



MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES



**PRODUCTION OF CONTINUOUS
FIBERGLASS REINFORCED UV-CURABLE
POLYMER MATRIX COMPOSITE
MATERIAL WITH 90 DEGREE ELBOW
PRODUCTS BY ROBOTIC ADDITIVE
MANUFACTURING**

AHMET İPEKÇİ

Ph.D. THESIS

Department of Mechanical Engineering

Thesis Supervisor

Prof. Dr. Bülent EKİCİ

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ÖZET

SÜREKLİ FİBERGLAS TAKVİYELİ UV KÜRLENEBİLEN POLİMER MATRİSLİ KOMPOZİT MALZEME İLE 90 DERECE DİRSEK ÜRÜNLERİNİN ROBOTİK EKLEMELİ İMALAT İLE ÜRETİMİ

Kompozit malzemeler hafif ve dayanıklı olma özelliğinden dolayı birçok alanda yapısal malzeme olarak tercih edilmektedir. Bu sebeplerle, kompozit malzemelerin üretim yöntemleri geliştirilmektedir fakat otomasyona uyarlı olsa da henüz kalıp ile imalat ihtiyacından kurtulamamışlardır. Özellikle dirsekler ve benzeri açılı ürünlerin üretimi kalıp ihtiyacından dolayı maliyetlidir. Ayrıca kompozit dirseklerin üretimi filament sarma yöntemiyle kısıtlı olarak yapılmaktadır. Filament sarma yönteminde dirsek geometrisinin tek bir doğrultuda olmamasından dolayı sarım açısı ve sarım stratejisi sınırlı olarak geodezik ve geodezik olmayan şekillerde yapılabilmektedir. Bu şekilde yapılan sarmada, kalıbın bağlantı bölgesinden dolayı tam dik açıda sarım yapılamamaktadır. Bu da dayanım konusunda düşüşe sebep olmaktadır. Ayrıca sarım stratejisinde dirseğin etrafında tam bir simetrik helisel sarım sağlanamamaktadır. Bu kısıtları aşmak için eklemeli imalat yöntemleri umut vaat etmektedir. Fakat tek başına eklemeli imalat yöntemini kullanmak problemi çözmekte yeterli olmamaktadır. Öncelikle kalıpsız imalat yapabilmek ve muadil kompozit dirsekler ile rekabet edilebilir ürün elde edebilmek için, fotopolimer reçine ve sürekli fiber elyaf kullanarak ultra violet kürleme yöntemiyle kompozit üretimi tercih edilmiştir. Bu sebeple özel bir takım tasarımı ve üretimi gerçekleştirilmiştir. Sonrasında, optimum üretim parametreleri ve mekanik özellikler incelenmiştir. Son olarak, dirsek geometrisinden dolayı geleneksel üç eksenli dilimleme işlemlerinden farklı stratejiler gerekmektedir. Bu sebeple düzlemsel olmayan dilimleme işlemi gerçekleştirilmiştir ve katmanlar halinde helisel sarım yapılmıştır. Tüm bunların yanı sıra filament sarma işleminde kullanılmayan fakat eklemeli imalat yönteminde uygulanan iç boşluklu yapı oluşturulmuştur. Böylece, farklı doluluk oranlarında, farklı fiber yoğunluğunda, farklı fiber sarım açılarındaki 90° açılı dirsekler üretilmiştir ve iç basınç dayanım testine tabi tutularak test edilmiştir. Sonuç olarak, bu yöntemle üretilen dirseklerde, kolay şekillendirme, istikrarlı ürün kalitesi, makul eksenel mukavemet ve çevrelenmiş mukavemet oranı elde edilebilmektedir.

Anahtar Kelimeler: Dirsek, kompozit malzeme, kompozit yapılar, mekanik özellikler, 3B yazdırma, robotik, eklemeli imalat, fiber glass.

ABSTRACT

PRODUCTION OF CONTINUOUS FIBERGLASS REINFORCED UV-CURABLE POLYMER MATRIX COMPOSITE MATERIAL WITH 90 DEGREE ELBOW PRODUCTS BY ROBOTIC ADDITIVE MANUFACTURING

Composite materials are preferred as structural materials in many areas due to their lightness and durability. For these reasons, the production methods of composite materials are developing, but although they are adapted to automation, they have not yet got rid of the need for molds for production. Especially the production of elbows and similar angled products is costly due to need for molds. In addition, production of composite elbows is limited by filament winding method. Due to the fact that the elbow geometry is not in a single direction in the filament winding method, the winding angle and winding strategy can be limited to geodesic and non-geodesic. In this way of winding, it is not possible to wind exactly at right angles due to the connection area of the mold. This causes a decrease in strength. In addition, a fully symmetrical helical winding around the elbow cannot be achieved in the winding strategy. Additive manufacturing methods are promising to overcome these limitations. However, using the additive manufacturing method alone is not enough to solve the problem. First of all, in order to be able to manufacture without molds and to obtain products that can compete with equivalent composite elbows, composite production by ultra violet curing method using photopolymer resin and continuous fiber fiber was preferred. For this reason, a special tool design and production was carried out. Afterwards, optimum production parameters and mechanical properties were investigated. Finally, different strategies are required from traditional three axes slicing operations due to elbow geometry. For this reason, non-planar slicing is performed and helical winding is made in layers. In addition to all these, a hollow structure, which is not used in filament winding but applied in the additive manufacturing method, has been created. Thus, 90° angled elbows with different filling rates, different fiber densities, different fiber winding angles were produced and tested by subjecting to the internal pressure strength test. As a result, elbows produced by this method can be easily formed, stable product quality, reasonable axial strength and circumferential strength ratio.

Keywords: Elbow, composite material, composite structures, mechanical properties, 3D printing, robotic, additive manufacturing, fiber glass.

CLAIM FOR ORIGINALITY

PRODUCTION OF CONTINUOUS FIBERGLASS REINFORCED UV-CURABLE POLYMER MATRIX COMPOSITE MATERIAL WITH 90 DEGREE ELBOW PRODUCTS BY ROBOTIC ADDITIVE MANUFACTURING

Elbow elements are difficult to manufacture and used in many fields as a necessity. When they are produced as plastic, they are not durable, and metal production has difficulties in terms of mold and production precision. For this reason, the production and use of composite elbows is becoming widespread today. In production of composite elbows, filament winding method is used with the help of mold. In this production, a separate mold is required for each different diameter. Also, there is limited winding possibility due to movement in two axes. Due to the parts where the mold is attached to the machine, 0 - 90 degrees fiber orientation can not be provided between the layers according to the main axis of the elbow. In the literature, it is observed that the highest strength properties are achieved when approaching this angle.

The originality of this work is that 90 degree composite elbows are produced without a mold and the winding directions between the layers can be adjusted as 0 - 90 degrees. To the best of the author's knowledge, there is no study in the literature on production of 90 degree composite elbows with continuous fiber-reinforced robotic additive manufacturing method.

In order to solve this problem, first of all, optimum production parameters, printing quality and mechanical properties of products were examined with the robotic additive manufacturing method. Then, by making nonplanar slicing, helical filling structure and different filling rates were obtained for the pipe and elbow group elements.

SYMBOLS

V_c	: Volume of Composite (m^3)
V_f	: Volume of Fiber (m^3)
V_m	: Volume of Matrix (m^3)
ρ_c	: Density of Composite (kg/m^3)
ρ_f	: Density of Fiber (kg/m^3)
ρ_m	: Density of Matrix (kg/m^3)
w_c	: Mass of Composite (kg)
w_f	: Mass of Fiber (kg)
w_m	: Mass of Matrix (kg)
W_f	: Fiber Mass Ratio (%)
W_m	: Matrix Mass Ratio (%)
v_f	: Void Volume Ratio (%)
v_v	: Void Volume (m^3)
v_c	: Void Volume of Composite Material (m^3)
ρ_{ce}	: Density of Composite Material (kg/m^3)
ρ_{ct}	: Theoretical Density of Composite Material (kg/m^3)
D	: Diameter of Nozzle (m)
ρ	: Density of Fiber (kg/m^3)
E_c	: Energy Requirement (J)
D_p	: Penetration of Resin (m)
C_d	: Depth of Curing (m)
P_L	: Resin Surface
L_w	: Line Width (m)
V_p	: Printing Speed (mm/s)
V_E	: Extrusion Speed (mm/s)
A_f	: Area of Nozzle (m^2)
A_p	: Area of Printed Line (m^2)
τ	: Shear Stress (MPa)
σ	: Normal Stress (MPa)
ϵ	: Strain ($\mu m/m$)

S	: Elasticity Matrix
C	: Stiffness Matrix
E	: Elasticity Modulus (GPa)
G	: Shear Modulus (GPa)
V^f	: Fiber Volume Ratio (%)
V^m	: Matrix Volume Ratio (%)
r	: Diameter of Cylinder (m)
t	: Thickness of Elbow Wall (m)
P	: Internal Pressure (bar)
σ₁	: Circumferential Stress (MPa)
σ₂	: Axial Stress (MPa)

ABBREVIATIONS

3D	: Three Dimensional
3MF	: 3D Manufacturing Format
ABS	: Acrylonitrile Butadiene Styrene
AF	: Aramid Fiber
Al	: Aluminum
Al₂O₃	: Aluminum Oxide
Al₂O₃/Pb	: Aluminum Oxide / Lead
AM	: Additive Manufacturing
ASTM	: American Society for Testing and Materials
AWWA	: American Water Work Association
B/Al	: Boron Aluminum
BaO	: Barium Oxide
BC	: Before Christ
BMC	: Bulk Moulding Compound
BMI	: Bismaleimide
C	: Carbon
C/Pb	: Carbon / Lead
CAD	: Computer Aided Design
CF	: Carbon Fiber
CFRP	: Continuous Fiber Reinforced Plastic
CH₂	: Methylene
CH₃	: Methyl
Cl	: Chloride
CMC	: Ceramic Matrix Composite
CNC	: Computer Numerical Control
DLP	: Digital Light Processing
EN	: European Standards
F	: Flor
FDM	: Fused Deposition Modelling
FRP	: Fiber Reinforced Plastic
FS	: Fume Silicane

FW	: Filament Winding
GF	: Glass Fiber
GFRP	: Glass Fiber Reinforced Plastic
Gr/Al	: Roentgenium / Aluminum
H	: Hydrogen
H₂O	: Hydrogen di Oxide
He-Cd	: Helium Cadmium
ISO	: International Standards Organisation
JFRP	: Jute Fiber Reinforced Plastic
LED	: Light Emitting Diode
Li₂O₂	: Lithium Peroxide
LOM	: Laminated Object Manufacturing
MgO	: Magnesium Oxide
MMC	: Metal Matrix Composite
MWNT	: Multi Wall Carbon Nanotubes
N	: Nitrogen
NF	: Natural Fiber
NFC	: Natural Fiber Composite
Ni	: Nickel
O	: Oxigen
OBJ	: OBJ File Format
PAN	: Polyacrylonitrile
PCL	: Polycaprolactone
PDMS	: Polydimethylsiloxane
PEEK	: Polyether Ether Ketone
PLA	: Poly Lactic Acid
PLC	: Programmable Logic Controller
PMC	: Polymer Matrix Composite
PN	: Nominal Pressure
PTFE	: Polytetrafluoroethylene
PVA	: Polyvinyl Alcohol
PVC	: Polyvinyl Chloride

R&D	: Research and Development
RAM	: Robotic Additive Manufacturing
REACH	: Registration, Evaluation, Authorization and Restriction of Chemical
RTM	: Resin Transfer Moulding
S	: Sulfur
SEM	: Scanning Electron Microscope
SGC	: Solid Ground Curing
Si	: Silicon
Si₃N₄	: Silicon Nitride
SiC	: Silicon Carbide
SiC/Al	: Silicon Carbide / Aluminum
SiCp/Al	: Silicon Carbide Particles / Aluminum
SiO₂	: Silicon Oxide
SLA	: Stereolithography
SLIM	: Standard Language for an Industrial Manipulator
SLS	: Selective Laser Sintering
SMC	: Sheet Moulding Compound
SPCF	: Steam Produced Carbon Fiber
STL	: Standard Triangle Language
SWNT	: Single Wall Carbon Nanotube
T_g	: Transition Temperature
TSE	: Turkish Standards Institution
USA	: United States of America
UV	: Ultra Violet
WPC	: Wood Plastic Composite

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1. INTRODUCTION

Today, there has been a great change in science and technology, and it has acquired a dimension by adding criteria such as aesthetics, economy and durability to the features expected from design. In cases where these criteria are insufficient, lightness in design, easy assembly and resistance to corrosion are now more priority. Due to the limited nature of materials, technological development has become inevitable in materials and materials science, which has a fundamental and important place for industry. For this reason, scientists have tried to produce economical, high-strength and light materials in the process of development of science with the innovations of the age. Composite materials developed in this way have gained a very important place in the manufacturing industry and new technological products [1].

However, the concept of "fibre-reinforced" is very old. Inscriptions written on straw-reinforced clay brick have been found in Ancient Egypt, but in 1970s composite applications were widely used in automotive, aircraft, and sport goods. Over past years, the composites industry has been growing steadily and on a global basis, the composites market has been found to grow more than anticipated [2]. This growth can be attributed that composite materials have unique advantages such as long fatigue life, high strength, low density, high stiffness and adaptability of the structure to its intended function. Further improvements can be made in thermal conductivity, corrosion resistance and sound isolation, thermal isolation [3].

Composite materials are produced by physically mixing the main phase, called matrix, and a second phase, called fiber, in a certain ratio and order, taking into account the desired material properties. All structures except single-phase structures are called complex-phase structures. In that case, all materials, except single-phase materials, fall into the composite group [4].

Fiber reinforced plastic composites are made of glass, carbon, aramid, etc. as a reinforcing element. Resin is used as matrix element. Plastic resins used as matrix material are the most used type in the industry, and polyester resins are preferred more in the industry due to their cheapness. Epoxy resin is preferred in applications that require high strength and chemical resistance.

The fiber material determines the strength property of the composite material. The fibers, which are brought together with the matrix material at a certain temperature and under

certain conditions, can be found in various arrangements and various structures. Matrix materials physically hold the fibers together and distribute the dynamic and static loads on the composite structure homogeneously on the fibers. Thus, the fiber material plays a role in preventing crack propagation that may occur in the transition to plastic deformation and delays the rupture of the composite material.

Composite material developments, driven by the needs of the aircraft industry for a long time, have recently been used for many different purposes in many new sectors [5].

In recent years, important studies have been carried out in automotive industry to produce light vehicles by preserving the strength values of existing structures, and accordingly to produce and develop these structures for sectoral targets such as carbon dioxide emissions and fuel consumption [6, 7]. Fiber Reinforced Plastic (FRP) materials have been used in many areas for structural applications as competitive alternative to improving and strengthening existing structures. There are many reasons to consider FRP composites in many civil engineering applications. The benefits of FRP composites vary depending on the resin, fiber selection and manufacturing process. In addition, there is need to optimize design of composite material because not all of best properties can be achieved at the same time [8].

If special applications are mentioned; Examples include sports equipment (such as sailboat hull, race car hull), high pressure composite tubes, large-diameter industrial pipes, fuel tanks of space vehicles, shafts, long propellers, rocket body. When the application examples are examined carefully, it is seen that; High strength and lightness is requested factor in the materials used for all these applications, and a high ratio of strength to weight of the material used is desirable. This ratio (strength / weight), also known as the strength performance of the materials, has gained a serious place in the industry because of the performance value of FRP materials compared to other materials and especially steel. According to the type of reinforcement element it has, FRP composite materials, which are the most common in the use of composite materials; can be classified as continuous fiber reinforced composites and chopped fiber reinforced composites.

Continuous fiber reinforced composites, as the name suggests, are based on the principle of continuous and uninterrupted production of the reinforcement element over a coil in composite production. Filament Winding (FW) technology, which is one of the production methods of continuous fiber reinforced composites, is a preferred and effective method in

fiber winding applications, and makes it possible to produce durable products. High-pressure tubes and tubular symmetrical elements are at the forefront of industrial products produced with fiber winding technology. The use and importance of such high pressure tubes (especially in hydrogen fuel technology used in new generation vehicles) are increasing day by day [9].

Glass fiber, which is used as a continuous fiber reinforcement element in fiber winding processes, has gained an important place in today's industry due to its superior properties. The fiber used in fiber reinforced composite structures is a fiber bundle consisting of thousands of long fibers with a diameter of 5 – 10 μm . This fiber can be used alone or made into fabric. The density of fiber is quite low compared to steel. This makes the fiber an ideal material for applications requiring a high specific strength. Glass fiber reinforced composite has the same strength as a standard AISI 1020 steel material in terms of breaking strength and has a lightness of 1/5. Likewise, while it is twice as durable as 6061 aluminum material in terms of breaking strength, it is twice as hard and 1.5 times lighter. In addition, the fatigue strength of glass fiber is better than most known materials, and the corrosion resistance of the composite obtained when coated with appropriate resin is very good. FRP materials are used in very important areas such as military, space and aircraft applications due to their high strength and low density. The fact that Boeing produces the majority of the Boeing 787 Dreamliner aircraft from FRP shows the place of this material in the industrial field.

The advancement of technology with each passing day has also diversified the manufacturing methods; Thanks to this diversification, a new production method has been created every day in plastic and composite manufacturing methods. A manufacturing method that has been mentioned frequently in recent years is AM. AM method, also called 3D printing, was first described by Charles Hull in 1986 [10]. AM is a modern manufacturing method in which physical parts are produced automatically in a computer-controlled manner using 3D solid model data, without using traditional manufacturing methods. In this method, the CAD data of the part designed with 3D solid modeling software is converted to STL data format and separated into layers with the help of slicing programs. By using the cross-sectional area data of each layer, motion vectors suitable for the production method are obtained. With this motion data obtained, the production of the relevant layer of the part in one layer thickness is carried out by adding material. Part production is carried out by adding all layers from the lowest layer to the top layer by adding them on top of each other. Thus, products with complex geometries can be easily

manufactured.

As a result of years of studies, examples of Additive Manufacturing (AM) technologies are seen in many fields such as aviation, automotive, biomedical, and architecture [11]. AM continues to develop rapidly with an exponential growth due to its ease of use and low costs in rapid prototyping and rapid production. The ability to easily produce complex geometries with precise tolerances has made the AM industry a billion-dollar industry in a short time [12, 13].

Although the products obtained by AM with ability to quickly transform model into a physical object were wanted to be used functionally, they could not be used functionally in the first years due to strength problems and were mostly used for prototyping [14]. Today, most of the studies on AM have focused on achieving acceptable values in terms of precision surface quality and strength, within dimensional tolerances, with the feature that the parts can be used directly [15]. This situation has paved the way for the use of this technology with functional and adaptation applications, master models and finally rapid manufacturing possibilities, apart from conceptual product design trials, rapid prototyping systems [16].

The demand for functional and direct use of the needed products have increased the importance of manufacturing, especially in engineering applications, and various research and development studies are carried out in order to use a wide range of materials as raw materials in these production methods. It is possible to see applications of 3D printing of polymers in the aerospace industry for complex lightweight structures [17], structural models, architectural industries [13], for reproduction or education [18], and medical fields for organs and tissues [19].

Until today, most of the studies in the AM industry have focused on production of products from a single material. The fact that the materials are uniform and limited has brought limitations in terms of the physical and chemical properties of the products. The desire to overcome these limitations has paved the way for studies that optimize the use of more than one material type in a single process in AM technologies.

In this thesis, polymer matrix composite material production methods briefly mentioned and studies on the production of polymer matrix composite materials by AM method examined. Then, the production of composite printing tool and polymer matrix fiber reinforced parts developed within the scope of the thesis by Robotic Additive Manufacturing (RAM) method introduced and the results of experimental studies and tests examined.

1.1. Aim and Significance

A structure consisting of two or more materials with different chemical properties is called composite. While the materials entering in this combination preserve their own structural properties, they add different features to the structure that emerges after the combination. Features such as high strength, dimensional stability, light weight, design flexibility, high dielectric resistance, corrosion resistance, ease of moulding, surface treatments, high thermal resistance, vibration damping, transparency, high chemical resistance, acoustic conductivity, sound retention or sound absorption are examples [20, 21].

