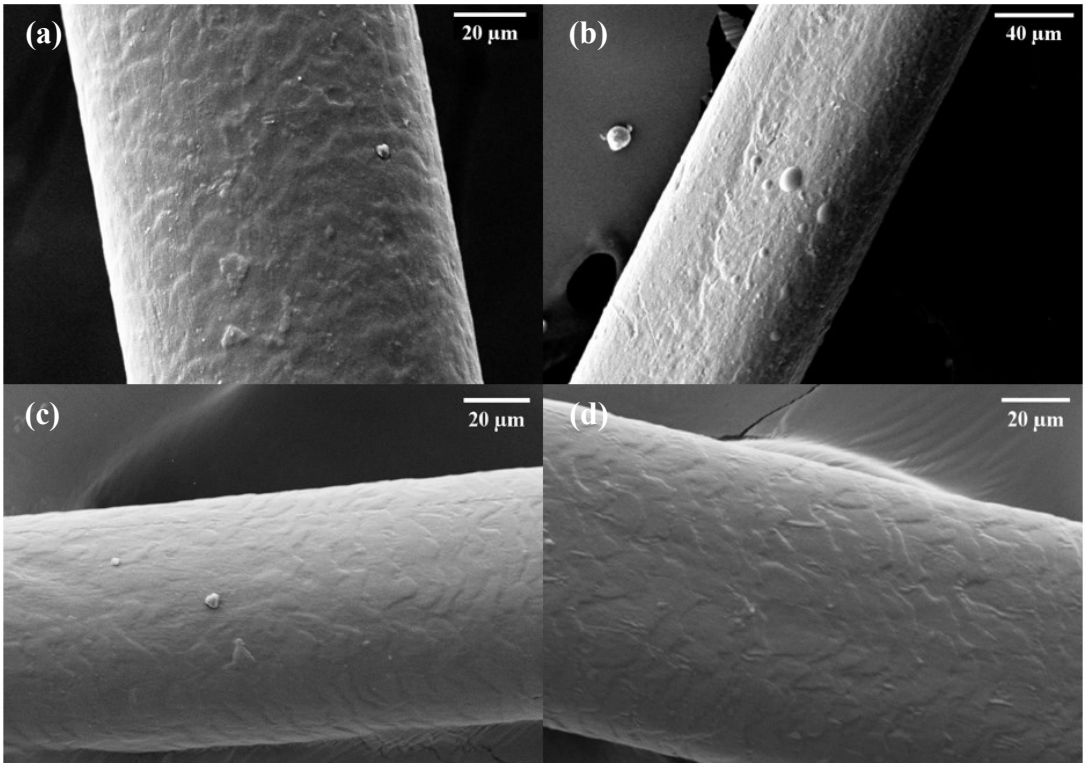


Figure 20: Morphology of human hair a) Neat fibers, b) POSS grafted fibers, c) 15s Air plasma treated fibers, d) 25s Air plasma treated fibers