Same-directional aramid and carbon fiber reinforced epoxy composite materials have a specific tensile strength about 4-6 times higher than steel and aluminum. The same directional graphite-reinforced epoxy has a specific tensile strength approximately 3.5-5 times higher than steel and aluminum. Depending on the place of use and its features, the required features are increased and controlled. Thus, the production time is shortened by reducing the interconnecting details and parts [1, 21].

On the other hand, some disadvantages; The raw material is expensive, the properties of laminated composites are not always ideal, and they have low durability in the thickness direction and between layers. The quality of the material depends on quality of the production methods, there is no standardized quality. Since composites are brittle materials, they can be easily damaged, and their repair may create new problems [22].

Composites consist of two basic components: the binder or matrix and the reinforcing element. While the reinforcement element provides strength and stiffness in the composite material, the matrix has more than one task in the structure. The matrix acts as the binder that holds the reinforcing element together, protects it against environmental factors and transmits the external effects and loads to the reinforcement element. It also helps to hold the structure together by guiding the reinforcement member. While the matrix and the reinforcement element preserve their own physical and chemical properties within this structure, they add different properties to the structure they form, independent of these properties. The most well-known carbon composite classes; metal-matrix composites, polymer-matrix composites and ceramic-matrix composites carbon-matrix composites.

One of the most important issue is the selection of the right matrix and reinforcement element in production of composites. The most common superior composites are produced with polymer-matrices. These composites contain thermoplastic or thermoset polymers

reinforced with aramid, glass or carbon fibers. Composite materials can be produced with different sizes and shapes. In this way; they can use their properties such as resistance to corrosion, high strength and hardness and in many different areas. In this study, polymer matrix – glass fiber reinforced composite material was chosen due to its wide usage area and superior properties.

Glass fibers widely used as reinforcing fibers in this field due to their structural properties. The most important features; It has good tensile strength, low density structure, high thermal and chemical stability in the absence of oxidizing agents, and resistance to creep [23]. Stress strain graphs of fiber and matrix materials and stress strain graph of produced composite are given in Figure 1.1.

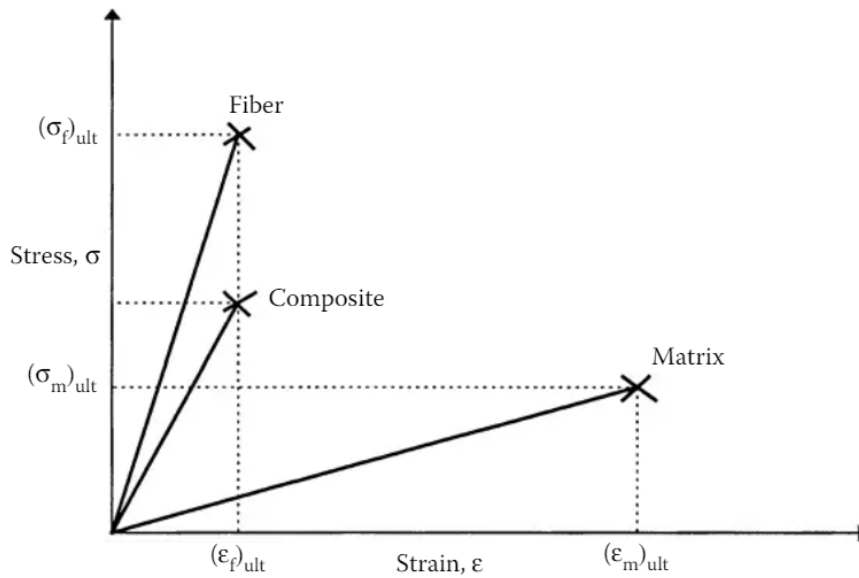


Figure 1.1 Tensile stress – strain curve of composite materials [24].

Glass, carbon, aramid, boron, polyethylene, polyamide, polyester, natural fibers or fabrics are examples of fibers used in composite preparation. In Table 1.1, the tensile strength and tensile modulus values of some fibers and metals that are frequently used for reinforcement are given. Among these fibers, glass fibers are mostly used in general purpose commercial composites, and carbon or aramid fibers are used in advanced composites [25].

Table 1.1 Tensile strength and elastic modulus of some fibers and metals [25].

Material	Tensile Strength (MPa)	Elastic Modulus (GPa)
Carbon Fiber	2000-3500	325-440
Aramide Fiber	300-3600	60
E-Glass Fiber	2400	70
S-Glass Fiber	3450	85
Aluminum	130-180	72
Titanium	25-400	105
Stainless Steel	205-520	196

By producing the fibers in fine diameter, the possibility of structural error is minimized compared to large mass structures. Therefore, they show superior mechanical properties. In addition, the reasons why fibers are high-performance engineering materials also depend on the following properties:

1. Superior microstructural properties, small grain sizes and small scale production.
2. As the length/diameter ratio increases, the amount of load transmitted by the matrix material to the fibers increases.
3. Too high modulus of elasticity [25].

Production methods for composites; hand lay-up, spraying, pultrusion, filament winding, infusion and Resin Transfer Moulding (RTM). The most widely used method in the production of large profile structures is the filament winding method. Pipe and profile production with FRP material was developed during the second world war. Some advantages of this material such as being able to be manufactured quickly and durability are used in bridges, sea boats, etc. allowed it to be used in manufacturing. After the Second World War, it found a widespread use in the pipe manufacturing sector, as in many other sectors. The first FRP pipe was manufactured in 1948. Until today, by member organizations of the FRP Pipe Manufacturers Association; 7.983 km of FRP pipes in Turkey, 5.718 km abroad and 13.701 km in total were successfully produced, shipped and put into practice. Although the pipe usage areas are very common, they can be listed as follows; drinking water, irrigation, wastewater, rain water, industrial, facilities, hydroelectric, power plants, energy projects. For these reasons, the subject of this study is on the pipe and profile production method with limited production method. The worldwide composite cylinder market is expected to remain the largest market by value for composite use for the transportation industry. The expected growth in alternative fuel vehicles and the increased need for weight reduction with higher gas carrying capacity are the main drivers of growth

for this sector [2]. In addition, the development of composite cylinder production technology is given in Figure 1.2.

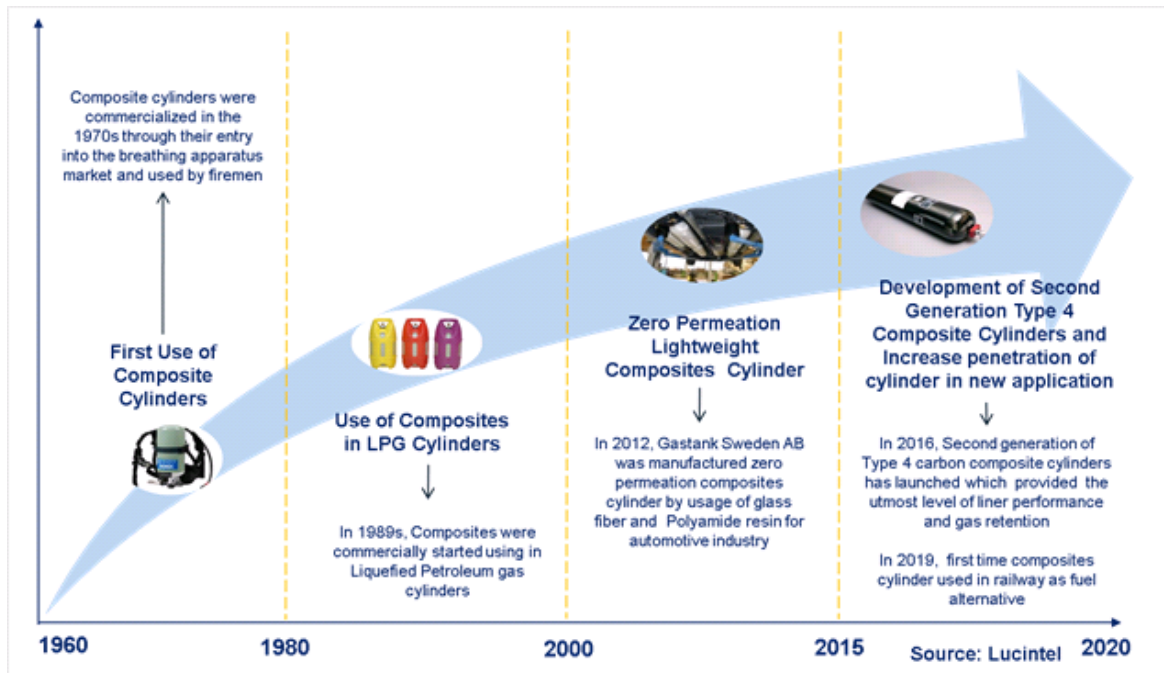


Figure 1.2 Evolution of composite cylinder technology [2].

With the decrease in fiber prices, the rate of use has increased in sectors such as automotive, aerospace and yachting, as well as sports, construction and biomedical. The most important application examples in the field of space aviation can be given as space vehicles. In aviation, it is widely used in both civil aircraft and military aircraft and helicopters. It is used in the automotive sector to reduce the total weight of vehicles due to its low density [26].

The chassis of Formula 1 vehicles are produced entirely with carbon fiber composites. By the top-class car manufacturers in the sector; It is used in many parts of the vehicle such as chassis, bumpers, axle, engine equipment and suspension systems. With the increase in use in the global arena, production technologies are also developing rapidly. Its use in daily life is also increasing day by day. In the coming period, it will be used more widely in sectors such as the space industry and aviation. With the development of the composite industry and the production of better composites with different properties, the sectors it uses will develop at the same rate [27]. Development of the composite materials and major industries over the years are given in Figure 1.3.

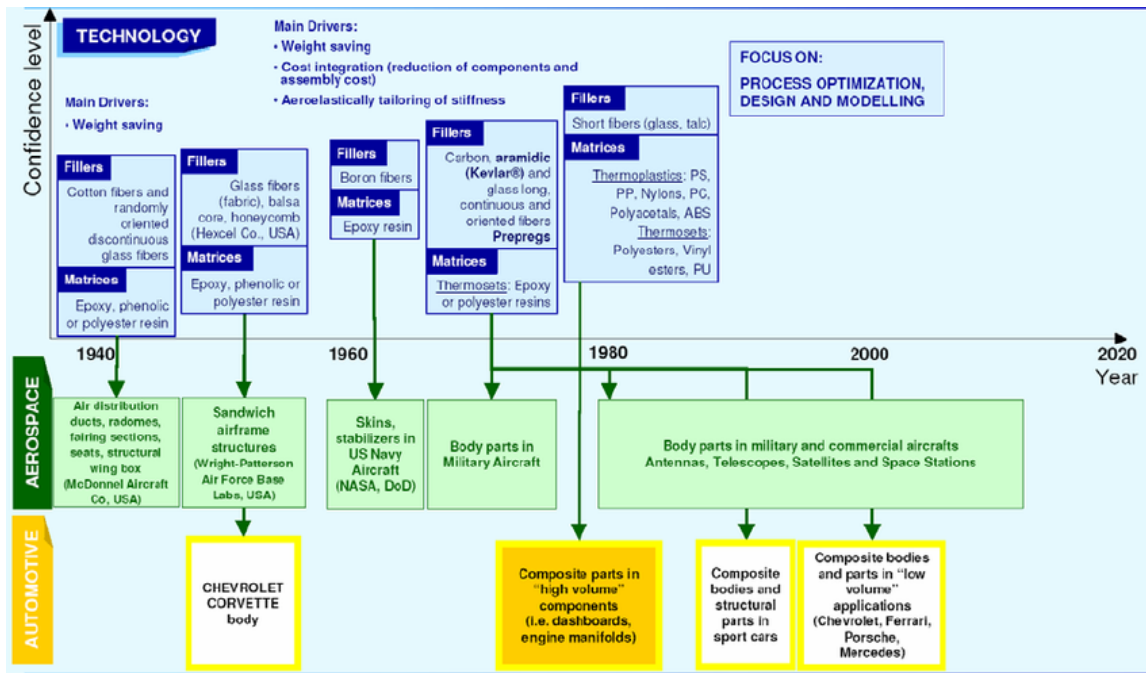


Figure 1.3 Development of the composite materials and major industries over the years [28].

The worldwide composite cylinder market has been observed to decline in 2020 due to the worldwide economic recession led by COVID-19. On the other hand, the market continued to recover and rise in 2021. Technological developments in the sector have also begun to shape the market. Thanks to the production technologies developed in an integrated manner with the market, it has helped the use of composite materials in new and different sectors [29].

Fiber is produced in different filament diameters and weights, depending on the production process. These yarns produced can be processed directly with resin to form composite material, and as an additional process, they are knitted in different types of knitting and used for the production of composite material in the form of fabric. These fabrics are in different weights, angles and weave types, depending on the design of the composite material.

1.2. Composite Materials

FRP composite materials, also called “advanced composite materials”, are increasingly used as structural engineering materials after the Second World War due to their excellent corrosion resistance, high specific hardness, light weight, high specific strength, impact resistance and fatigue resistance. In addition, thanks to their ability to be produced in complex shapes, they reduce the number of parts to be used during production and assembly.

All these reasons explain the interest in composites compared to traditional metal alloys, despite the high production cost [24].

The composites market is widely used in the transportation, aerospace, construction, marine, pipe and tank, consumer goods, electrical/electronics and wind power industries. In the global composite industry, construction industry; represents the largest consumer of composites in terms of bulk shipments. After the construction sector, the transportation and electrical/electronics sectors represent a significant consumer of composite materials. The construction industry is seen as the largest potential market for composites. Bridge deck repair and re-installation, concrete repair and reinforcement, composite hybrid technology (use of composites with wood, steel and concrete), offshore piling and pier upgrade programs are some of the areas being developed [30].

Reinforced composite materials; It is a subgroup of composite material class within the four basic engineering material classes [31] called polymers, metals, ceramics and composites. A composite material is defined as a multiphase material consisting of two or more components with different properties that are combined to optimize some specific properties [24, 32, 33]. The reinforced composite material is the reinforcement phase in the matrix phase, and the matrix secures the reinforcement in place, providing load transfer and distribution, while protecting the reinforcement from external environmental conditions. Typical matrix materials; metal, thermoplastic polymer, thermoset polymer, carbon and ceramic. Reinforcement plays an important role in controlling the strength and stiffness properties of the composite materials. Reinforcement types can be made from long (continuous) fibers or short (discontinuous) fibers in three forms; It may consist of particles, flakes, and fibers, as shown in Figure 1.4 [24].

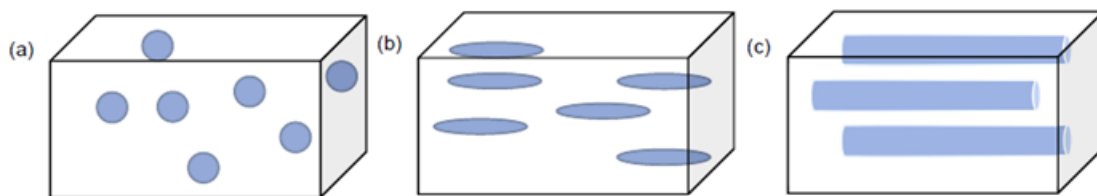


Figure 1.4 Reinforcement types are a) Particle, b) Flake, c) Long fiber form [24].

Fibers with high strength and modulus are added to polymers, metals, carbons and ceramics, which have a sensitive structure, and are used to create a solid structure. The most important criterion for an efficient reinforcement is the bonds formed between the fiber tissues and the

matrix. In a unidirectional composite, the axial tensile force is independent of the fiber and matrix bond. However, the cross-tension force and the bending force are directly affected by the bonds between the fiber-matrix. However, in some special cases, if the bonds between the fiber and the matrix are too strong, it can cause the material to become more brittle. The reason for this is that the strong bonds formed cause cracks on the surface. Bonds between fiber-matrix; includes mechanical bond, chemical bond and van der Waals forces. Chemical bonding is the strongest bond here. This force can be increased by varying the size of the fibers used and the chemical treatment applied [34].

If the fiber and matrices form a three-dimensional plane, the mechanical property of the formed part depends on the bond between matrix and fiber. This bond creates a roughness on the surface between the fiber and the matrix, allowing them to stick together. The slightest change in this bond affects the mechanical properties [35].

For chemical bonds and van der Waals bonds to form, the matrix and fiber must be in close contact. To achieve this, the matrix or precursor matrix must wet the surface of the carbon fibers during penetration. For this process, chemical intervention or coating can be applied depending on the type of matrix. High pressure can also be used during the penetration process to increase wetting. Wetting agent can be used as a method [26].

Typically used fiber materials are carbon, quartz, metal, glass, boron and organic (synthetic and natural) fibers. In addition, continuous fiber reinforcement can be specially prepared in various forms and structures according to application conditions (type and direction of loads that product will carry) of final product.

In the literature, classifications related to the different alignment and directions of fibers have been introduced for the structure of the fabric reinforcement, depending on the manufacturing technology. In this way, traditional fiber weaving technologies are used, as in the examples shown in Figure 1.5, to design and manufacture fiber reinforcements such as weaving, sewing and knitting [36]. In addition, many new technologies have been developed to produce special shaped composites [37].

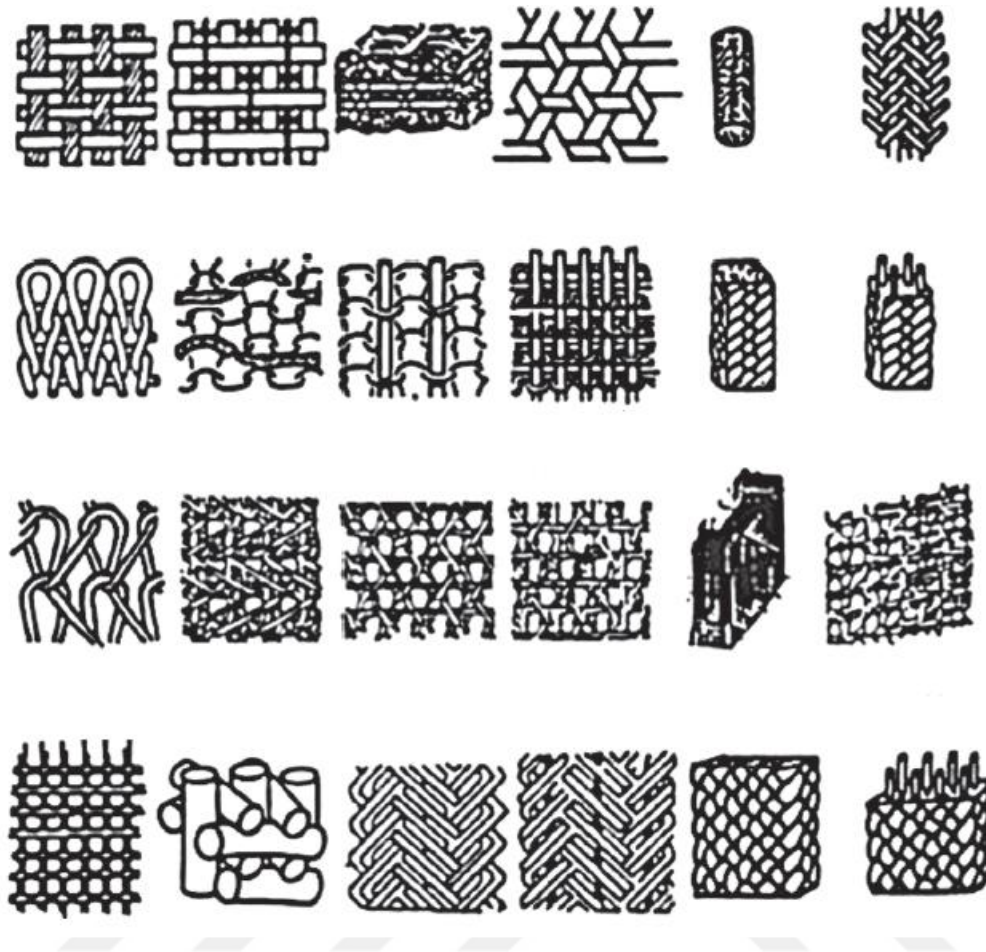


Figure 1.5 Types of fiber weaving [36].

In terms of alignment of structural fibers, fiber reinforced composites are divided into three groups. These; one-dimensional fiber reinforced composites in which fibers are aligned in one direction, two-dimensional fiber reinforced composites in which the fibers are aligned to a plane of XY plane, and another set of fibers, in addition to fibers aligned in one plane of the structure (XY plane), corresponds to the thickness axis of structure. They are three-dimensional fiber reinforced composites that also contain reinforcement or fibers aligned along the incoming vertical axis (Z-axis). Regarding the orientation of the major axis of the structural fibers, fiber reinforced composites; They are classified as uniaxial, biaxial, triaxial and multiaxial structure [36].

FRP are used for numerous reinforcement applications in a variety of industries. Nevertheless, common applications for bridge components include externally bonded composite fabrics on beams, pillars and bridge decks [38].

Fiber reinforced composites display a number of structural properties that make them an alternative to many engineering materials. Tensile strength may be around that of mild steel

and better than that of prestressed steels. However, the specific strength values used to make comparisons between materials can be 40-60 times that higher strength steel [39].

These properties are of great importance in applications such as cladding panels and low-density framing materials. Thanks to its low weight, it enables the assembly and disassembly of structures to be done much easier and in less time than similar structures made of wood or steel. When considering bridges, low weights are advantageous, which can save money throughout the structure and foundations. The strength of an FRP bridge deck can be up to 20% of the structural equivalent of a reinforced concrete deck [40]. Also, the specific strength modulus is high and can provide effective damping of vibrations where this property is important. A material's measure of damping is its damping factor, and in general, FRP composites have a higher damping factor than metals [41].

Polymeric composites can be divided into two groups as advanced composites and engineering composites. They differ mainly in the type and length of fiber reinforcement and the performance characteristics of the resins used. A summary of the differences and similarities in material technologies of engineering and advanced composites is given in Table 1.2 [42].

Table 1.2 Comparison of composite material technologies [42].

Specification	FRP Composites	Advanced Composites
Fiber Reinforcement	Mainly E-glass products Use of C-glass for corrosion Corrosion versions of glass E and C Limited use of “natural” fibers fiber reinforced plastics Glass reinforced plastics Glass fiber reinforced plastics	High strength S glass (R and T glass versions) carbon and graphite Aramid, Boron Quartz (fused silica) polyethylene Advanced polymeric fibers ceramic fibers
Typical Fiber Forms	Continuous fiberglass and chopped fibers Woven fiber products Tight glass woven fabrics Glass fiber materials Commercial matte and stitched/glued materials	Continuous fiber roving and drawing materials Preparation materials (unidirectional tapes and fabrics) Higher fiber volumes (55%-65%) Complex structural weaving products
Matrix Resin	Polyester and vinylester Wide variety of polyester formulations Phenolics for fire applications Limited use of epoxy in certain areas All thermosets except some glass fiber thermoplastics	Epoxies Bismaleimide (BMI) and cyanate esters for higher temperatures polyimides Numerous high-performance thermoplastics Hardened resin system
Application temperature and conditions	Ambient temperature range (4-60 °C) UV and weather exposure Exposure to fuels, waste materials, water, seawater and process chemicals	Exposure over a wide temperature range space environments Aviation service conditions Fuels, solvents, liquids Extreme conditions: 82 °C–371 °C environmental conditions cryogenic conditions
Use of core (core) material	Balsa and foam core materials Core materials suitable for close environment conditions Core usage technology based on marine and boat market	Intensive use of honeycomb core materials Aluminum aramid carbon fiber Comprehensive design and manufacturing technology

FRP composites consist of two main components: load-bearing fibers and polymeric matrix, which acts as the binder and protector of the fibers. The matrix facilitates load transfer between fibers and ensures that the embedded fibers maintain orientation and directional

stability [43]. Composites are generally anisotropic, exhibiting different mechanical properties in three orthogonal directions. The properties of FRP composites vary somewhat depending on the manufacturing and manufacturing processes used [44]. The roles of matrix and fiber reinforcement in composites are summarized in Table 1.3 [42].

Table 1.3 Matrix and reinforcement roles in composites [42].

Matrix	Reinforcement
• Gives shape to the composite part • Protects the fiber reinforcement from environmental conditions. • Transfers loads to fibers. • Contributes to properties such as strength, which depend on both the matrix and the fibers.	• It gives strength, hardness and other mechanical properties to the composite material. • Provides mastery of other properties such as thermal expansion coefficient and thermal conductivity.

Among the types of loading that civil structures must withstand, fatigue loading plays an important role. The fatigue properties of a material represent its response to cyclic loading and it is well known that the force decreases significantly under cyclic loads. The response to such loadings is complex and affected by various variables such as stress level, repetition mode, material composition, environmental conditions, and the like. Fibre-reinforced composites seldom exhibit defects along a crack path. Instead, multiple defects can occur in the form of fatigue damage, fiber breakage, delamination (layer separation), bonding, and matrix cracking. Depending on the stress level, fiber orientation, and component properties, some of these defect/failure modes occur singly or in combination just before causing the composite to defect, causing a progressive growth of the defect to rupture. When working with FRP composites, take into account the properties that cause a phase difference between stresses and strains, and that the polymers do not disperse easily due to their viscoelastic structure and low thermal conductivity, thus creating a temperature difference between the center and surfaces of the polymer composites, causing energy dissipation as heat in the material should be taken. This temperature gradient can reduce the fatigue life of composites [45].

With the developments in composite material technology, composites have been increasingly used in industry and technology applications. Scientific studies on composites, which are used significantly in the aircraft industry and many other sectors, continue intensively today. Composite materials are used in a wide variety of fields thanks to their structures and properties. Since each sector has different needs and expectations, product flexibility of composite materials is an important advantage. Composites are used as raw

materials in different sectors as well as as manufacturing auxiliary equipment. Space technology, maritime industry, manufacture of medical devices, robotics, chemical industry, electrical-electronic technology, musical instruments industry, construction and building industry, automotive industry, defense industry and aviation industry, food and agriculture industry, sports equipment manufacturing (high jump poles, tennis rackets, surfing, racing boats, skiing, etc.) [46].

Hybridization is an approach to meeting competing and diverse design requirements more cost-effectively than traditional engineering materials. The term "hybrid composites" refers to a compound containing at least two different types of fibers reinforced in a single matrix, or polymer blends reinforced with a single fiber, to provide a synergistic effect such as improved mechanical properties [47]. Hybrid composites offered balanced thermal stability, low weight/cost, balanced strength and stiffness, better fatigue resistance, impact strength, fracture toughness [48]. Using various techniques such as hand lay-up, compression molding, RTM; Various studies have been reported on epoxy hybridization reinforced with natural/synthetic fibers produced to improve mechanical, thermal, physical and flame retardant properties [49].

1.3. History of Composite Materials

Today, when it comes to composite materials, materials that are kneaded with engineering knowledge, difficult to produce, high in cost and with very complex structures come to mind, but the origin of composite materials produced by human beings goes back to ancient times. One of the oldest known composite materials is the plywood materials produced by combining and gluing wooden pieces in the Mesopotamia region before Christ. (BC) Archaeological studies in Egypt and Mesopotamia show that adobe, which is formed by combining straw with mud, was used even in the years 2181-2055 BC. Portland cement concrete, which is still used today, is mentioned in the book named 'De architectura', which is estimated to have been written around 25 BC.

In the 1200s, the Mongols invented bows that fit today's modern composite definition, which were very effective in winning wars. Wood, horn, leather, antlers, tendon and bamboo are used in this bow. While the horns form the main body, the task of the tendon and skin is to hold the main body together. Fish glue was used as adhesive. Mongolian bows were used as the weapons with the longest range until firearms were used in wars. In the 1800s, the use of resins with cross-linkable molecular structures such as celluloid, bakelite and

melamine became a turning point in the development of composite materials.

The 1930s were accepted as the years when the production of modern composite materials began. The Owens Corning company produced the first FRP composite in 1935. The first patent was obtained in 1936 for polyester resins, which are widely used in composite production today due to their curing properties. Epoxy resins with superior properties started to be used in 1938.

Especially in 1940s, World War II, interest in composites increased. Glass fiber reinforced composites have become widespread especially due to their high strength and low weight. Composite parts started to be used in automobile production in 1947 and different composite production methods were developed in the 1950s.

In 1961, the first carbon FRP composite with superior properties compared to fiberglass reinforced composites was patented. Kevlar, which has high chemical resistance, impact resistance and heat resistance, was introduced to the market by DuPont in 1971. After the 1980s, traditional materials have begun to be replaced by composite materials, which are made easier to produce with the development of different production methods and designed to perform multiple functions [50].

The successful use of composite materials, especially in military aircraft, has also ensured the reliability of commercial use. Thus, with the improvements in design and production, it has taken its place in the market with lower cost products. First of all, the composite materials used in the 2nd degree important parts of the existing parts have started to be used at a higher rate and in more areas with the increase in their reliability. In addition, improvements have been made in the field of use at high temperatures, which is one of the most fundamental problems of plastic matrix composites. While the operating temperature was maximum 120°C with the first used epoxy resins, it can be used at temperatures close to 200°C with bismalemid resins used in the following years, and up to 300°C with polyimide resins today.

Premium materials can only be used if its performance compensates or exceeds its high cost, and can find its place in new application areas. With the easier production of complex shaped parts, the provision of mass production and the decrease in material prices, both the areas of use and the amount of use of composite materials, which are a distinguished material type, have shown a high increase.

1.4. Advantages and Disadvantages of Composite Materials

In composite materials; superior properties often cannot be achieved on their own. By producing a new material from materials with certain superior properties, some of the following properties can be achieved. These can be broadly listed as follows:

- Composite materials have very high specific strength values. Thanks to these features, they are widely used in airplanes and automobiles and provide fuel savings.
- Composite materials have high fatigue strength. While the fatigue strength of steel and aluminum alloys can reach up to 50% of their static strength, this rate reaches 90% for carbon/epoxy composites.
- Composite materials have high corrosion resistance. Iron and aluminum corrode easily in the presence of water and air. While additional processes such as coating alloying are needed to prevent corrosion in iron and aluminum, corrosion can be easily prevented by choosing the appropriate material in composite production.
- One of the most outstanding features of composites is that they are impact resistant. Glass and Kevlar composites have higher impact strength than steels and aluminum alloys.
- Composite materials have high rigidity and hardness values besides their lightness.
- Composite materials have better vibration damping properties than traditional engineering materials.
- Composite materials can be a good insulator or a good conductor depending on the electrical properties of the components used in production.
- Composite materials have a good surface quality at the end of production.
- Crack propagation in composite materials can be minimized by selecting suitable material components.
- In composite materials, the desired color can be given with appropriate chemicals added to the resin during production. In this way, additional labor and expense are avoided.

Composite materials do not have all these properties together. The mechanical properties of the produced materials may vary according to the usage areas or usage conditions. The use of composite where specific strength and modulus is really needed is a significant source of advantage and provides flexibility in design. In a fiber reinforced composite material, the difference in strength or fiber modulus between fiber and matrix is important for the

mechanical properties of the composite. Classification and properties of composite materials are given in Table 1.4.

Table 1.4 Comparison of mechanical properties of composite and classical materials [51].

Material	Specific Weight (g/cm ³)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Specific Tensile Strength (G/ρ)	Specific Elastic Modulus (E/ρ)	Percentage Elongation (%)
Aluminum	2.8	84	71	30	25	-
Al-2024	2.8	247	89	88	25	8-20
Al Alloy	2.8	600	71	210	25	-
Titanium	4.51	700	117	192	21.1	20
Ni Alloy	8.18	450-1200	204	147	24.9	26-45
Unalloyed Steel	7.86	460	210	60	27	20
Low Alloy Steel	7.8	600	207	80-250	26.5	20-30
Carbon/Epoxy (%60)	1.62	1400	220	865	135	0.8
Kevlar/Epoxy	1.38	1310	83	950	60	-
Glass/Epoxy (%60)	1.66	1510	165	910	99	-
Glass/Polyester (%50)	1.9	750	38	390	19.8	1.8

For composite materials, matrix and reinforcing element, production technique, optimization technique applied, strength properties of the components and other factors should be considered. In addition, the compatibility of the components and the wettability of the matrix must be suitable in order for the interfacial bond formed between the matrix and the fiber to be strong.

Composite materials have disadvantages as well as advantages. The disadvantages of composite materials can be listed as follows;

- Besides being difficult to process, high cost and required surface quality are not obtained.
- It is not recyclable like other materials.
- Elongation at break is low.
- The production of composite materials is quite expensive compared to the production of aluminum and steel. Considering the price per unit weight, the price of composites is between 5 and 20 times higher than the price of aluminum and steel.
- Behaviors of traditional engineering materials such as elastic deformation and plastic

deformation under impact could be explained. However, the behavior of composites under impact is very different from each other. Therefore, the behavior of composites under impact has not yet been standardized and fully explained.

- Traditional materials have standardized production methods. Since composite materials consist of unlimited combinations, it is difficult to standardize production methods.
- The thermal resistance of composite materials depends on the properties of their components. The thermal resistance is low in composites where polymers are used as matrix material.
- Composite materials are affected by moisture. With humidity, the strength values of composite materials decrease [52].

1.5. Application Areas of Composite Materials

Composite materials have a wide range of uses today. Composite materials are widely used in almost all areas of industry. It is used instead of metals, especially where high strength is required. This situation increases the interest in composite materials. For this reason, composite materials have found their widest use in the transportation industry. Application areas of composite materials are given in Table 1.5.

Table 1.5 Application areas of composite materials [51].

Industry	Application Areas	Composite Materials Used
Aeroplane	Aircraft wings and fuselage, landing and exit doors, struts, trusses, frames, ventilator and turbine blades,	B/Al, SiCw/Al, Gr/Al, B/Al, glass/epoxy, C/epoxy, B/epoxy, K/epoxy, super alloy
Automotive	Body parts, bumper and fenders, front and rear panels, axle shaft, springs, pushrods and piston rods	Kevlar/epoxy, SiCp/Al, SiC/Al, B/Al
Ship	ship hull, ship deck	Kevlar/epoxy, Carbon/epoxy
Chemistry	Pipes, pressure vessels and tanks	Glass/epoxy, Carbon/epoxy
Sport	Fishing rods, golf clubs, swimming pools, tennis rackets bike and motorcycle body	Gr/Al, B/Al, C/epoxy, B/epoxy, SiC/Al, B/Al, Gr/Al, SiC/Al
Medicine	X-ray tables, prosthetics and wheelchairs	B/Al, SiC/Al
Space	rocket nozzles, turbine propellers, rocket launch systems, Space structures, antennas, robot arms, shuttles	Carbon/Carbon Composites
Other industries	Machine body	C/Pb, Al ₂ O ₃ /Pb

Although the use of thermoset composite materials is common in the automotive industry, thermoplastic materials have been used frequently in recent years due to their recycling, easy shaping and high specific strength. Automotive body parts, some engine parts, mirrors in the interior equipment, instrument panels and vehicle parts that require strength during a collision can be given as examples.

1.5.1. Construction industry

Composite materials are also widely used in the construction industry. Sink, bathtub, doors, door handles, balcony railings, cold storage, building cladding panels are examples of composite material use.

1.5.2. Marine industry

Composite materials have very superior corrosion resistance. For this reason, it is widely used on surfaces that come into contact with water. At the same time, its light weight, easier movement of marine vehicles on water, more fuel consumption and faster movement can be

shown as the reason for the frequent use of composite materials in the marine industry. Sailboat hull, yacht and boat steps, fore and aft platforms are the places where composite materials are frequently used in the marine industry [53].

1.5.3. Electric-electronic industry

Composite materials are used as a production material in the electrical-electronic industry due to their insulation properties [54].

1.5.4. Sport equipment

Composite materials are frequently used in sports equipment due to their light, durable and high vibration damping properties. Golf clubs, racing boots, tennis rackets, ski equipment, fishing rods, bicycles, etc. sports equipment can be given as an example [53].

1.5.5. Home appliances

Composite materials are used in many household appliances such as kitchen appliances, ornaments, table cabinets.

1.6. Types of Composite Materials

Composites can be divided into three different classes according to the function of their matrix: Metal Matrix Composites (MMC), Ceramic Matrix Composites (CMC) and Plastic Matrix Composites (PMC). PMCs; They exhibit relatively low raw material cost, simple production methods and an excellent cost/performance ratio compared to MMC and CMC. There are two different types of matrices, thermoset and thermoplastics [55].

Fiber-reinforced polymer composites are still an evolving class of engineering materials. They usually contain a wide variety of types, grouped broadly according to the appearance of reinforcing fibers and matrix properties (thermoplastics or thermosets). Composites are defined as materials consisting of two or more distinct phases with a recognizable phase. Accordingly, composites consist of at least three phases. Fibers are inherently stronger than bulk materials because the probability of defects decreases as the size decreases. The stiffness and strength of the most important reinforcing fibers such as glass (GF), carbon (CF), aramid (AF), natural fibers (NF) are significantly higher than that of polymeric matrices. High-strength inorganic fibers include glass, carbon and ceramic fibers. However, due to its practical importance in fiber-reinforced polymer composites, attention is focused here on glass and carbon fibers. The matrix transfers the loads to the fibers and distributes

the stresses between them. The matrix is also responsible for protecting the fibrous reinforcement from the environment and ensures the necessary positioning of the fibers. The fiber/matrix interface ensures stress transfer from the "weak" matrix to the "strong" ones and from the matrix to the fibers.

Polymer-matrix composites have advantages over carbon-matrix, ceramic-matrix and metal-matrix composites due to their ease of manufacture. Continuous carbon fiber polymer-matrix composites are more dominant in structural applications. They are usually in the form of laminates. The interface is the weak link in a laminate, but due to the effects of these parameters on the contact electrical resistance of this interface, they are temperature, damage sensors [56].

The term interface, meaning a finite intermediate layer between fiber and matrix with different physico-chemical properties, emerged in the 1970s [57]. This phase controls the interactions between fiber and matrix and thus the mechanical property profile of structural composites. Mechanical properties such as tensile strength and modulus are mainly controlled by the tensile properties of the fiber, its volume fraction, orientation (relative to loading), and length. There are some general design concepts for interphase engineering. For example, a strong bond between fiber and matrix is recommended to achieve high stiffness and strength, while a relatively weak interfacial bonding generally improves energy-absorbing performances under impact conditions. However, stress transfer and energy absorbing mechanisms appear to be completely different in polymer composites [58].

The load transfer ability of the interface is dependent on fiber/matrix adhesion, which can be physicochemical or frictional (or both) in nature [59]. Chemical reactions, intermolecular interactions, surface-induced crystallizations, phase separation events, etc. Physico-chemical additives, including friction, appear to be more important than friction in polymer composites. However, some concepts strongly induce "roughening" the fiber surface and induce differential thermal shrinkage of fiber and matrix with appropriate curing/cooling cycles. Since this interphase is a key factor in composite performance, engineering design is of interest to both academia and industry. The characteristics of the interphase are the locally dominant stress field, possible environmental attack, service temperature, etc. should be adapted based on various parameters. In addition, early detection and even recovery of the dominant defect mode in the fiber-reinforced polymer is often the main goal. Different features have been created to take into account adaptive (one-way response to environmental

change) and intelligent (two-way "communication" due to environmental change) developments in phase changes [60]. However, "interfacial engineering" appears to be a more appropriate term to encompass developments in this field.

1.6.1. Metal matrix composites

Metals are soft in their pure state and have low strength, but alloyed, hot-cold formed metals are durable. When metal materials are subjected to a load, they do not suddenly break, they just flow and distribute the load throughout the system, making it safe to use. Metals, in which the toughness and strength property pair are the most suitable, are the materials widely used in the field of mechanical and metallurgical engineering.

Some metals can be composites by being reinforced with fibers or particles. For example, metal alloy composites reinforced with fibers made of tungsten alloy can withstand temperatures as high as 1000°C and these composites are used in jet engines [1].