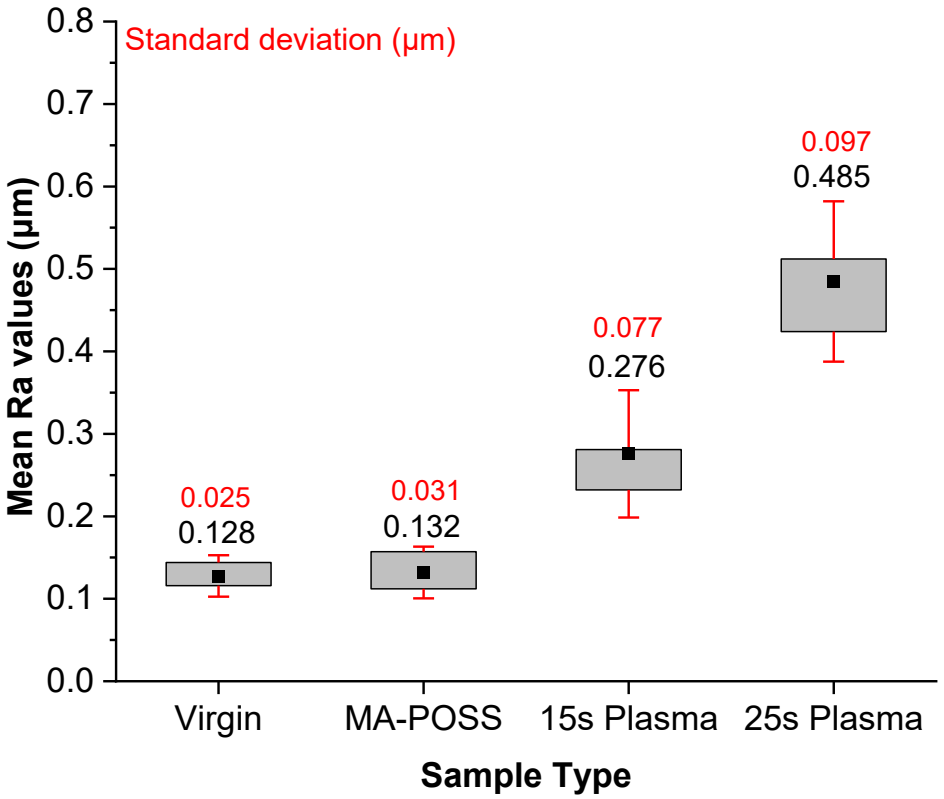


Figure 21: Surface roughness data for all samples.

4.3.4 Tensile test results

Figure 22a shows the tensile test results for clear, virgin human hair, MA-POSS grafted, and plasma-treated human hair fiber composites. Figure 22b also shows the ultimate tensile strength of the specimens with single-ply and double-ply human hair fibers. The average tensile strength of a clear sample (neat resin) with no fiber reinforcement was 17.62 MPa, and the tensile modulus was 874.4 MPa, similar to the results published by the manufacturer in their technical data sheet [197]. When virgin human hair was added as reinforcement, the tensile strength and the modulus increased to 21.54 MPa and 1446.02 MPa, respectively, which indicates that the human hair fibers were good candidates for reinforcement among natural fibers and with the appropriate surface treatment, the tensile properties can further be substantially increased.

As shown in Fig 19 (a), the results clearly indicate that the composites with plasma-treated human hair fibers had an approximately 100% increase in the ultimate tensile strength. They were also at least 35% better than that of the composites with virgin human hair. The increase in the tensile strength of the plasma-treated fiber specimens may be due to the increase in the surface roughness of the fibers and better interfacial adhesion between the fibers and polymer matrix due to the cleaning properties of the plasma arc [185–187]. Composite samples with MA-POSS grafted fibers also showed improvement in ultimate tensile strength by approximately 25%, which this behavior may be due to an increase in the interfacial bonding between the fibers and the matrix [189]. When the fiber loading was increased by adding an additional layer of hair fibers, the tensile strength also increased slightly, as shown in Figure 22a. However, this trend may change as the fiber loading increases beyond a critical fiber loading percentage [139,140,178].

As shown in Figure 22(b), the tensile modulus of the composites also improved with surface treatment. The results for virgin human hair and the plasma-treated fiber reinforcements indicated that Young's modulus increased slightly with the increase in fiber loading. However, it was the opposite in the case of MA-POSS grafted fibers. This may be due to the changes in the fiber orientation, as the young's modulus decreases with the change in the fiber orientation from the loading direction [198]. Although, in our case, most of the fibers are aligned with the direction of loading, some fibers are skewed, as evident from the fiber orientation data discussed in the next section.