Metal matrix composites with the matrix function of light metals and alloys such as aluminum, copper, magnesium, titanium; It occurs when carbon, boron and some other metals form the reinforcement phase in the fiber, particle, platelet, hair-crystal (whisker) structure. These composite materials are used in nuclear power equipment, gas turbines, aerospace and automotive industries with their superior strength, wear, corrosion and hardness properties. Ceramic matrix composites are a group of materials with superior thermal resistance and strength, formed by the reinforcement of ceramic matrix materials (such as Al_2O_3 , Si_3N_4 , SiC) as ceramic or metal particles, platelets, bristle crystals or fibers [61].

Carbon fibers conduct electricity and heat quite well compared to polymer and ceramic matrices. For this reason, carbon fibers can not only serve as reinforcement in the structure, but also add conductivity to the composite. At the same time, since their thermal expansion coefficients are close to zero, they can also give these properties to the material. They can be used comfortably in space shuttles with their very low thermal expansion and good heat conductivity. Because of the increase in thermal conductivity of carbon fibers by graphitization, graphitized carbon fibers are used where high conductivity is required. Since they are more cathodic than all metals, they form a galvanic structure in which the metal acts as the anode in every structure they form with metal matrices. This causes corrosion in the metal structure. To prevent this, coating is generally used in metal-matrix carbon fiber composites [26].

1.6.2. Ceramic matrix composites

Although ceramics are low density, durable and hard, they are very brittle, in other words, they do not flow plastically. Their brittleness makes ceramics potentially unsafe. In addition, ceramics generally have high thermal and chemical resistance. However, their high melting temperature and hardness make them difficult to process. In addition to their higher costs, parts made from these materials have to be designed more carefully and accurately. Ceramic composites are prepared from matrices such as $\text{Li}_2\text{O}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$, SiO_2 and $\text{BaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Si}_3\text{N}_4$. As reinforcement, mostly Al_2O_3 , SiC , Si_3N_4 are used [1].

Although ceramics are low density, very durable and hard, they are extremely brittle. They are generally resistant to thermal and chemical effects. However, their high melting temperature and hardness make them difficult to process and they are insulators. Their vulnerability makes them potentially unsafe. Polymer matrix composites are formed as a result of reinforcement or reinforcement of advanced plastic-polymer group matrix materials, mostly with hard, durable materials in the form of fibers [1].

Carbon fiber ceramic matrix composites are more resistant to oxidation than carbon-carbon composites. The most used area of this structure is carbon fiber-reinforced concrete. Although the structure of concrete is alkaline, which causes oxidation, there is no harm in using it because the chemical stability of the carbon fiber used is much better than other fibers (glass, polypropylene, etc.) [62].

The production of carbon-carbon composites is generally done by liquefying the carbon structure and combining it with carbon fibers. In this process, carbon fiber and carbons are impregnated and become sequentially wound on the mandrel [63].

1.6.3. Polymer matrix composites

Polymer literally means multi-part. A polymer material can be thought of as a solid containing many chemically bonded parts or units, or as parts or units bonded together to form a solid. Plastics are a group of artificial materials that are shaped or molded in a certain way [64].

Organic polymers form the main material of plastics. These are usually large molecule organic compounds. When examined chemically, it is seen that generally carbon (C), hydrogen (H), nitrogen (N), oxygen (O), silicon (Si), sulfur (S), chlorine (Cl) and fluorine (F) elements are present in plastics. When these elements react with various methods, very

large and complex molecules called macromolecules are formed and thus polymers are formed [65].

Chemically large polymer molecules cannot be obtained directly. First of all, active groups called monomers must be produced. For example, when heat and pressure are applied to the ethane molecule with its chemical formula ($\text{CH}_3\text{-CH}_3$), it loses 2 hydrogen atoms and a double bond ($\text{CH}_2 = \text{CH}_2$) is formed between the carbon atoms by rearranging the electrons in the molecule. In this way, the four energy bonds of the carbon atom are saturated and a stable compound called "ethylene monomer" is obtained [65].

In order to obtain high molecular organic compounds called polymers from monomers through polymerization, millions of monomers are kept under the influence of temperature and pressure in a reactor. In this environment, where certain catalysts are also present, the double bonds of the carbon atoms forming the monomers are rearranged and the double bond between the carbon atoms turns into a single bond by forming a free bond on each side of the carbon atoms. The free bonds are linked by the free bonds of other monomers to form a stable chain-like compound. With the monomer continuously attached, the chain grows larger and the reaction continues until it encounters stray hydrogens attached to the free ends of the chain. At this moment, the reaction stops and the chain is completed [65].

The length of the chain significantly affects the properties and technology of the plastic material. As the chain length increases, the toughness, creep strength, melting temperature and viscosity of the plastic increase. Not all chains that make up the plastic can be produced in the same length, so there are certain differences between them. In this respect, the length of the chains that make up the polymer shows a certain statistical distribution [65].

To examine the physicochemical properties of plastics:

- Specific gravity: One of the most important features of plastics is that they are light as a building material. Most of the plastics have a specific gravity between 1-2 and this provides a great advantage over metals with a specific gravity between 1.7-12.
- Specific heat: Since the production of various articles from plastics generally requires heating of the raw material, the cost of the heating process increases as the specific heat of the material increases, and the specific heats of plastics are generally higher than metals. In this case, plastics heat up more difficult and cool down later than metals.
- Thermal Properties: The characteristic of plastics that differs from other materials is their

thermal conductivity. The thermal conductivity coefficients of plastics are very low and therefore they are used in thermal insulation works.

- Thermal expansion coefficient: The thermal expansion coefficients of plastics are much higher than metals, in many cases the expansions that occur as a result of temperature changes cause problems. Especially in molded production, significant problems arise due to shrinkage and therefore they cannot be molded and cast in small tolerances such as plastics and metals.

- Useful temperature limits: Thermal decomposition temperature; It is the temperature at which the plastic starts to decompose. Another important temperature for plastics is the Vicat softening temperature, and depending on this temperature, the temperature at which the plastic material will soften is determined and the material is used in suitable areas that do not exceed this temperature.

- Melt Index: The melt index value of a plastic depends on the average molecular weight of the polymer. Accordingly, as the molecular weight increases, there will be a decrease in the MI value, and the plastic material will have less fluidity.

- Flammability: The combustion characteristics of plastics are very important. The rate at which the combustion spontaneously spreads after the plastic starts to burn is as important as the temperature at which the combustion starts.

- Weathering: Chemical deterioration causes the polymers to wear out over time. This deterioration may occur due to thermal, mechanical, photochemical, biological and chemical factors.

- Light and permeability

- Refractive index

- High energy radiation effects

- Water absorption: Most plastics are insoluble in water, but they can absorb some water. Water absorption can change the properties and therefore the effectiveness of the plastic can be reduced. For example; A significant deterioration in electrical properties is observed, and mechanical strength decreases. In raw plastic, moisture makes production difficult and causes defects in the final product.

- Solvent resistance: In order for a solvent to dissolve plastic, this solvent must overcome the intermolecular forces in the plastic. Solvents dissolve by getting between the plastic

molecules and separating them. The weaker the intermolecular bonds in the plastic material, the easier the solvent separation process.

- Distortion: When stress is applied to a material, a deformation (a contraction in cross section) occurs in the material and this can be found experimentally. Distortion; It is the sum of the microscopic changes that occur in the material at the atomic and molecular scale.

- Electrical Properties: In general, the electrical conductivity of plastics is weak. In order for polymers to conduct electricity, they must have free electrons or ions in their structure, and these electrons or ions must be able to move freely in the structure. However, because of the rigid and rigid chains in the structure of polymers, the strong influence of these chains on each other, the high crystal structure and orientation, the electrons in the structure can move freely and this causes plastics to have low electrical conductivity [65].

If it is necessary to examine the chemical properties of plastics;

Amorphous structure: It is the formation of an irregular structure by making random rotation and bending movements of the polymer chains. The structure is glassy and brittle. When voltage is applied to such a structure; It is expected to show very little deformation.

Crystalline structure: In crystalline polymers, atoms are located at certain points and are in an immobile arrangement.

Orientation: Orientation, the third form of intermolecular order, is observed in polymeric fibers, films and foams. If a molten polymer is cooled, randomly oriented an amorphous or crystalline structure is formed. During solidification; If the polymeric material is pulled, the polymer chains are oriented in the direction of attraction. In order for orientation to occur, the chains must have mobility within the structure. Therefore, the orientation takes place over amorphous regions. If the crystalline structure does not contain enough amorphous regions, no orientation is observed in this material [65].

The mechanical properties of plastics are greatly affected by temperature. Accordingly, it can be said that the mechanical properties of plastics are temperature-controlled. Some mechanical properties of plastics are as follows [65].

- Tensile properties: The tensile stress-elongation test of a plastic is similar to the tests performed on metals. The difference is the upload speed. In order to accurately measure the elongation in tensile tests on plastics, it is necessary to load at a constant speed.

- Stress-strain curves: Stress - % elongation, graphed in binary coordinate system, gives

important information about the mechanical properties of plastics [65].

- Young's modulus: The modulus of elasticity of a plastic material is the rate of elongation caused by the applied stress in the material. It is also the slope of the initial linear region of the curve.
- Tensile strength: It is the maximum tensile stress that the material can withstand without breaking.
- Yield stress: It is the stress value at which inelastic deformation, that is, plastic deformation, begins.
- Elongation at Break: It is the size change of the material at the breaking point and is always determined as a % of the initial length.
- Breaking energy per unit volume (Toughness): It is the amount of area under the tensile stress - % elongation curve and is a measure of the durability of the material [65].

Depending on the above parameters obtained in the experiments, the mechanical properties of plastics can be explained in these terms [65].

- Hard / Soft: Indicates that the Young's modulus is high or low. A material with a higher Young's modulus has stronger bonds, therefore a higher rigidity, it is harder. The opposite is true for soft materials.
- Strong / Weak: Indicates that the yield stress is high or low.
- Brittle: Indicates that the material will break or break before it reaches the yield stress.
- Durable (Ductile): Indicates that the unit energy required for the material to break is very high [65].

Plastics are important engineering materials for many reasons. Many of its properties are not available with other materials and are often relatively inexpensive. Other reasons for choosing plastics include: the possibility of design with fewer parts, reduced surface finishes, simplified assembly methods, weight gain (or ease of transport, light weight). Plastics are particularly suitable for many electrical engineering designs, as they have excellent insulating properties [64].

Depending on the chemical bond in their structure, plastics are divided into two classes: thermoplastics and thermoset plastics. For this reason, polymer matrix composites are divided into two main groups depending on the polymer used as the matrix phase:

thermoplastic and thermoset based composites [64].

Hundreds of plastics with different structures and properties have been developed to be used for various purposes in the industry. However, many of these are very expensive or difficult to process plastics. Most of the plastics used today are thermoplastic materials such as polyethylene, polypropylene and polyvinyl chloride. In recent years, polymethyl methacrylate and acrylonitrile butadiene styrene plastics from thermoset materials have been used as engineering materials in the form of plates, rods and pipes [65].

Polymers are classified in several ways:

- 1) By chemical composition: Organic, inorganic
- 2) According to their structure: Homopolymers, copolymers, terpolymers
- 3) By processing basis: Thermoplastic, thermoset
- 4) By area of use: Plastics, fibers, coatings
- 5) According to their physical structures: Amorphous, crystalline, semi-crystalline [65].

1.7. Basic Components of Composite Materials

A composite material consists of matrix materials reinforced with fibres. To understand the behavior of a composite material, it is necessary to know the functions of the fibers and matrix materials in the composite material. Important tasks of fibers and matrix materials are given below.

Duties of matrices in composite material are given below [66].

- Matrix material holds the fibers together, thus preventing the individual movement of the fibers.
- Transfers dynamic and static loads on the composite material to the fibers.
- The matrix material gives the shape of the composite material and also ensures that the material remains solid.
- Matrix material protects the composite material against chemical and physical damages caused by environmental factors.

The duties of the fibers in a composite material are given below [66].

- The fibers carry most of the load of the force applied to a composite material.

- Fibers make the composite material stable with its high elastic modulus, stiffness and resistance at high temperatures and other structural properties.
- The fiber material used in the composite determines the electrical conductivity or insulation properties of the composite material.

1.7.1. Matrix materials

Resins are polymeric additives found in fiber reinforced composites. The common point of all polymers is that they are composed of small molecules that bind together to form a long chain structure. Resins that are not natural and result from a certain production process are called synthetic resins or resins. Polymers are divided into two according to their reaction to heat: thermoplastic and thermoset.

Thermoplastics: Thermoplastics are called solid materials at room temperature. It softens when heated, and its viscosity decreases as the temperature increases. This feature makes the products made from them more economical and allows them to be shaped easily. It hardens again when it is cooled again. The viscosity state is high at temperatures where it is in liquid form. Therefore, interfacial bonding is more difficult than thermosets. However, their use is widespread due to their good forming capacity. These polymers can be crystalline or amorphous. In those with crystalline form, the molecules form highly regular shapes over large distances. In amorphous polymers, on the other hand, long chains are entangled at many points. It is used with pulp or sheet molding method in a small volume environment with short fiber [1]. Table 1.6 contains the physical and mechanical properties of thermoset matrix materials.

Table 1.6 Mechanical and physical properties of some thermoset materials [1].

Specifications	Epoxy Resin	Polyester Resin
Density (g/cm ³)	1.11	1.04 – 1.46
Elastic Modulus (MPa)	7000	3400
Tensile Strength (MPa)	70	41 – 90
Ultimate Strength (MPa)	3 – 6	4.2
Thermal Conductivity	0.19	0.19
Thermal Expansion Coefficient (1/C°)	45 - 65	55 - 100

Thermosets, on the other hand, form a hard and durable structure as a result of the chemical interaction of two separate components, and this reaction is irreversible. In some thermosets, volatile by-products may be formed as a result of this chemical reaction. Since there is no formation of these by-products in resins such as polyester and epoxy, this type of thermoset

is more preferred in the industry. After the curing process is completed, thermosets cannot be reheated to their original state. However, the mechanical properties of the thermoset change significantly above a certain temperature. This temperature is called the "Glass Transition Temperature" (T_g) and is different for each resin. At temperatures above T_g , the rigid structure of the thermoset deteriorates and a transition to a more flexible and amorphous structure occurs. This physical change is restored when the temperature is lowered below T_g . The water impermeability, color stability, shear and compression strength values of the resin are also negatively affected at temperatures above T_g [67].

Thermoset matrices are formed as a result of a chemical reaction that turns small monomer molecules into long polymer molecules with strong bonds between them. Thermosets are obtained by polymerization in two stages. While the first one starts in the reactor where the monomers containing the material are brought together by the linear chains, the parts that do not react with the temperature and pressure during the molding process of the second polymerization process become liquefied and the molecular chains have a three-dimensional structure. A solidifier is usually used for this reaction to take place.

With the addition of a thickener, they first become gels and then solidify. These cannot be softened by reheating. Thermoset resins are isotropic. Thermal stability, chemical resistance, low density are the advantages of thermoset resins. Limited working time at room temperature, long fabrication time for solidification, low elongation at break are disadvantages [68].

Epoxy and polyesters are matrix materials commonly used in fiber-reinforced composites. Their physical and mechanical properties depend on the size and density of the molecules and the length of the crosslink. However, polyesters wet fiberglass well and fillers can be used. The disadvantage of these is that they shrink (shrink) by 10% during hardening. This shrinkage causes the fibers to buckling under compressive stresses [68].

Thermoset materials cannot be remelted and shaped after curing. During the curing process, molecular chains cross-link while thermoset materials solidify. Therefore, molecules cannot be remelted and shaped.

The higher the crosslinking density, the more rigid and thermally stable the material. Polyimides are moldable polymers with the highest thermal resistance among plastics [68].

Common thermosetting resins; epoxy, polyester and vinylester. These materials can be a one-piece or two-piece system and are generally in liquid form at room temperature. These

resin systems are raised to high temperatures or finalized at room temperature.

Advantages in processing thermoset composites;

1. Because the initial resin system is in liquid form, thermoset composites are easy to process.
2. Since the fibers can be easily wetted with thermosets, the gaps and pores are less.
3. In the processing of thermoset composites, heat and pressure requirement is less than thermoplastic composites. This provides energy gain.
4. Simple and low-cost equipment can be used in the processing of thermoset composites [68].

Disadvantages of thermoset composite processing;

1. Thermoset composite processing requires long curing times, resulting in lower production rates than thermoplastics.
2. Thermoset composite parts, once cured and solidified, cannot be reshaped.
3. Recycling of thermoset composites is a problem [68].

- **Phenolic resin**

The most important feature of phenolic resins is their high flammability (ignition) resistance. They show good dimensional stability when the temperature drops suddenly. They have high chemical resistance and abrasion resistance. Unlike other thermoset resins, water is formed in the environment during production (condensation reactions) and this water must be removed from the environment most of the time. Their electrical insulators are good and their densities are low. They are widely used in electronic applications, ballistic applications, joining wooden structures. The most well-known is bakelite.

- **Epoxy resin**

It began to be produced simultaneously in Europe and the United States in the early 1940s. The first epoxy resins were often used in coating and molding parts. Due to their many varieties, they can be found in many physical forms from low-viscosity liquid to solid with relatively high melting temperature.

In this case, it makes them different from other thermosets used for composites and provides a wide range of production and application areas. Epoxy resins generally have high strength,

low shrinkage, chemical resistance and low cost compared to polymers. Epoxies, which can be cured with many chemicals, can also bond well with many materials. Because of these properties, epoxies are good matrix materials for composite materials.

Today, epoxy resins are used as adhesives, coatings and molding materials. Epoxy resins have provided the desired properties in plastic-based composites used in the aerospace industry. Now these epoxy resins are used in many fields from automobile to musical instrument.

When choosing a thermosetting resin, tensile strength modulus, compressive strength and modulus, notch sensitivity, impact resistance, glass transition temperature, flammability, and material accessibility are taken into account [69]. In this context, epoxy resins have a balanced composition in terms of chemical and mechanical properties.

Epoxy resins are a wide family of thermosetting polymers whose basic building block is a cross-linked oxygen and a two-carbon cross-linking compound. Unannounced carbons in this basic molecule bond with other molecules to produce epoxy resins. The most commonly used substance in the production of epoxy resin is epichlorohydrin. The first thing to consider in the use of produced epoxy resins is the glass transition temperature. While it exhibits a brittle structure below this temperature, it exhibits a more rubber-like behavior above it [70]. Above the glass transition temperature, the strength modules of the epoxy resin are several times lower than the values below the glass transition temperature. In this context, the glass transition temperature is an important factor in the choice of epoxy resin. The glass transition temperature generally depends on the molecular structure of the cured epoxy resin during curing and the density of crosslinks. Generally, as the curing temperature is increased, the glass transition temperature rises, but only up to a certain point. It should also be noted that the pure resin, curing agent and modifiers are important factors. There are many epoxy resins with different chemical and mechanical properties depending on the type of production and the place of use, except for the temperature of use. In epoxy resins, amine, amine derivatives and anhydrides are generally used as curing agents. The curing temperature ranges from 5 to 260°C, while curing can take as little as minutes or even days.

Apart from curing agents, other important additives affecting epoxy resin are modifiers. These provide specific physical and mechanical properties to the resin. As a rubber additive, it provides fatigue resistance, flexibility and toughness. However, it reduces the values in strength and modules and lowers the glass transition temperature. Thermoplastic additives

are generally added to increase fracture toughness. Thermoplastics do not affect the glass transition temperature like rubbers. Some resins are also used as diluents. Generally, epoxies with very low viscosity are added to other epoxy resins as diluents. However, their use causes a decrease in thermal and mechanical properties.

Flame retardants reduce flammability by using as filler or matrix material in epoxy resins. In general, the more C and O in the polymer structure, the more flammable it is. The presence of halogens or charring aromatics in the structure reduces flammability.

Another additive material added to epoxy resins is non-reactive filling materials. They are used especially as reinforcement material to change certain physical properties such as low density, thermal and electrical conductivity, and shrinkage-reducing effect. These filling materials can be in the form of powder, spheroid, short fiber, flake, crystalline filament. While these are added to the epoxy resin, attention is paid to their grain characteristics, mechanical strength, ratio by volume, adhesion by bonding with epoxy.

Finally, pigments or dyes can be added to give color to the epoxies. Paints can be dissolved in epoxy resin while pigments are insoluble in epoxy resin. However, the paints are not resistant to high temperatures. Apart from these, it is used as an additive in flexibilizers, plasticizers, antioxidants and antifoams.

- **Polyester resin**

Polyester resins are the most widely used resin type in the composite industry. They are used in the construction of composites used in the construction of boats, especially in the maritime industry.

Polyester resins are generally unsaturated and can be cured with various reinforcements under the right conditions. After this curing, they reach a hard and durable structure. Depending on the type of reinforcement used, they can add different properties to the resulting composite structure.

There are two types of polyester resins used in the composite industry. Orthophthalic polyester is widely used because of its lower cost. Isophthalic polyester, on the other hand, has started to be used frequently in places where very high water resistance is required and especially in sea vehicles [71].

- **Vinyl ester resin**

Although they are very similar to polyester resins in terms of molecular structure, they are

more resistant to shock loads than polyesters, with fewer reactive ester groups and presence at the two ends of the molecule. At the same time, it differs with its more flexible structure compared to polyesters. Since the ester groups at the ends of vinyl esters are more sensitive to water loss by hydrolysis, vinyl esters show higher resistance to water and other chemicals than their polyester counterparts. With this feature, it can be used in pipes passing chemicals, chemical tanks and pipelines.

With its water-resistant feature, it can be used as a coating on polyester in some cases, adding extra water-resistance in boat manufacturing [71].

- **Cyanate resin**

Cyanate ester resins have very good strength and toughness properties. Their toughness can be further improved by the addition of thermoplastic materials. They are less affected by moisture than other resins. Cyanate esters can be cured more easily than epoxy resins. They are used in space vehicles, microelectronic systems, missiles, radar systems.

- **Bismaleimide and polyimide resins**

Bismaleimide and polyimide resins are used in high temperature environments, especially in missiles, spacecraft and electrical circuits. The glass transition temperatures, where they lose their glassy properties and start to gain viscous properties, are higher than polyesters and epoxy resins. However, they are less preferred than epoxy resins due to their lower toughness values, difficulties in production and high moisture retention properties.

- **Polyurethane resin**

Polyurethane resins can have thermoset and thermoplastic properties. Thermoplastic polyurethanes have linear molecular bonds while thermoset polyurethanes have cross-links. Polyurethane resins can have different properties with appropriate formulations. They are preferred because they have high abrasion and chemical resistance, elasticity, toughness and impact resistance. Automobile bodies and tires, furniture parts are the places where they are most commonly used [72 - 74].

1.7.2. Reinforced materials

Fiber-reinforced composite materials are composites that are produced by equipping them with fibers that will improve these properties for purposes such as improving the weak aspects of the weakly structured brittle material, removing the fragility, and making the

material ductile. The fiber definition is made as macroscopically homogeneous, flexible materials with a length of at least 100 times the cross-section, and different fibers are used for reinforcement in composites. In fiber-reinforced composites, the main component that meets the external loads is fiber, and the polymer matrix creates the environment that holds the fibers together in the desired geometry [21, 25].

While preparing fiber reinforced polymeric composites, some basic points should be considered in terms of fibers. These points are: the mechanical properties of the fiber, the amount of fiber, the fiber thickness and the orientation of the fiber. The strength of the fibers is very important for the strength of the composite structure. In addition, as the length/diameter ratio of the fibers increases, the amount of load transmitted by the matrix to the fibers increases. As a general rule, the mechanical strength of composites increases as the fiber content increases, and starts to decrease after the fiber ratio reaches a certain value. The reason for this is that the amount of polymer in the composite decreases depending on its increase. When the ratio of polymer in the composite falls below a certain value, it loses its matrix function and cannot hold the fibers together [25].

Fiber thickness is another important factor affecting composite properties. In composites prepared with thin fibers, the area where the polymer wets the fiber is large. Increasing the fiber-polymer contact surface facilitates the load (energy) distribution within the composite by increasing the fiber-polymer interactions. For this reason, among the composites reinforced with thin and thick fibers in the same mass, the one reinforced with fine fibers is more durable.

Morais et al. determined the effect of layer thickness on the resistance of composites reinforced with glass, carbon and aramid fabrics against repeated low-energy impacts for two degrees of impact energies. The obtained results showed that under a certain energy level, the most variable impact resistance determined on the subject is the cross-section of the layer [75].

When fibers are bundled, they are always more durable than the bulk form of the polymer used in their manufacture. When an external effect is made on the fiber bundle, some of the fibers in the bundle may break or crack, scratch, etc. defects may occur on their surfaces. Such damages of the bundle in the face of external forces are limited to the affected fibers only and are not transferred to other fibers in the bundle. A defect occurring in any part of a bulk material (glass piece, polymer piece, etc.) progresses through the material and may

eventually render the material unusable. This feature is one of the advantages of fiber reinforced composites.

The placement of the fibers in the matrix is an important factor affecting the strength of the composite structure. By placing the long fibers in parallel to each other in the matrix, high strength is provided in the direction of the fibers, while very low strength is obtained in the perpendicular direction to the fibers, equal strength is provided in both directions with two-dimensionally placed fiber reinforcements, while it is possible to create an isotropic structure with homogeneously dispersed short fibers in the matrix structure. By placing the fibers in the composite in suitable geometries, it is ensured that the composite gives different responses in different directions to loads such as tensile.

For example, the tensile strength of the composite will be greatest at loadings made at an angle of 90 degree to the axis to which the fibers are oriented. Similarly, behaviors such as impact strength, thermal conductivity and thermal expansion are angularly dependent on the orientation axis of the fibers. The reinforcement made with the fibers allows the directional control of the mentioned properties by adjusting the fiber orientation [25]. All of the fibers used in the composite material structure are called reinforcing elements.

- **Glass fiber**

Glass fibers are currently used in almost 90% of reinforcement applications to thermoset and thermoplastic matrices and are used in industrially produced space vehicles, submarines, etc. There are many products. The oldest and still the most used form of glass fibers is E glass. Other fiber types can also be used when different properties are required, such as S glass, where particularly high strength is required.

Fiber-reinforced materials generally have a stronger structure than their unreinforced counterparts. As the glass fiber ratio increases, the strength of the material also increases [76].

Normal glass fibers are three times stronger than steel and show a tougher behavior compared to the weight of the steel. In general, hand lay-up products produced using non-woven glass fiber have 40-50% less strength than products made from woven fibers. However, in some structures, composites produced with specially arranged fibers show similar or sometimes better properties than composites produced using weaving [76].

Reinforced plastics are generally applied in several layers in laminate construction. In this

application, there are many important parameters that will affect the properties of the final product. A few of these are the number of layers (felt) applied, the matrix type, the fiber/matrix ratio, the fiber type and the orientation of the fibers. Only filaments or fibers have limited use in engineering. A support is needed to hold them in a structure or mechanism. In this case, a polymer matrix is used in which the fibers can be embedded and placed, which can keep the fibers in the same shape and constant, prevent the fibers from bending and break, and provide force transfer between the fibers. The matrix will often be weaker, lower elastic modulus, and lower density than the fibers. Without fibers it cannot withstand high stresses. When the fibers and matrix are in a composite material, they create a synergy and create combinations of high strength, rigidity and toughness, very different from using them separately.

Long and short cropped, continuous etc. Glass fiber types have a wide range of uses, and they improve the strength, dimensional and thermal stability, corrosion resistance, dielectric properties, etc. of both thermoset and thermoplastic materials. increase their properties. Apart from compression and impact properties, glass fibers have high strength and low elongation, higher elastic modulus and better bending strength. In addition, thanks to their high temperature resistance and low moisture retention, the dimensional change is very small and their resistance to ambient conditions is very good. Finally, its low moisture retention makes it easy to prepare mold components with good electrical properties in a wide variety of weather conditions. However, there must be a suitable bond between the fiber and the matrix. Otherwise, a great decrease in the mechanical properties of the polymer is observed as moisture escapes between the resin and the fiber.

In addition to all these, the fiber itself also shows elastic properties. It will stretch uniformly to the breaking point when force is applied and will return to its original dimensions when the load is removed. This lack of hysteresis, combined with high mechanical stresses, allows the fibers to store and release large loads without loss of energy. At the same time, if there is protection against abrasion, this feature increases the dynamic phatic resistance to very high levels, making it effective for use in a wide variety of applications [76].

It is composed of glass silica sand, limestone and oxide-containing materials. By adjusting the chemical composition at different rates and using different production techniques, very different glass fiber structures can be obtained. However, these different glass types show typical glass properties such as hardness, corrosion resistance, reluctance to chemical reactions and lightness, easy to form. In addition to these features, glass is a cheap material.

All these features make glass one of the indispensable materials of the industry.

While glass types have approximately the same stiffness values, they have different strength values and different resistances to the negative effects of the environment. Due to its low alkaline properties, E glass has better electrical insulation than other glass types. It has high tensile strength, good corrosion resistance and is also inexpensive. Although S glass has the highest strength values among glass types, its applications are limited because it is an expensive glass type. However, they are still an alternative to carbon fibers in terms of both strength and price. C glass has high corrosion resistance while D glass has low dielectric constant. D-glass is used as core material in high voltage ceramic insulators. While A-glass is resistant to alkalis, R-glass is the American equivalent of E-glass used in Europe.

Glass fibers have higher strength before they are placed in the matrix. While the yield strength of E-glass fibers alone is 3.5 GPa, this strength in the matrix decreases to 1.75 GPa. Similarly, the yield strength of S-glass fibers is 4.5 GPa outside the matrix and 2.1 GPa inside the matrix. These remarkable reductions in yield strength are usually due to damage during production. While the tensile strength of glass fibers decreases with increasing temperature, their corrosion resistance also depends on the components that make up the glass fibers.

- **Silica and quartz fiber**

Silica fibers and Quartz fibers differ from conventional glass fibers due to the amount of silica component they contain. While the silica in glass fibers is in the range of 46%-75%, this ratio is in the range of 96%-98% in silica fibers and in the range of 99.95%-9.97% in quartz fibers. While the mechanical properties of silica and quartz fibers such as stiffness and strength are better than glass fibers, their prices are 25%-50% more expensive than glass fibers. While silica fibers can perform their duties for long periods of time at 900°C, quartz fibers can be used at temperatures up to 1050°C. While silica and quartz fibers are less affected by humidity and chemical environments, another feature is that they pass radio frequency. Silica and Quartz fibers are used in spacecraft because of all these properties.

- **Boron fiber**

Boron fibers are actually composite in themselves. They are produced by coating boron on a thin filament called the core. This is because boron has a very hard and brittle internal structure. The core is usually tungsten. Carbon core can also be used but this is a new application. Boron fibers are the thickest fiber type used in composite materials and are

approximately 20 times thicker than carbon fiber. It has high buckling, tensile and compression strengths. It is generally used in metal matrices [77].

- **Carbon fiber**

Carbon is a crystalline material with a density of 2.268 g/cm^3 . Carbon fibers are a group of fibers that developed after glass fibers and are widely used. The most important properties of carbon fibers, which are generally used with epoxy resins and polyester resins, are high toughness as well as density. Carbon fibers are not affected by moisture and their creep strength is very high. They have higher strength than steel and are extremely solid. For this reason, they have a widespread use in military and civil aircraft structures, automotive industry and sports equipment.

The use of carbon fibers as a reinforcing element is due to the characteristic feature of the graphite crystal. The crystal lattice plane of the carbon graphite crystal has a hexagonal hexagonal fold structure, and the angular carbon atoms have a covalent bond. The floors are connected by Van der Waals bonds.

Carbon fibers are one of the most important reinforcements used to achieve high stiffness and high strength. The term carbon fiber covers a wide range of strength and stiffness. Due to their excellent mechanical properties and light weight yet low density, carbon fibers are mostly used in high-end products in aerospace, military and some medical and sports applications. For this reason, they have a relatively high cost. However, they are also used in new environmental regulations to reduce the weight of cars, trucks, airplanes and even trains as the main solution to reducing gas emissions in transport. For this purpose, it is aimed to replace metallic parts with composite parts and to realize hybrid metallic composite parts. The United States, Western Europe, and Japan have leading aerospace and defense industry-related carbon fiber reinforced composite markets. There are three main markets in Western European countries: aerospace and defense, automotive and windmills industries. Japan is the main producer of carbon fiber as a raw material and the third largest market for carbon fiber-based composites. On the other hand, China is a very fast growing market due to the development of wind energy and aerospace and military applications [78].

The main problem of the industry in the use of carbon fiber is that the required cost per kilogram of carbon compound is too high compared to other fibers. Possible solutions that could increase carbon fiber production and lower the price include developing the supply chain for carbon fibers that are cost-effective enough for automotive applications; There

may be issues such as strategic alliances and organization of joint ventures between automakers and carbon fiber manufacturers [79].

- **Aramid fiber**

Aramid fibers are generally characterized by having very high strength, medium modulus and a very low density. Aramid fiber composites adapt well to the stress curves left by the carbon fiber family on the one hand and the spacing between the glass fibers on the other hand. Aramid fibers are fire resistant and perform well at high temperatures. They are both electrical and thermal insulators. They are resistant to organic solvents, fuels and lubricants. A major difference to aramid fibers is that in their non-compound form they are highly sensitive and do not behave as brittle as in both carbon and glass fibers.

The tensile curve of aramid fibers is basically linear versus defect. It has two distinct categories where the modulus of elasticity is approximately the same 60-70 GPa as glass fiber and a modulus of approximately twice that level. They are generally higher modulus materials that can find use in composites. It has applications in composites, especially in ballistic applications, where high strength is required. The specific performance, strength/weight and hardness/weight ratios of aramids are their primary advantages. Because the density of aramid is in the range of 1.39-1.44, high modulus aramids may have higher specific modulus than some carbon fibers and all glass fibers [80] and medium to ultra high strength, medium to low elongation and they are characterized by moderately high to ultra-high modulus [80].

Its very low density, high tensile strength and high strength make aramid fibers highly suitable for ballistic applications as a "dry" fabric or as a composite. It should be noted that some aramids have a relatively low compressive strength. Therefore, they require special care when used in compression or bending.

The breaking strength of aramid yarn is 3045 MPa, ie five times that of steel (under water, aramid is four times stronger) and twice that of glass fiber or nylon. The high strength is a result of the aromatic and amide group and high crystallinity. Aramid maintains its strength and modulus at high temperatures up to 300 °C. Aramid fiber applications articles are used in composites such as aircraft, military vehicles and others in the category of fabrics in clothing such as reinforcement and fire protection clothing or bulletproof vests. In addition to aramid fibers; It is also used in products such as protective gloves, helmets, body armor, pressure vessels, flame and cut resistant clothing, ropes, cables, tennis racket strings and

hockey sticks [81].

Environmental regulation of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) application in recent years has significantly restricted the use of aramid fibers, even though they are still mainly used for some military and security applications such as armors and helmets [82].

- **Natural fiber**

The market for bio-composites with bio-based fiber reinforcements and/or bio-based matrix is growing rapidly, especially in Europe. These composites can be classified into two main categories: Wood Plastic Composites (WPC) and Natural Fiber Composites (NFC). The USA and Canada and North America are the main markets for WPCs, with key applications in decking, siding and fencing in the construction industry. NFCs dominate the European market for automotive applications [83].

The biggest driver of the growth of this market is the increasing demand for lightweight and environmentally sustainable composite materials in various applications such as automotive and construction. Increasing concerns about passenger safety, government demands for better fuel economy and end-of-life directives and high acceptance of environmentally sustainable composite materials are the main drivers of growth for this segment [84].

Among natural fibers, flax, hemp and kenaf natural fibers can be considered as potential composite reinforcement materials instead of glass fibers due to their good mechanical properties such as certain modulus and strength. Scientific studies are carried out to find solutions to improve the natural variability of natural fiber quality and their poor compatibility with matrix polymers. However, properties such as poor service life and very low thermal stability are important issues that need to be addressed and investigated in the future regarding the use of natural fibers in composite structures [85].

- **Polyester fiber**

Polyethylene terephthalate-based polyester fibers are generally used with glass fibers and provide higher hardness, abrasion and impact resistance to the material [86].

- **Ceramic fiber**

Ceramic fibers are produced from metal oxides. They have high thermal resistance, high elastic modulus and chemical resistance. They are generally produced from aluminum oxide, aluminum-boron-silicate, aluminum-boron-chromium. They are generally produced

in the form of cloth and felt [86].

- **Basalt fiber**

Basalt fibers are obtained by melting and extruding volcanic basalt rocks. While the mechanical properties of basalt fibers are better than glass fibers, their price is lower than that of carbon fibers. They show very good thermal and chemical stability, have high strength and stiffness values, have good corrosion resistance. They can form a strong bond with the matrix and are not affected by radiation. Like other fiber types, they do not have a long history of use. However, future usage areas for heat applications and structural applications are seen to be wide.

- **Metallic fiber**

Metallic fibers are obtained by producing metal materials in fiber form for different needs. For example, Aluminum fibers can be used for applications where lightness is required, Steel fibers for strength applications, and Tungsten fibers for applications where rigidity is important. Metallic fibers can also be used in situations where electrical and thermal conductivity are important [87].

1.7.3. Filling materials

Fillers are materials added in solid form, different from the composition and structure of the matrix. In general, it constitutes 40-65% of the laminate material by weight. They are the materials that have the least cost among the products and are used as a cost reducer. In addition, fillers are important in controlling the mechanical or physical properties of the final product [88].

They are generally found in inorganic form, but there are also organic ones. Inert fillers have the effect of increasing density and reducing cost. Active fillers, also known as reinforcing fillers, have significant contributions to mechanical or physical properties [88].

Fillers and reinforcing materials, which are widely used today, make clear differences where they are used. Although the main goal is to reduce the cost of mold components, today the priority has been to change the plastic properties as desired [88].

Ineffective fillers directly affect the density. With the addition of fillers, the molecular chains of the material to be reinforced cannot be found as they should normally be. The bonding of the polymer segments to the surface of the fillers by primary or secondary bonds,

respectively, causes the bonding segments to become immobilized and the polymer matrix to have a proper alignment [88].

It is important that the fillers have a regular distribution in the matrix, rather the polymer chain comes into contact with the free filler surface. In addition, the free surface energy and the polarity of the bond between the filler and the matrix are important in this respect [88].

The main difference between them is that tensile strength can be increased only with active fillers, except that inert and active fillers, as well as spherical fillers such as glass spheres and talc, all slightly increase the elastic modulus and toughness values. Addition of spherical structured fillers increases toughness etc. at high temperatures. It is not as effective as reinforcement fillers in increasing properties. However, leaf-shaped fillers such as talc and mica can increase these values [88].

The most important issue in using filler can be considered as cost. Because reinforcement materials are only used when an improvement in the mechanical properties of the product is desired or when situations that cannot be reinforced with different methods are encountered. Homogeneous distribution of the added filler in the matrix to prevent shrinkage, internal stresses, cracks and easy removal from the mold during composite production; It should also impart low specific heat and low thermal expansion properties to the composite.

Apart from this, it also affects the good bonding of reinforcement and plastic. The low hardness value of the fillers to prevent wear in the production machines, the spherical structure to have low surface energy, and the high thermal resistance to surface treatments contribute to the production process [88].

It has been mentioned that fillers have a partial effect on mechanical properties. For example, in order to increase the tensile stress and elongation of the composite, the filler used must have higher strength than the matrix. Apart from this, the fibers used should have a high length/diameter ratio, good bonding of the fiber and matrix, and good distribution in the matrix. Small and spherical fillers can be used to improve the compressive stress. In order to increase the toughness, fillers with higher elastic modulus than the matrix should be used. In addition, they must have a high orientation [88].

Long fibers can be used if high impact strength other than these mechanical properties is desired. Hard fillers can be added to increase the hardness of the composite. In addition, by controlling the particle size distribution, a tight-packed structure can be created that can

achieve high density. By adding fillers that are soft and have good sliding properties, low wear properties can be added to the composite [88].