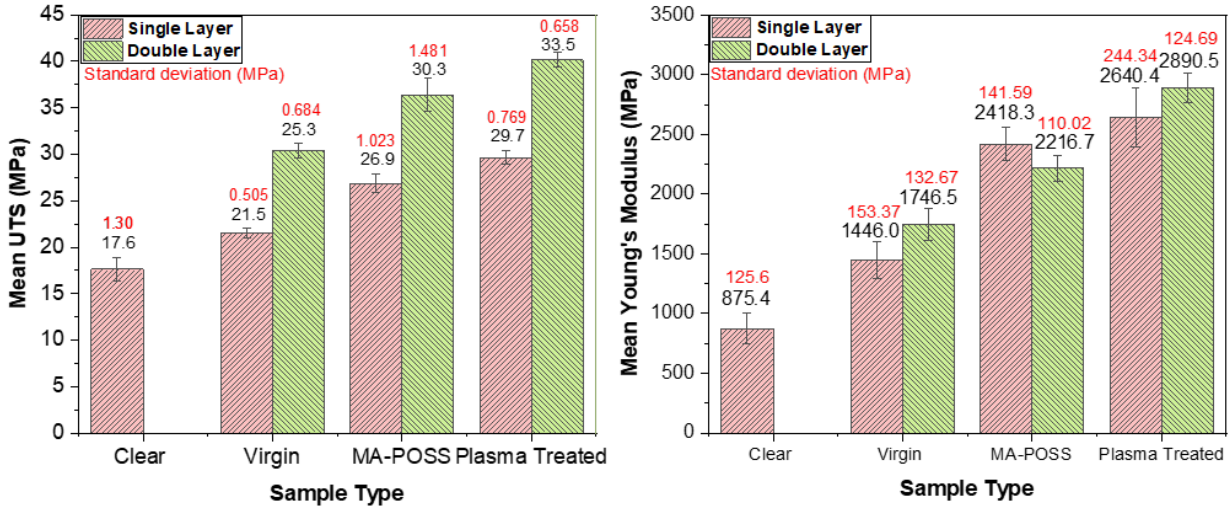


Figure 22: a) Ultimate tensile strength for all the samples b) Elastic Modulus for all samples.

4.3.5 Fracture and Micro CT Analysis

Micro-CT characterization of all the tensile coupons was performed to detect and quantify the void percentage and exact fiber loading. The data obtained from the imaging were also used to identify the fiber orientation. Figure 23c shows an example of the segmentation performed on a sample with voids identified in pink and fiber in blue. Dragonfly software was used to identify the actual fiber volume fraction and the void percentage based on the segmentation performed on each sample. Figure 23(a) and 23(b) represents the average void percentage and the average fiber loading in the case of all the composite specimen, respectively. The data shows that the average void percentage in the MA-POSS grafted human hair composite slightly decreased compared to that of the composites with virgin hair. However, the average void percentage was significantly reduced in the case of the composites with plasma-treated fibers. However, the void percentage increased when the trend remained the same in the case of both single- and double-layer fiber laminates. Voids in the most part were found at the interface of the fiber and the matrix, as evident in Figures 23c and 23d. Better fiber-matrix adhesion results in lower void formation in composites [199]. The average fiber loading for single-layer fiber laminates and double-layer fiber laminates were consistent at 1.5% and 3%,

respectively. Hence, no significant overlapping was noticed in the fiber loading between the two types.

The fiber orientation data is shown in Table 7, in which fiber orientation data can also be a good indication of process repeatability. OrientationJ plugin available on the ImageJ software was used for detecting the orientation of fibers. A segmented image, as shown in Figure 23(c), was used to obtain the pixel count vs. orientation data (as shown in Figure 24). As can be seen in Table 7, all the fiber layers in all the samples have an orientation close to the desired 90º and the standard deviation (mean of means) to be less than ±1º. This also confirms the repeatability of our 3D printing process. The fiber orientation for single-layer MA-POSS composites shows a greater deviation from 90º, which explains the deviation in Young's modulus trend. The high tensile strength of the plasma-treated fiber composites could also be explained by the lower void percentage and good fiber orientation in these samples.

Figure 25 shows examples of fractured samples during the tensile test. In the case of the composite specimens, the matrix failed first due to a brittle fracture. However, the hair fibers continued to elongate/break or were pulled out depending on how long the test (elongation rate was kept constant throughout the test) was continued after the fracture. For all the composite specimens, the fracture occurred along the gauge length or just at the beginning of the gauge length after the fillet radius. In the case of the neat polymer samples, the fracture occurred at the center, as shown in the figure, and was a brittle fracture, as expected.