Recently, the use of fillers and reinforcing materials has become a very important factor in technical applications. This situation also provides a great profit in the production of plastics in high tonnages. However, unfortunately, almost no sector in the world, except the glass fiber sector, has not announced a figure that will indicate the economic importance of fillers [88].

- **Calcium carbonate filler**

Today, carbonate fillers are generally used as cost reducers. It has an extremely important place especially in the plastics industry in terms of its extraction from the quarry, its purity, the impurity rate and types it contains, the processing method and the subsequent surface smoothing processes.

In addition, by applying a suitable surface treatment to calcium carbonate, an oil-loving feature can be gained. This is a feature that makes it preferred in the plastics industry [88].

Calcium carbonate is the most commonly used filler with polyester resin systems. It is found in nature in the form of chalk, limestone and marble and may contain very small amounts of other minerals [88].

In terms of weight, ground calcium carbonate is the most important filler added to plastics. A very finely ground type is also used especially in Polyvinyl Chloride (PVC). Calcium carbonate helps both to reduce costs and to increase physical and mechanical properties [88].

- **Talc filler**

Talc occurs in nature as a magnesium silicate in the form of a water-containing compound with the formula $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. Talc; It has four different particle shapes: fibrous, lamellar, needle-like and plate-shaped, but commercially only lamellar talc is commonly used [88].

The composition of talc varies according to the source from which it is obtained. The most important factor here is the amount of tremolite it contains. E.g; Montana talc does not contain asbestos and tremolite, while sheet California talc contains less than 3% and hard talcs 5-25% tremolite [89].

The main content of talc is magnesium hydroxide and oxide compounds, which are sandwiched between two silicon oxide layers.

The good sliding properties of talc are largely due to this lamellar structure and its low hardness. This sandwich-shaped structure ensures that each layer has a certain degree of water removal and is resistant to chemical reactions. If we heat talc around 800°C, it loses the water it contains, but if this happens, the sheet-shaped structure is lost and the properties change. Since the layers in the structure are connected to each other by weak Van der Waals bonds, they can be delaminated and separated from each other even under the influence of low shear forces. Due to the existence of these weak bonds between the layers, talc gives a slippery feeling to the hand and can be easily dispersed in the structure when added.

In the form of a plate, talc gives properties such as high resistance and less gas permeability in the plastics to which it is added. In addition, it causes less wear because it is the softest mineral in the Mohs hardness scale and its surface does not like water [89].

Talc is one of the most preferred fillers in the polymer industry, especially when it comes to toughness. In this respect, the function of talc depends not only on its filling purpose, but also on its fine-grained and layered structure [88].

Unlike other silicates, the desired results have not yet been obtained in the experiments to improve the mechanical properties of talc with surface applications.

- **Kaolin filler**

Kaolin is a product formed as a result of the decomposition of granite and feldspar. It is very abundant on earth, but its purity is low. Also known as "china clay". This includes primary and secondary kaolinites. It has a lamellar structure. Primary kaolinites have a value of 10:1 in their length to thickness ratio, and the remaining lamellar structure is hexagonal.

Kaolin is the second most important filler in the tire industry after carbon black. In tire chemistry, whether kaolin is "hard" or "soft" can be distinguished according to whether the end product has a high or low modulus. The grain size is very low. From the morphological point of view, the main difference is; The reason is that almost 75% of hard kaolin grains are smaller than 2µm, while soft kaolin grains are larger.

It is highly white, does not show electrical conductivity, is resistant to chemicals and very resistant even to strong acids. It also reduces the water absorption feature of the product it is used in. It reduces the crack tendency that may occur in the final product. Apart from that,

it provides better shock resistance and surface quality. Having a lamellar structure makes the final product harder [88].

1.8. Production Methods of Composite Materials

Composite material is a material system that combines one or more of the same or different groups of materials to complement each other's weaknesses or reinforce their superior properties. The fact that composite materials can be produced by AM methods is important in terms of eliminating the limitations of standard (one-component) parts obtained by AM methods. With the introduction of composite materials to this technology, it is aimed to use the products produced functionally. There are many different production methods to meet different needs in the production of composites. Each of these methods has several advantages and some benefits. For this reason, finding the appropriate production method is one of the important parameters affecting the quality of the final product.

Before explaining the details of some of these methods, some parameters that are important in composite production should be explained [90].

Gel time: It is the time it takes for the resin added to the catalyst to harden after the necessary processes are done. At the end of this period, the resin becomes a gel-like consistency. Many factors affect gel time:

- The amount of catalyst. If the amount of catalyst “Initiator” increases, the gel time becomes shorter. The catalyst initiates the cure of the resin or gelcoat.
- The amount of “Accelerator”. If the amount of “Accelerator” increases, the gel time will be shortened. If “non-accelerated” resins are used, a sufficient amount of catalyst should be used, otherwise the gelling time will be too long or the resin will be undercured.
- Pigment content. Some pigments extend the gelling time, while others shorten it.
- Presence of inhibitor. The inhibitor prolongs the gelation time.
- To mix up. Improper mixing of the catalyst and accelerator leads to molding and curing errors.
- Ambient temperature. As the ambient temperature increases, the gelation time becomes shorter.
- Monomer loss by evaporation. If there is not enough monomer, proper polymerization will not occur. Fast gel time reduces evaporation

- The use of fillers. Most fillers prolong gelling time.

Thixotropic: It is the ability of polyester to stand without slipping from the vertical surfaces of the mold.

Wetting: It is the complete penetration of polyester into the glass fiber, which is the reinforcement material.

Exothermic Heat: It is the heat released during the cure time. If not controlled, the material or the mold used may crack.

Pooling: Resin, which does not have a thixotropic feature, flows under the mold as droplets and forms a pool of the drops accumulating under the mold.

To summarize these methods briefly;

Hand laying is based on the basic principle of laying the reinforcement material, which is generally knitted in the form of fabric, into the mold and applying liquid resin on the open mold. Composite materials can be used in mold making, just like in the product. As the process names suggest, in manual laying, the addition of resin and reinforcement materials is done manually. In order for the curing process to be carried out, certain proportions of catalyst must be mixed into the resin. In order to accelerate the curing, curing can be performed for certain periods at different temperature levels higher than room temperature [91].

In the vacuum infusion method, the reinforcement material knitted in the form of fabric is laid in the mold, as in manual laying. In order for the resin to reach all parts of the reinforcement material, channels that will create flow paths are placed on the mold and placed in an airtight bag. The resin chamber is placed in such a way as to allow resin entry from a central part of the mold and vacuum is applied from the other parts of the mold by means of a vacuum pump. With the vacuum effect, resin is drawn from the outside on the reinforcement fabric on the mold, and the reinforcement material is wetted and impregnated with a certain amount of resin. The process is continued until the resin wets all the reinforcement elements and reaches the vacuum hose, and it is put on hold for curing in a suitable time period [92]. For the curing of the resin, it is necessary to add a catalyst to the resin, as in manual laying, and early curing can be achieved by keeping it at different temperature levels when desired.

In cases where flat shaped composite materials are desired to be obtained, pressing can also

be applied between two molds. For this, the composite material is first laid by hand and a catalyst mixed resin is applied on it. After laying the fabric with the desired properties, pressing is done and it is waited until the end of curing. Heat can also be applied to the press molds to increase the temperature during the pressing process so that curing takes place in a short time. Materials with thermoplastic properties can also be used as matrix material in the production of composites by hot pressing. For this, a thermoplastic film material is laid between the reinforcement material layers. Layer by layer laying process is carried out until the desired thickness is achieved. The resulting bundle is compressed between two flat molds under a certain temperature, and the thermoplastic film layer melts and adheres to the reinforcement element [93].

In spraying, the resin and reinforcement material is added to the mold with a spraying device. Fiber-shaped materials are sprayed onto the mold surface together with the added resin by cutting small pieces [94]. The reinforcement materials obtained in this way consist of particles of discontinuous structure.

In the pultrusion method, as in the extrusion process, the fibers are continuously passed through a longitudinal mold, while the polymer material is allowed to penetrate between the reinforcement fibers, and composite profiles can be produced in a solidified form at the exit of the mold with the effect of temperature [95].

A composite type called prepreg has been developed, especially on the basis that the amount of polymer added to the reinforcement material cannot be adjusted well in manual laying and vacuum infusion, and the molding procedure is troublesome. In this type of composite, the reinforcing material is pre-impregnated with thermosetting polymer and then cured under temperature and pressure. In this way, the rate of polymer additive can be adjusted as desired [96].

Various fibers are used in composite materials. Glass fiber; it is a silica-sand-based material and contains certain amounts of elements such as sodium, calcium, aluminum, boron and iron. Composites by using polymers are often used as reinforcement elements in material production. Glass fiber is a preferred fiber in terms of cost and can be found quite often and easily. There are variants such as E, S and C. Carbon fibers have high strength properties due to the strong covalent bonds between atoms and therefore they are used in composite materials. Carbon fibers were first used by Edison in incandescent lamp wires by carbonization of cellulose-based materials such as cotton and bamboo. The basic production

technique in carbon fiber production is based on the separation of various organic precursor materials. Although many materials can be used in the production of carbon fiber, the most suitable raw materials are polyacrylonitrile (PAN), pitch and rayon. Carbon fibers are generally low density, low thermal conductivity, structurally effective and high fatigue resistance materials. Boron fiber is one of the light elements and is solid at room temperature. It is a fiber that is difficult to produce. Its density is high due to the tungsten wire inside. It can be easily combined with high-strength metals. Although it is expensive, it is mostly used in the space industry. Alumina fibers; They are used in metal matrix composites. Elastic modules with a density of 3300 kg/m³ can reach up to 380 GPa. One of the most important organic reinforcement elements is Para-aramid (Kevlar). Its elastic modules can reach up to 130 GPa. It is frequently used in bulletproof vests, vehicle tires and ropes and cables. It is a fiber resistant to chemical effects.

Thermosets are generally used as matrix material. Some of these materials are mixed with hardener/catalysts in certain proportions and some are solidified by heat and/or UV light. During this condition, which is called curing, irreversible chemical reactions and bonds occur. Different thermoset resins are available. Some of those; They can be listed as Epoxy, Phenolic, Polyester, Silicones, Amino resins [90]. Comparison of some aspects of composite production methods is given in Table 1.7.

Table 1.7 Comparison of some aspects of composite production methods, 10: largest value, 1: smallest value [97].

Method	Equipment Cost	Production Speed	Importance of Labor	Possible complexity of the part	Reproducibility
Hand Lay-up	1	3	10	9	1
Sprey-up	4	4	10	8	1
Pultrusion	7	9	2	2	10
Filament Winding	6	6	2	4	9
Resin Infusion	10	10	2	1	10
Resin Transfer Moulding	10	10	2	1	10
Compression Moulding	10	8	4	9	10

1.8.1. Hand lay-up method

Hand lay-up was one of the first methods to use polyester resins. Although the process is very simple; It is the wetting of the fiber reinforcement in the form of glass fiber mat or woven fabric in a female mold with matrix resin containing accelerator and initiator. Different reinforcement forms such as woven glass fiber, glass fiber mat and knitted fabrics can be used alone or in combination with each other. This process often uses room temperature curing resins that contain precursors and only require the addition of the catalyst, which is a ketone peroxide such as methyl ethyl ketone peroxide. Although the raw materials and equipment used are quite simple and not expensive, there are significant labor costs as all work is done manually. This may also lead to some quality differences depending on the qualification, skills and experience of the performing operator. Hand lay-up is often used for prototyping and is suitable for small batches or very large objects that cannot be easily produced using other standard techniques. Figure 1.6 shows the hand laying process [98].

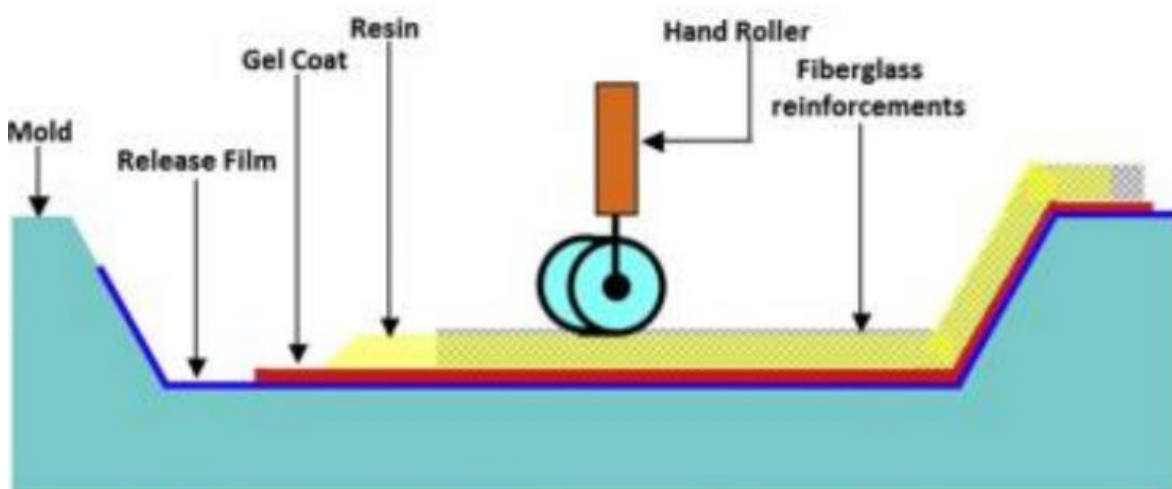


Figure 1.6 Hand lay-up process [99].

Often, after applying a release agent (typically PVA, wax, or PTFE/silicone) to the mold surface, the mold is coated with a pigmented gel denim resin and allowed to gel and partially cure before reinforcing and laminating with the resin. The function of the gel denim coating is to prevent printing from the fiber surface to the final surface and to protect the fiber material from external factors. In room temperature gel denim coatings, it is usually applied using spray equipment using gel denim coating groups with small catalysts or a catalyst injector gun that injects and blends the gel denim coating resin while spraying the required

amount of catalyst onto the mold. The thickness of the gel denim resin coating layer can vary from 1 mm to 15 to 20 mm in the cured state. It is difficult to achieve precise thickness control in molding. The process gives a high grade surface on the die side. For particularly high-quality surfaces, a fiberglass fabric can be embedded in the partially reinforced gel denim coating for surface reinforcement. After application and partial curing of the gel coat, the liquid resin and reinforcement material are applied alternately in layers. The resin is applied by hand roller wetting or spraying. After each layer, the fibers absorb the resin and compact it with brushes or hand rollers. It is important to exclude air bubbles from this process, as trapped air creates mechanical micro-defects through small nicks in the composite. Resins for hand lay-up are generally thixotropic to minimize resin drainage in the vertical sections of the flooring. Room temperature curing systems are almost always used. Any type of styrene-containing polyester can be combined for hand lay-up work. It is also possible to replace some of the styrene with methyl methacrylate to increase decomposition or paramethyl styrene to reduce monomer emissions. Vinyl ester resins containing styrene may be recommended for use in hand lay-up molding at room temperature. Hand layup is often used with vinyl esters, largely because large and chemically resistant pieces of equipment for which they are intended are easily produced with this molding method. The degree of fiber reinforcement varies depending on the type of fiber material used. Typically, around 35% to 45% by weight of fiberglass reinforcement is common when using glass fiber fabrics [99]. The major disadvantages of hand lay-up are (1) that it only has one good surface on the molded parts, (2) it is labor intensive and therefore not economical for all products, (3) the reproducibility of the parts produced is not perfect, and (4) there is generally little mechanical It is the inability to completely avoid the problem of air entrapment during hand laying, which causes performance parts.

1.8.2. Sprey-up method

In the spray method, which is a partially automatic form of hand lay-up, the spray guns are fitted with initiator injection spray equipment and small fiber cutters. These developments enabled the simultaneous application of accelerator and initiator resin and cut glass fiber to molds. The cut fiber reinforcement is partially wetted by the resin during spraying. Typically, the fibers are cut into lengths of 20 to 50 mm. Air removal by wetting and compression is completed with special hand rolls, similar to the laying process [98]. An example of industrial applications is given in Figure 1.7.

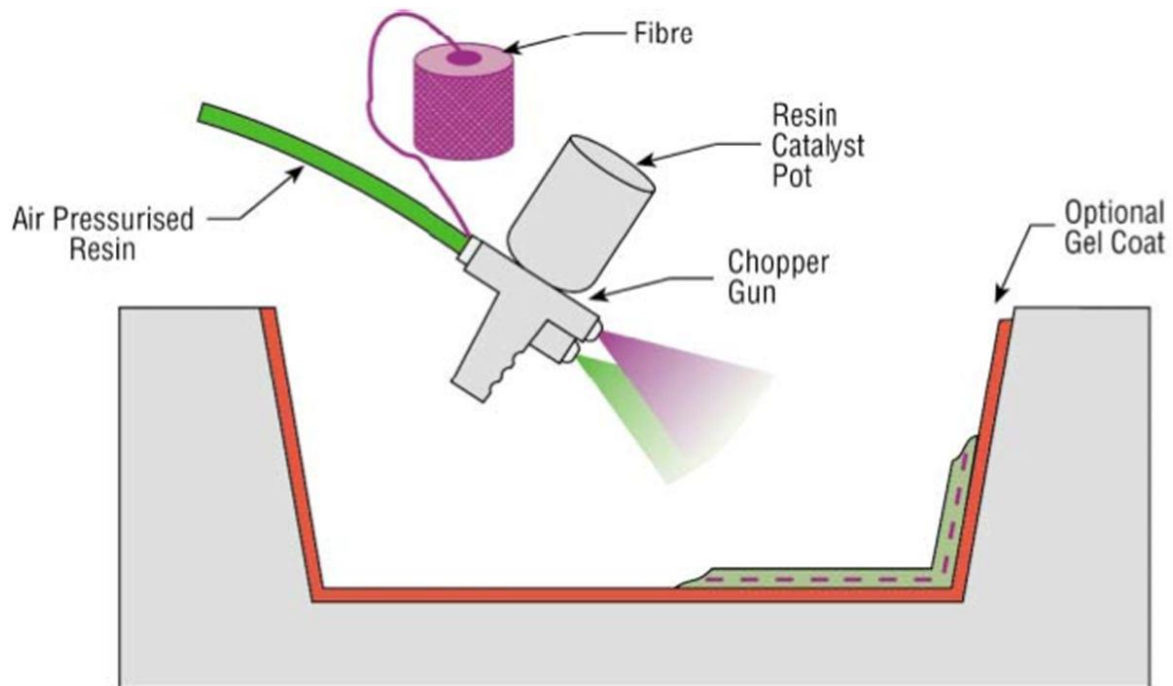


Figure 1.7 Spray-up process [100].

The spray gun usually delivers the resin accelerator and resin hardener mixtures together from two separate reservoirs to prevent the matrix system from temporarily curing. As with hand lay-up, room temperature curing resins are used with pigmented gel denim resin coatings. Similarly, the molding has only one good surface and it is difficult to precisely control the thickness in the mold. Fiber control and reproducibility in the resin layer can be improved using computer-controlled molds or spraying robots. The tools used for spray placement are also relatively simple; Again, it is one piece, worked with open molds and is more economical than hand lay-up due to its potential automation. One advantage over hand lay-up is the extremely high material application rates. However, the relative percentage of fiber reinforcement in the final composite is lower. Spray flooring is suitable for producing small product batches and oversized parts. It can also be used for the application of fiber-reinforced surface coatings by spraying the resin fiber mixture directly onto the substrate. Vacuum formed acrylics become the service surface of the molded work and serve as a mold for backing up polyester and chopped fiberglass during production, which is usually applied by the shear gun spray laying method. The development of good adhesion between the acrylic and the polyester glass fiber replacement laminate is crucial to the success of this fabrication technique. For curing at room temperature, specially formulated thixotropic resins are often used to maximize adhesion.

1.8.3. Pultrusion method

The pultrusion process, which started to be used for the first time around 1948, is a low-cost mass production method in which composite profile products with continuous constant cross-section can be produced.

It is derived from the words Pull and Extrusion. After the continuous reinforcement material fed to the system is passed through the resin bath, it is hardened by passing through the forming mold heated to 120-150 °C. Molds are usually made of chrome-plated bright steel. Due to the use of continuous fibers, very high mechanical strength is achieved in the reinforcement direction. Around 60-65% fiber can be used because wetting is not complete with more glass fibers. It is necessary to use special weavings in order to meet the transverse loads [5, 101]. Profile pultrusion process is schematized in Figure 1.8.

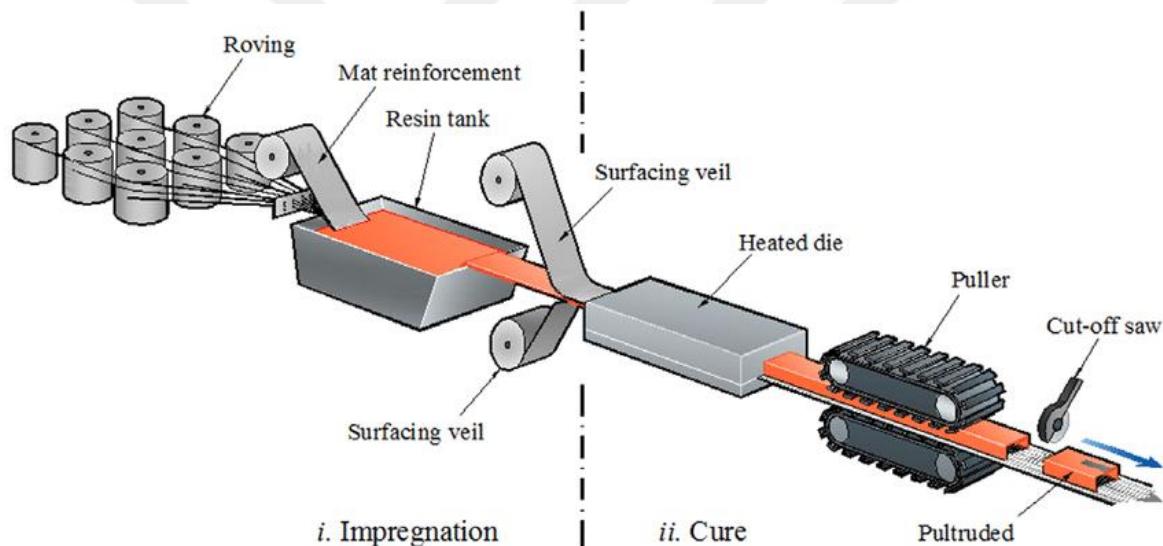


Figure 1.8 Profile pultrusion process [102].

Advantages of the Profile Drawing method:

- The fiber is oriented
- High longitudinal strength
- There is automation
- Low operating cost
- Low investment cost
- Medium and high production volume

Parts produced by pultrusion are used in many areas of industry [103]:

- Electrical: stair components, cable trays, rail guards, lighting poles, pole parts
- Anticorrosion: Grates, manure separators, suction rods, pipes, reinforcement beams
- Construction industry: Frames, windows, roof reinforcements, patio doors, trims, roofing plates
- Automotive industry: Sliding doors, bus license plates, interior arrangements, instrument panels, slide shaft, storage shelves.

1.8.4. Filament winding method

FW is one of the composite material production methods and is generally used in the manufacture of cylindrical parts. These methods are based on the technique of winding the continuous fiber dry or wet on a rotating part by pre-stretching it from the reels. This manufacturing method is used to produce high strength and lightweight composite products [104]. Continuous fiber materials (such as glass fiber and carbon fiber) and resin are used in fiber winding technology. In Figure 1.9 the filament winding process is given schematically.

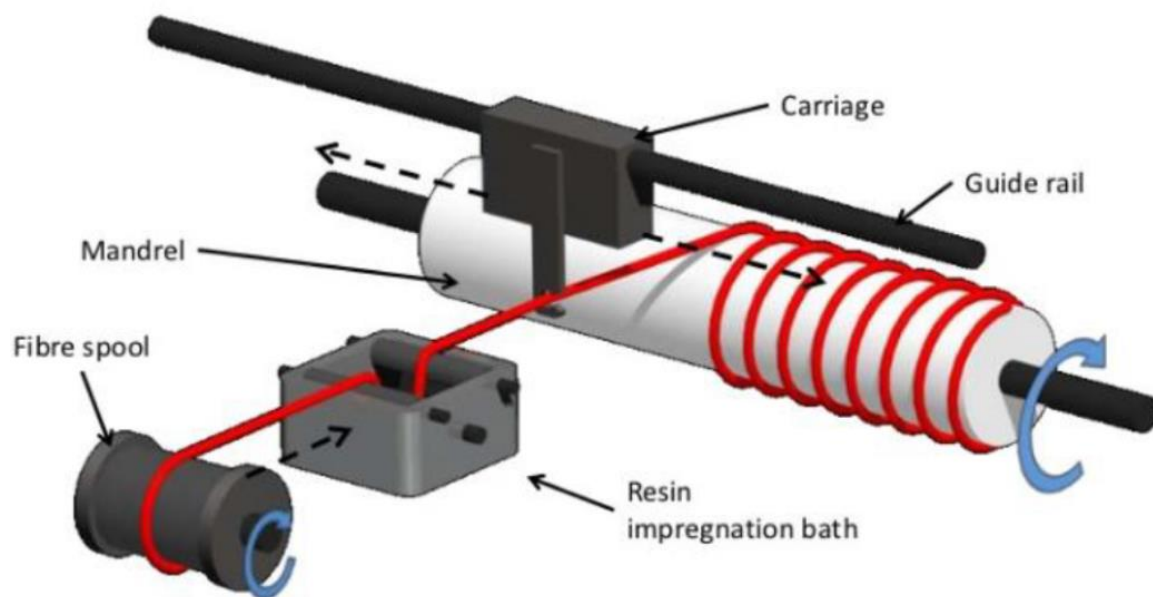


Figure 1.9 Filament winding process [105].

Winding a pressurized container with carbon fiber in a fiber winding machine [106]. This winding technique is mostly used for the production of symmetrical and circular products. An example application for this production is given in Figure 1.10. It is possible to produce products with very high mechanical properties by applying the resin reinforced fiber

winding process on these symmetrical and circular products. The general usage areas of the products produced by this method;

- In the production of cylindrical and symmetrical parts,
- In the production of cannons used in the defense industry,
- In the production of high pressure tubes (These tubes are used in aviation, space and military systems)
- In the manufacture of fuel tanks in the aerospace industry,
- Hydrogen and fuel tank production in new generation vehicles,
- Especially in the design of parts of vehicles that require high speed and mobility,
- It is used in many areas such as the production of vehicles used for sports purposes (such as the hulls of sailboats, skeletons of bicycles).

Winding a pressurized container with carbon fiber is given in Figure 1.10.

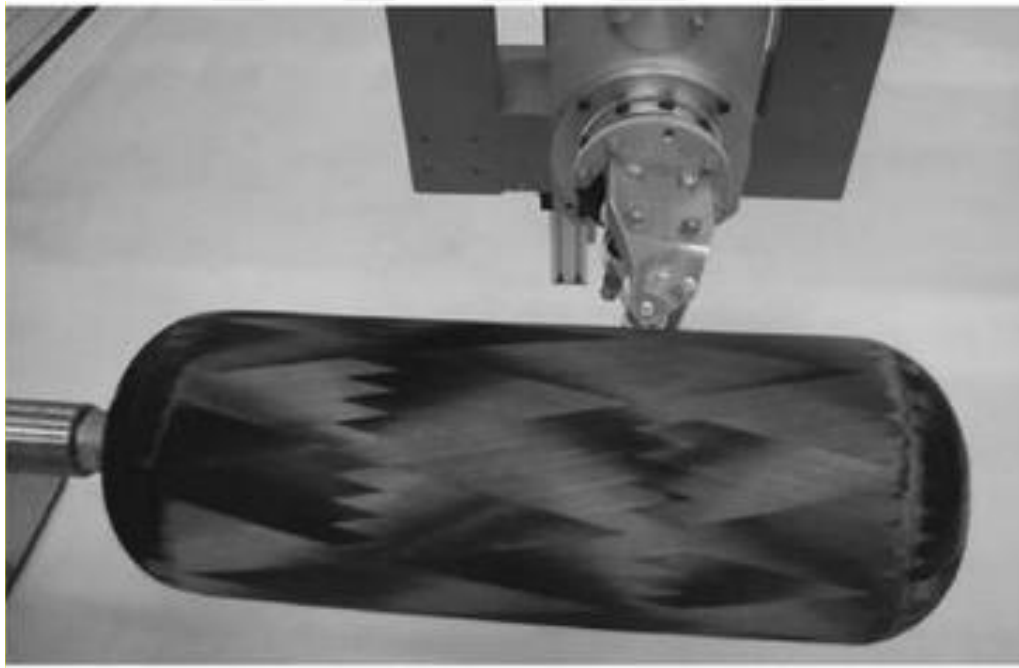


Figure 1.10 Winding a pressurized container with carbon fiber in a fiber winding machine [106].

Products such as low and high pressure pipes, water and chemical storage tanks, pressure tubes, automobile shafts have an important place in the industrial applications of products produced with fiber winding technology. Examples by filament winding method that will operate under high pressure is given in Figure 1.11. In addition, in space and industrial

applications, it is used in areas requiring high strength such as rocket engine boxes, missile and rocket heads, airframe and wings. In addition, in the fields of entertainment and sports, examples such as golf tools, archery, firearms, and bicycles can be given.



Figure 1.11 Vehicle Gas Tank (Left) Hydrogen Fuel Tube (Right) Fiber winding method in composite production [107, 108].

Depending on the development of technology, fiber winding machines have also undergone a great change. The fiber winding process, which was previously done with conventional looms, is now computer-controlled. Geodetic wrapping method is used in computer aided production. Mathematically, the geodetic wrapping method is based on the curve fitting equation to the shortest path through two points. The geodesic winding method has been a very effective and highly sensitive method, especially in the production of high pressure tubes, in determining the fiber winding direction during the winding process [109]. The fibers are wound on the product with three basic winding techniques: circumferential, helical and polar. Fiber winding techniques are given in Figure 1.12. The purpose of these methods is to capture and produce the winding shape that will increase the strength performance of the product to be produced.

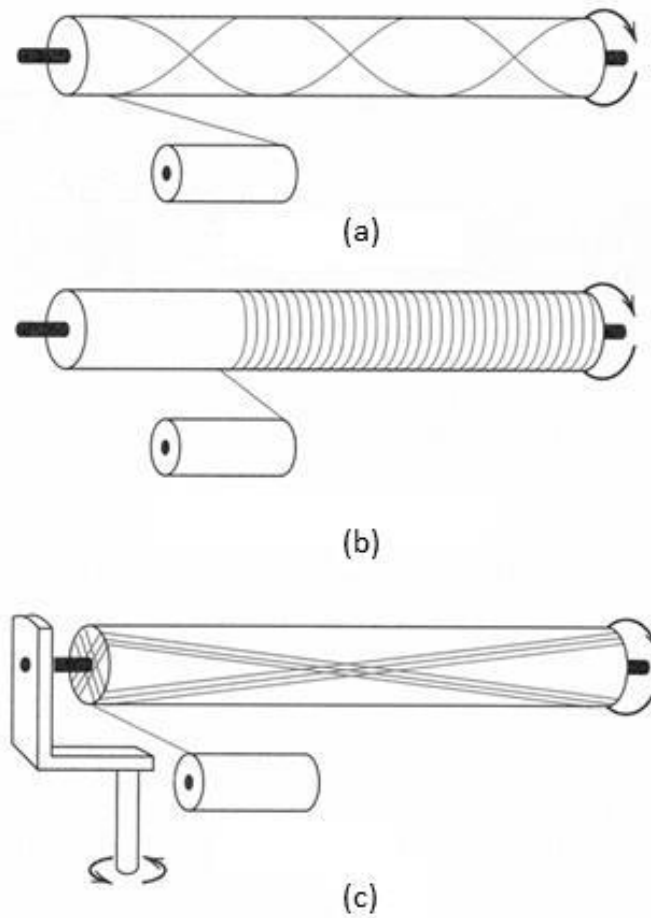


Figure 1.12 Fiber wrapping techniques; a) Helical b) Peripheral c) Polar Coil [110].

Today, fully automated fiber winding machines are used in order to perform complex geodetic orbital windings under a certain pre-stress during the winding process of the fiber. These machines can be produced with 2, 3, 4, 5 or 6 axis depending on the part to be wound. The winding process is carried out on the part as a result of the movements of the winding eye in the desired axis, passing through the resin bath by creating a certain tension on the fiber in order to wrap the fiber smoothly and without gaps. Today, such machines are controlled by Computer Numerical Control (CNC) control units. These CNC-controlled machines act with codes that define the fiber winding paths suitable for the part to be wound, thanks to various programs (Cadfil, Cadwind, etc.). An example of generating motion codes for fiber winding is shown in Figure 1.13.

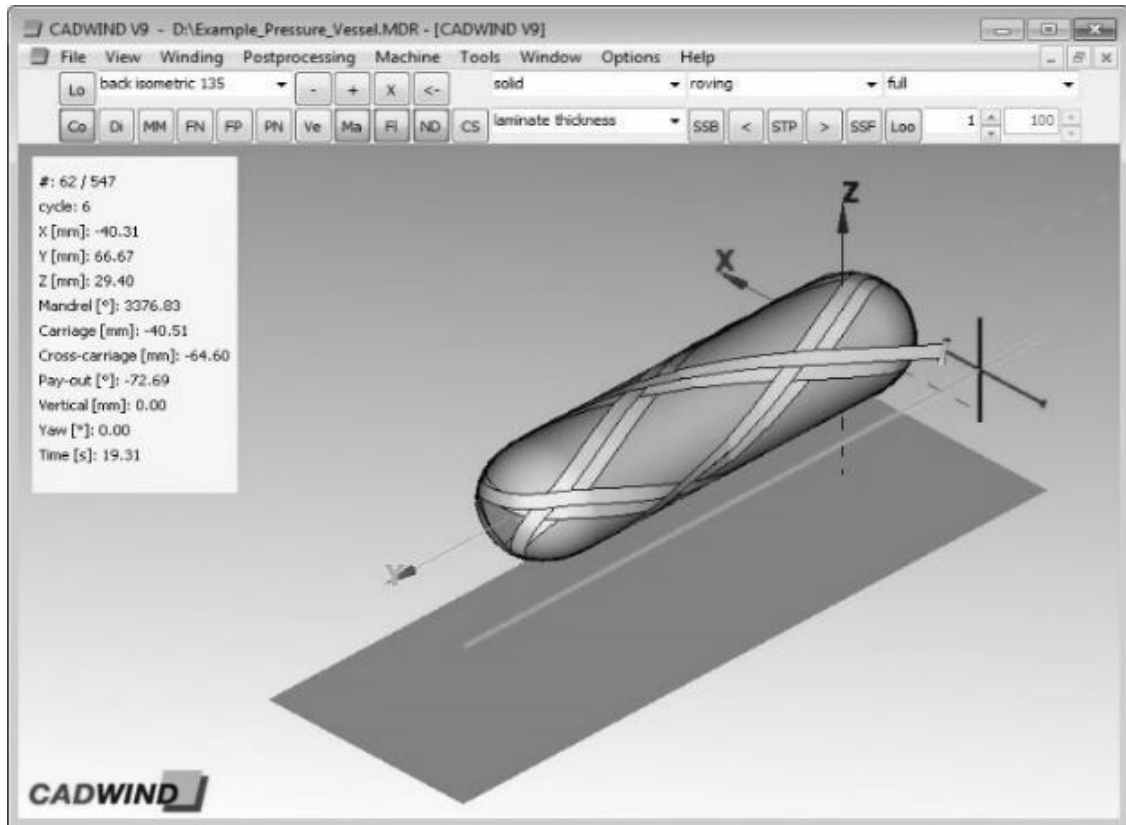


Figure 1.13 Example of software that generates winding codes on fiber winding machines [111].

1.8.5. Resin infusion method

In this method, which works with the principle of progressing the resin in a vacuumed environment, it is aimed to produce the product whose production preparations have been completed, untouched by human hands. Vacuum infusion process consists of 4 parts: vacuum pump, vacuum tank (resin collection tank), mold and resin bucket [112]. Resin infusion process is given in Figure 1.14.

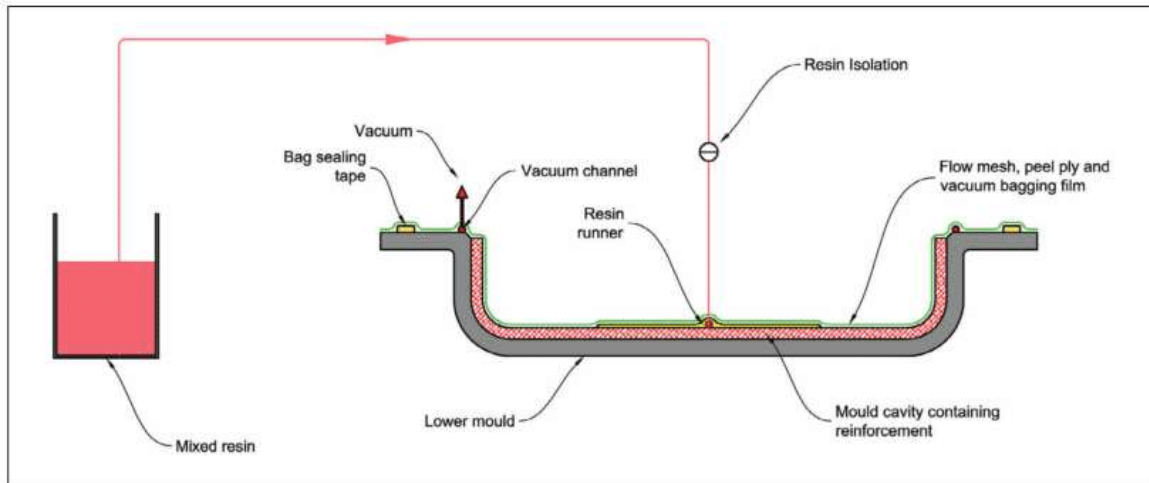


Figure 1.14 Resin infusion process [113].

In the literature, there are various methods based on the logic of resin infusion in a vacuum environment and named with different names. Although there are some minor differences between them, the basic process steps are as follows:

- Carbon fabrics are stacked on top of each other in a fiber mold to form the thickness of the material.
- A release film and resin dispersing layer (usually felt) are placed on these stacked fabrics.
- By using specially designed vacuum film and double-sided adhesive sealants, a leak-proof structure is obtained by placing it on the top.
- With the help of vacuum, it is ensured that the resin is absorbed into dry fabrics. Generally; Epoxy, polyester and vinylester resins are used in this method.

All known fibers can be used in this method.

1.8.6. Resin transfer moulding method

RTM is a modern version of an old molding method called the “Macro Method” developed in 1950. In principle, the process is a low-pressure approach combining both injection molding and pressing features [98]. Schematic RTM process is shown in Figure 1.15.