Table 7: Fiber orientation data for all samples

TYPE	**MEAN FIBER ORIENTATION**							
	Fiber treatment	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mean	S.D
SINGLE	Virgin	90	89.6	89.6	89.8	89.6	89.7	0.14

LAYER	MA-POSS	88.9	89.1	87.1	89.2	89.6	88.7	0.89
	Plasma	89.8	88.4	89.8	89.9	89.5	89.5	0.57
DOUBLE	Virgin	90	89.8	89.4	89.1	89.1	89.5	0.35
LAYER	MA-POSS	89.6	89.4	89.2	88.9	89.6	89.4	0.26
	Plasma	88.4	89.1	89.8	89.6	89.6	89.3	0.48

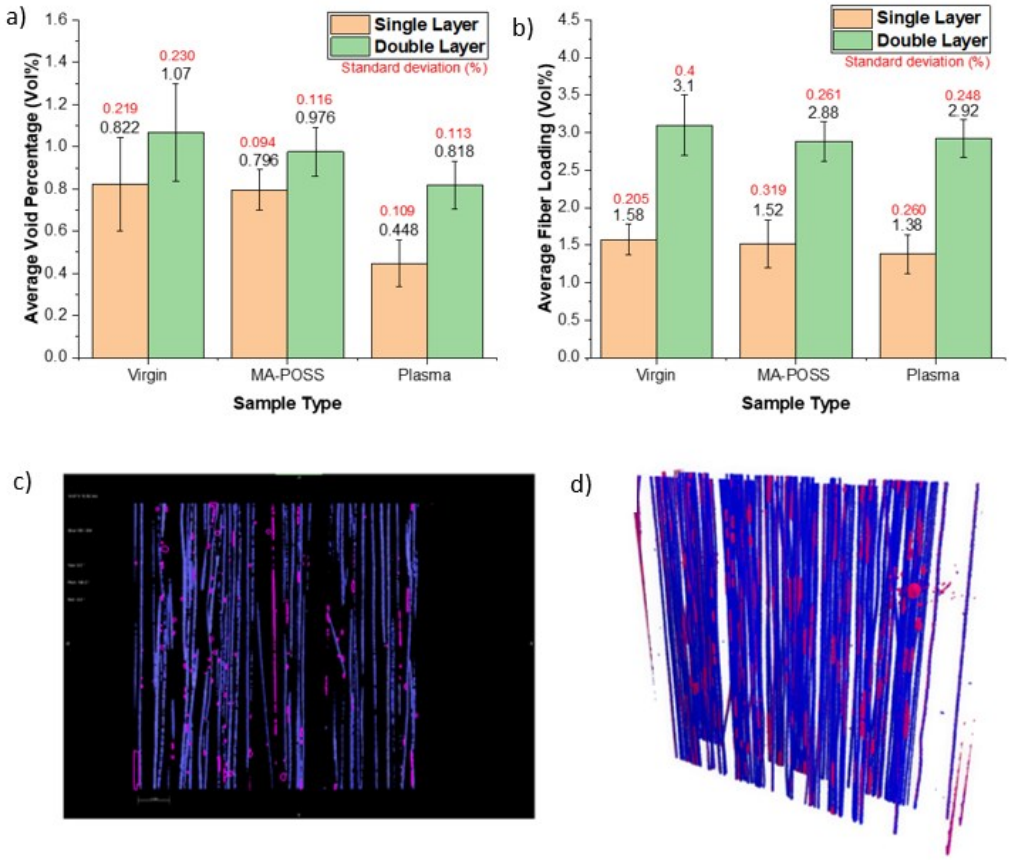


Figure 23:a) Ultimate tensile strength for all the samples b) Elastic Modulus for all samples c) Example of the fiber orientation distribution for one sample d) Example of the segmentation done on the ORS Dragonfly

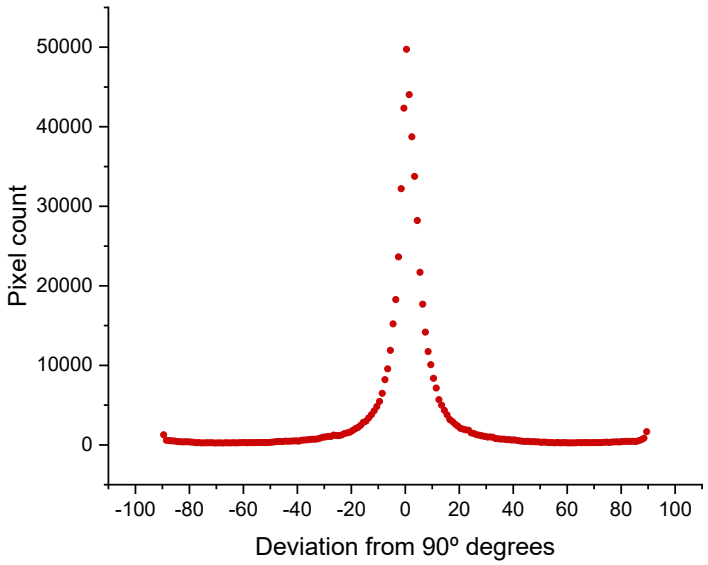


Figure 24: Example of the fiber orientation vs pixel count obtained from OrientationJ

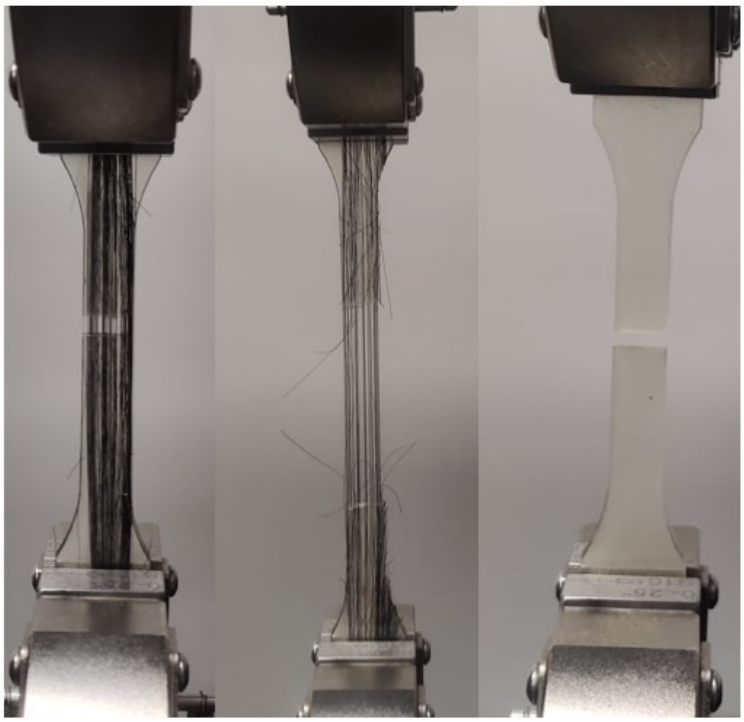


Figure 25: Examples of fracture during the tensile test a) Double layer composite b) Single layer composite c) Neat polymer sample

Chapter 5

Conclusions and Future Work

5.1 Conclusions

The feasibility of employing additive manufacturing as a method to fabricate natural fiber composites has been explored in this research work. The stereolithography (SLA) technique was used to fabricate randomly oriented short human hair, and continuous human hair composites were fabricated. Based on the initial hypothesis, technical contributions related to composites, natural fiber composites, 3D printing, and surface modification techniques were reviewed with guidance from the literature available.

Stereolithography (SLA) based additive manufacturing process was utilized to validate the initial hypothesis. A commercially available 3D printer – Autodesk Ember, capable of printing UV curable resin, was employed for the initial phase of the research to fabricate random short human hair fiber reinforced composites. Composites were 3D printed with different fiber loading to understand the effect of fiber loading on the strength of these composites. Tensile tests confirmed that the composites manufactured were significantly weaker than the samples with no reinforcement. From this study, several challenges were identified in the process of manufacturing short fiber-reinforced composites, which led to inferior composites. Firstly, the composites manufactured had a significant number of voids embedded in them. This could be due to the poor interfacial adhesion between the fiber and the matrix. Secondly, it was also identified that in order to maximize the tensile strength of these composites, it was required to first identify the critical fiber length and then modify the surface of the fibers to improve the interfacial adhesion between the fiber and the matrix.

Based on the results from our initial study, Continuous human hair composites were 3D printed successfully using Stereolithography (SLA) additive manufacturing technique for the first time. To overcome the problem of small print volume on the Autodesk Ember 3D printer, another commercially available 3D printer- ELGOO MARS 2 Pro, was employed in this study so that larger specimens can be 3D printed. To solve the problem of poor interfacial adhesion between fiber and the matrix, suitable surface modification techniques (plasma treatment and MA-POSS grafting) were used to enhance the fiber-matrix interaction. A set of single hair-pull-out tests were performed with custom single fiber pull-out test coupons developed to quantify the interfacial shear strength between the fiber and the matrix. The interfacial shear strength increased from 0.07 MPa for untreated human hair fibers to 0.24 MPa in the case of 25s plasma treated fibers; this increase in shear strength can be attributed to the increase in the surface roughness of the fibers. Tensile tests were performed on all the samples with two different fiber loading. The following conclusion was drawn: 1) Human hair fibers act as an excellent reinforcement given that the fibers and matrix have good interfacial adhesion. 2) Composites reinforced with 25s plasma treated hair fibers showed the highest tensile strength of 29.6 MPa because of improved interfacial adhesion with the matrix. 3) MA-POSS grafted hair composites also showed an improved tensile strength of 26.7 MPa compared to the strength of virgin hair-reinforced composites of 21.5 MPa but were inferior to plasma-treated hair-reinforced composites. 4) The tensile strength slightly increased with the increase in fiber loading from 1.5 volume percentage to 3 volume percentage by about 12%. 5) Addition of human hairs as reinforcements also showed significant improvement in the young's modulus of the composites.

Micro-CT analysis was performed on all samples before tensile tests to determine the void percentage, fiber volume fraction, and fiber orientation. It was determined that the voids decreased if the interfacial shear strength between the fiber and matrix increased. Human

hairs are an excellent and economical reinforcing material, and 3D printing composite provides a cost-effective way to manufacture composites without complex and expensive equipment. Plasma surface modification which is relatively easy to perform provides good interfacial adhesion between the fiber and the matrix. However, further studies are required to understand the interaction of fibers and available matrices in the case of short fiber reinforced composites and the effect of fiber length on the composite strength. Studies are also required to understand the effect of 3D printing process parameters on the composites to further develop 3D printing as a preferred choice of manufacturing composites. Natural fiber composites are emerging materials that are eco-friendly and cheap compared to other alternatives, and 3D printing of these composites will further make this an attractive option.

5.2 Future Work

The results presented in this work are key starting points for the development of the SLA 3D printing technique for the fabrication and development of natural fiber-reinforced composites. This manufacturing technique makes obtaining the desired composite properties feasible because of the flexibility 3D printing offers. Considering these factors, the following are some of the recommendations for future research.

- Identifying the process parameters in the 3D printing process to optimize the strength of natural fiber composites. This will lead to a further fundamental understanding of the process.
- Redesigning the SLA 3D printing apparatus to better suit the fabrication of fiber-reinforced composites will lead to faster processing and improved manufacturing.
- In the present work, only simple tensile loads were considered for characterizing the mechanical properties of the natural fiber composites. Future work can include

impact testing, bending, and fatigue testing to further understand the applications of the composites.

- There are a wide variety of UV curable resin available commercially, and it is important to identify or develop appropriate resin and additive combinations suitable for the fabrication of 3D printed composite
- A major challenge in the understanding of the behavior of short fiber reinforced composites was to determine to critical fiber length for elastic fibers like human hairs. To maximize the load transfer between the fiber and matrix, research in this area is required.

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