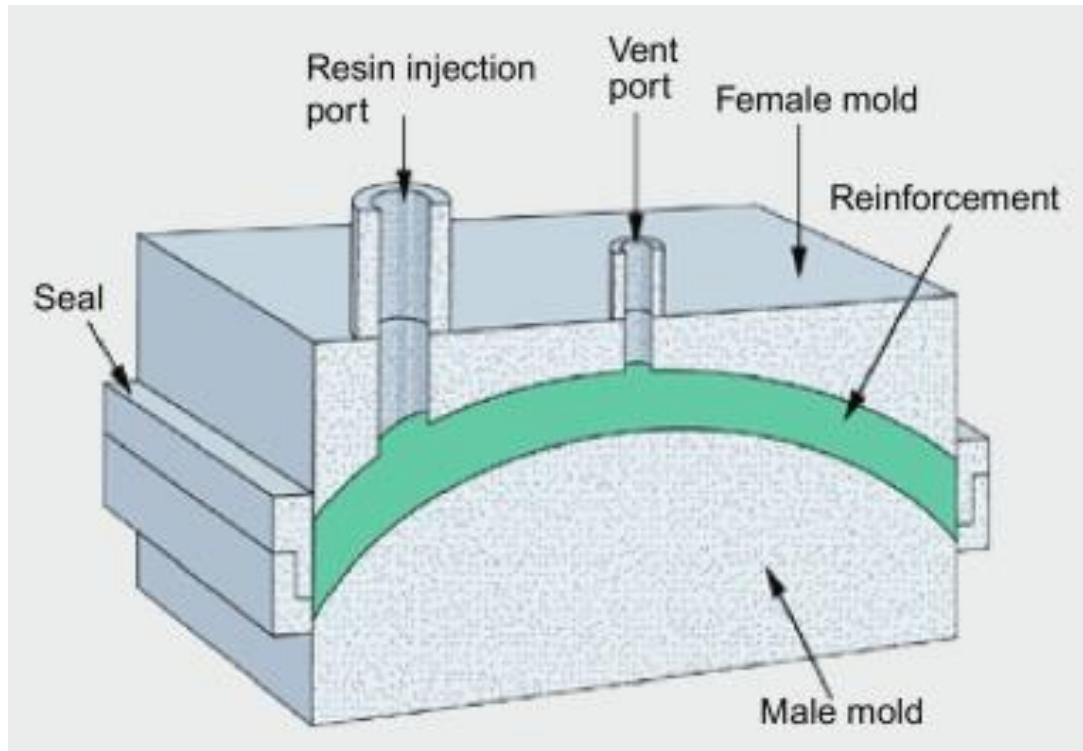


Figure 1.15 Schematic RTM process [114].

In this method, a male and a female mold are used. The reinforcement used is placed between two molds. Any desired reinforcing material can be used, such as fiberglass fabrics or structural foams. The gel denim resin coating can be used on one or both mold halves. After compressing the mold with a tight seal around the mold periphery, the initiator-added resin is applied to the mold with a pump through a clear tube inserted into a vent located at the highest point of the mold. Resin "transfer" and air removal are assisted in some processes by adding a vacuum source to the vent line. The process is suitable for manufacturing medium-sized production volumes. The quality of manufactured products is typically good because the applied vacuum or pressure conditions favor the removal of air bubbles and relatively high fiber reinforcement can be made. The process usually uses room temperature curing resins. Both polyesters and vinylesters can be used. Stronger mold construction is required for RTM rather than by hand or spray series because pressure (and perhaps vacuum) is used to apply the resin to the mold and into the reinforcement. Elevated processing temperatures can be used to further improve resin flow, particularly when using highly complex molds and long flow paths. Low viscosity resins are required to moderate the pressure requirements and facilitate wetting the reinforcement material. Resins with a low to moderate exothermic reaction are preferred because during curing the polyester composite is completely covered and isolated by molded parts, which are usually resin

composites. Excessive exothermic reaction can cause damage or reduce useful die life. Therefore, in many cases, stainless steel is also used, especially when producing large lots or developing high processing temperatures during curing.

1.8.7. Compression moulding method

Composite materials, called ready-to-molding compound, containing glass fiber, resin, additives and filling materials within ready-molding, become products with hot press molds.

It has advantages such as producing complex shapes and embedding metal parts into the body. In compression molding, it is shaped with a mold on two surfaces. It is possible to obtain complex shapes such as holes that other composite material production methods do not allow. The reject rate is low. The disadvantages of this method are that the molding compositions need to be stored in refrigerators, the molds are more costly than other molds because they are metal, and large and expensive presses are needed to produce large parts.

Although the compositions used in the ready molding method vary according to their content, two types of ready molding compounds are used at most:

- Sheet Moulding Compound (SMC)

SMC is a material in the form of pulp formed by pre-combining chopped fiber as reinforcement material and a resin containing filling material. Conceptually, the SMC composition is the composite equivalent of sheet steel.

Continuous fibers are used as clipped 25-50 mm and 25-30% of the total weight of the composite. Resins and reinforcement form a sandwich appearance between the film layers. Usually 1m wide and 3mm. Thickness [5, 101]. SMC manufacturing process is given in Figure 1.16.

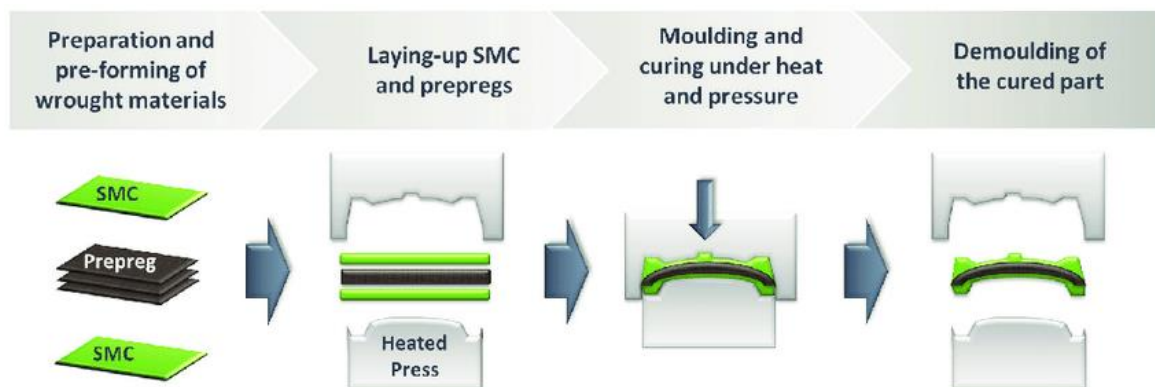


Figure 1.16 SMC production process [115].

- Bulk Moulding Compound (BMC)

BMC is a pulp-like material formed by pre-combining a resin containing chopped fiber and filling material, catalyst, pigment, lubricant as a reinforcement material.

This method is similar to RTM. The difference is that the resin/fiber mixture is mixed outside the mold and melted and injected into the empty mold under pressure. Only low viscosity thermoset resins can be used in this method. It is faster than other methods. Many products from children's toys to aircraft parts can be produced by this method in the production of small and large household appliances, in the automotive sector [5, 101]. BMC manufacturing process is given in Figure 1.17.

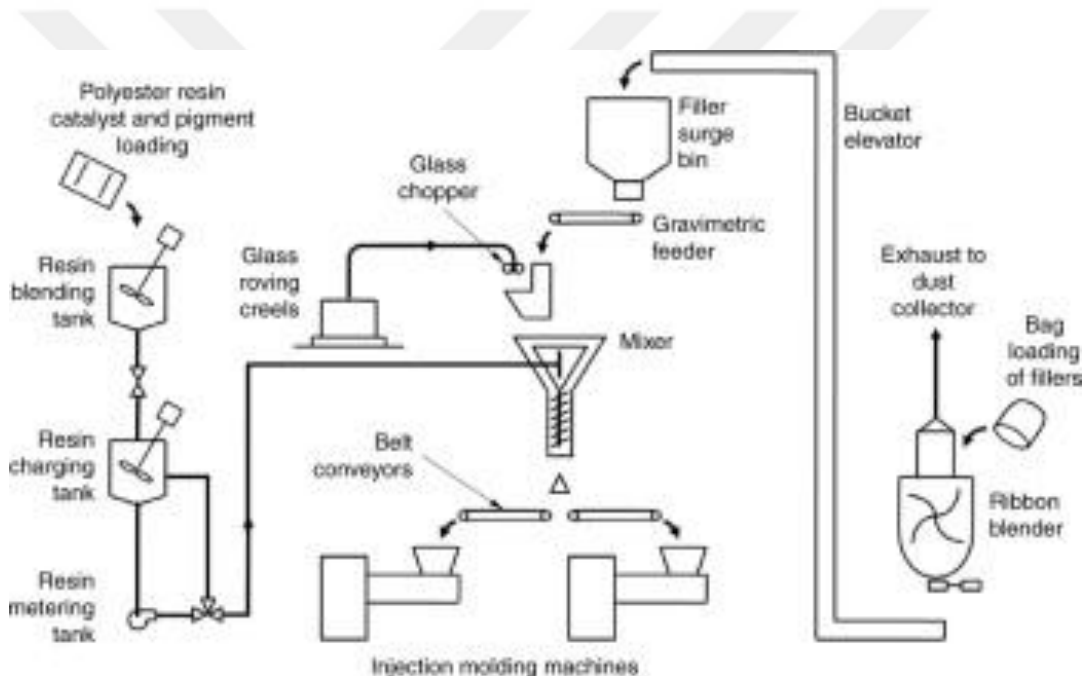


Figure 1.17 BMC production process [116].

Advantages of BMC:

- Huge design flexibility
- Smooth surface
- Easily paintable and surface coating in the mold
- Being able to be recycled and using recycled materials in production
- Ease of assembly with insertion of metal inserts
- Superior hardness and flame resistance with the addition of high filler material

- Temperature resistance

Disadvantages of BMC:

- A wall thickness less than 1.8 mm is not provided
- Rapid prototype production is limited.

1.9. Additive Manufacturing

Until the last 50 years, manufacturing methods were examined under two main headings. These two categories are machining methods and chipless manufacturing methods. As the name suggests, in machining methods, methods that remove chips from the rough part are used to produce the final part. The leading of these methods are turning, milling, cnc machining and wire erosion. These production methods are generally suitable for mass production. Another advantage of these methods is their high sensitivity.

However, the efficiency is relatively low due to the sawdust formed during production. And complex shaped parts are difficult to manufacture because of the size and shape of the cutting tools. The other category is chipless manufacturing methods. Although the process contents of the methods under this title are very different from each other, their basic common feature is that no machining is done while shaping the rough part during the production of the final part. The main production methods used under this category are casting, rolling, extrusion and pressing. These methods generally have a high initial cost but are suitable for mass production. In addition, they are not suitable for the production of complex shaped parts, except for a few casting methods. However, metals, plastics and ceramics can be processed in chipless manufacturing methods, which constitute the majority of engineering materials used today. Machining methods are disadvantageous in this sense and mostly produce with metals.

In general, more than one production method is used together during the production of parts. For example, in order to obtain a simple shaped coin, the specified alloy is prepared by melting and poured as slab by casting method. Then, this slab is thinned in rolling and sheet metal of desired thickness is obtained. The surface of the resulting sheet is milled to remove dirt and roughness. Then the sheet is sent to the presses and round stamps are cut in the desired size. After the flakes sent for washing are polished here, the desired shapes are pressed on the flake surface in the next press, and the desired money is obtained. Even this example alone shows that production in general is a complex intertwined process. With the

studies that started about half a century ago, a new perspective and method has been brought to this production approach. This method, which is called AM, has developed without slowing down until today and has become an important part of manufacturing methods. So much so that it has now formed the 3rd category in manufacturing methods.

The feature that forms the basis of AM methods and distinguishes it from other production methods is that the part to be produced is produced by adding material to the material. Thus, while the amount of scrap during production is close to zero, complex shaped parts can be produced easily. All production is collected in a single process. Thus, the production of a solid model, previously designed with the help of 3D CAD software, can be achieved without the need for any production planning. Although AM methods have facilitated the production of especially complex parts, it is still necessary to have a good command of the production process in AM methods. The working principle of AM is to decompose the solid model into layers by using the data obtained from the CAD model, and the layer is created by adding material over the previous layer. Of course, the layers have a certain thickness and therefore the dimensions of the parts produced are not the same as the model actually designed. As the layer thickness decreases, dimensional accuracy increases, resulting in a product that is closer in size to the 3D solid model. In addition, the initial cost is relatively low compared to other production methods. This situation facilitated the end user's access to this production technology and enabled the production to be personalized by entering the houses.

Despite this, the relatively low variety of materials used, the relatively low strength of the obtained parts, and the lower surface quality of the final product compared to machining are the main disadvantages. However, considering that additive AM technologies are still in their infancy, these problems will be resolved over time [117].

The features that distinguish AM technologies from each other are basically the material used, how the layers are produced and how the layers are joined to each other. All of these properties are factors that directly affect the mechanical properties, dimensional accuracy, production speed and cost of the final product produced. In this study, samples produced by using Fused Deposition Modeling (FDM), an extrusion-based process from AM methods, were chosen as the subject of examination or continuous fiber reinforced 3D samples produced with the help of this method were tested. In this context, first the development common components of AM methods will be discussed and the development process will be discussed, then the production methods will be classified and the basic methods will be

briefly explained and the FDM method, which is the subject of this study, will be discussed in detail.

In this context, AM processes generally consist of 8 main steps.

- Design and 3D modeling of the product

All product development processes begin with the idea of what the product will do and how it will look. The product needs to be designed according to the need and this design can be presented in different ways such as text, 2D drawing. The part to be produced with AM should be designed as a solid model with 3D CAD software.

In other manufacturing methods, there are factors that limit the 3D solid model design, generally due to the manufacturing method. However, in AM, these limitations are almost non-existent. In this case, it provides a great convenience and opportunity to the designer.

- Conversion of solid model to .stl format

Today, all AM technologies process files with .stl format. Apart from the .stl format, .amf, .obj, .x3d, .3mf and .vrml formats are also used [24]. However, since .stl is one of the oldest and most common formats, and the .stl format is also used in this study, all definitions and processes will be explained based on the .stl file type. The created solid model cannot be directly transferred to the 3D printer. Instead, it is first saved as a .stl file type. The .stl file type consists of geometrically triangulating the surfaces of the solid model and saving these triangles together with the surface normals.

- Transferring the .stl file of the solid model to the 3D printer and editing it

Technically, the .stl type solid model file can be produced directly by transferring it to the 3D printer. However, it is usually printed on a 3D printer by making partial changes to the .stl file. Among these changes are parameters such as changing the size of the model, printing direction, and printing position [118].

- Preparation of the 3D printer

After the .stl file is transferred to the 3D printer, the printer must be prepared for production. In general, 3D printers are mechanically ready, but data such as layer thickness, material, material parameters of the part to be produced are transferred to the 3D printer through a software [11]. This process is done with the editing of the 3D model in many software used today. In addition, whether there is enough material for the production of the model in the 3D printer and other mechanical controls are made at this stage.

- Production

Production starts with the 3D printer running. Today, all 3D printers make automatic production. Production continues as long as no errors are encountered in the production process. The 3D model is produced layer by layer until the whole part is complete.

- Removing and cleaning the model from the 3D printer

Technically, the 3D-printed part is the final product and is ready for use. However, in some productions, production is made using support and/or raft. In such cases, the support and/or the raft must be separated from the model. Also, some production methods use powder material as production material. In this case, the dust on the manufactured part is cleaned.

- Finishing

The parts produced in 3D printers can be subjected to surface polishing or surface coating if deemed necessary. In addition, in some 3D production methods, the part is subjected to a thermal or chemical finishing process in order to have the desired properties.

- Use

The manufactured, cleaned and finished part is now ready for use. However, a point to be considered during use is that the mechanical properties will be different compared to the parts produced by conventional methods [119].

1.9.1. History of Additive Manufacturing

Although studies on AM started in the mid-1950s, its real development was in the 1980s with the support of technologies such as computers, lasers and control systems. The first patents for this technology were obtained in 1984 in Japan, France and the USA. However, 3D Systems, the first AM company, was established by Charles Hull with a patent obtained only in the USA. The method commercialized by this company is stereolithography. In 1986, 3 more companies were established. These are Helisys using Laminate Object Manufacturing (LOM) technology, Cubital Corp. using Solid Ground Curing (SGC) technology and DTM Corp. using Selective Laser Sintering (SLS) technology. Of these technologies, only SLS is used today. In 1989, Scott Crump patented FDM and founded Stratasys.

Many AM methods have been developed to date. Some of them were successful and commercialized. With the expiration of the license period of the first patents in AM

technologies, studies on AM have accelerated since 2010. In addition, standardization studies have started by the F42 committee established under ASTM and ISO in 2009 [120].

If we briefly explain the most important AM methods below;

1.9.2. Vat photopolymerization

It is an AM process that uses radiation-curable liquid resins or photopolymers. Usually UV rays are used for curing. Photopolymers, which were developed towards the end of the 1960s, have gained a place in many fields, especially in coating and printing. As mentioned earlier, the first AM method developed by Hull using photopolymers was stereolithography. The beam can scan the material by passing through only one point at the same time with the laser scanner, or there are varieties that can be applied to the entire surface at the same time with the masking method. In addition, in another method, the focal point of two beam sources is combined for more precise production and used to cure pointwise [121].

Photopolymers started to be developed in 1960 and research and development (R&D) studies gained momentum especially with the widespread use in the electronics industry. Photopolymers are available in types that can be cured by UV, x-rays, gamma rays, visible light or electron beams. Photopolymers have a cross-linked structure. In other words, polymer molecules are not linear or branched, but interconnected. That's why photopolymers are thermoset materials. In other words, they cannot be melted with heat and used again. The first polymers in AM were acrylic-based. However, due to the shrinkage of acrylic-based photopolymers between 5-20% and the deformation of the part due to this shrinkage during production, the strength values were low [121]. In order to overcome these problems, there has been a tendency towards epoxy-based photopolymers. However, the curing speed of epoxy resins is low, the brittleness of the curing part and their sensitivity to moisture are the disadvantages of epoxy resins. For this reason, AM photopolymers used today are epoxy resins containing some acrylic resin. Thus, while providing the required strength for the part, sufficient speed and precision is provided for curing.

It should be noted that; Photopolymers are not just composed of liquid monomers. They also contain photoinitiators, stabilizers, reactive diluents, and softeners. Curing occurs when photoinitiators, activated by energy provided by UV or other radiation, react with monomers to form long, cross-linked large polymers. Today, the most common photopolymerization techniques are two. It is free radical photopolymerization used in acrylics and cationic photopolymerization used in epoxies. What distinguishes these methods from each other are

the elements that initiate the polymerization process. The liquid photopolymer in the tank is cured by beam. Then, the focal point of the beam is shifted up one layer thickness or the production table is moved down one layer thickness to pass to the second layer. The layer is cured with the beam again. The process continues until the piece is complete.

1.9.3. Powder bed fusion process

Powder bed fusion was the first commercialized AM method. This method is a process that proceeds by sintering the powdery material, adding a new powder layer on it, and then combining this layer with the substrate by sintering. In this method, a heat source is needed for the particles and layers to combine with each other. This joining occurs in the form of partial melting of the powders and the heat required for this melting is usually provided by laser. Since many materials can be used as raw materials in powder form, many materials such as polymers, metals and ceramics can be processed in this way.

For production, the material powder is laid on the production table with a thickness of ~ 0.1 mm. In order to prevent oxidation, the powder is heated to a certain temperature in a closed environment and/or in the presence of inert gases. Thus, less energy is consumed for laser melting and it prevents distortion due to thermal reasons during the cooling of the layer.

After the powder is laid and preheated, the laser creates the desired layer slice of the relevant model by melting the powder and combining it. The powder around the layer stays in the chamber, acting as a support structure. After the layer is completed, the build table is reduced by one layer thickness and the hopper is filled with powder again. The laser processes the new layer onto the powder. The process repeats until the piece is finished. After the part is completed, it is made ready by controlled cooling.

In powder bed fusion method, PEEK, PLA and PCL polymers, especially polyamide 11 and polyamide 12, are used as production materials. As metals, some of the Al Alloys, Ti Alloys, stainless and tool steels can be used as production materials. Other than that, some of the carbide, nitride and metal oxides are suitable for powder bed fusion.

In powder bed fusion process, the coalescence mechanics of powders can occur in 4 different ways [122].

The first of these is solid phase sintering. The driving force of solid phase sintering is the minimization of the total free energy.

In this process, the sintering rate decreases as the process progresses. The smaller the

particle size, the faster the neck formation and coalescence. Chemical sintering is seen in powders that can bond with each other and/or atmospheric gases. It plays a major role in the sintering of ceramic materials. For example, when SiC is sintered in atmospheric environment, SiO₂ is also formed and SiC and SiO₂ are bonded together to form composite material.

The third mechanism is liquid phase sintering and partial melting. For this process, a material that will melt and solidify and act as a binder can be added to the material. For metals with low melting temperatures, non-eutectic alloys and plastics, no binder is needed. Binders can be incorporated as a separate powder, composite (in combination with the base material), or as a particle coating. In these methods, porosity is an important problem in general. In addition, when the part is subjected to heat treatment to reduce this porosity, it is seen that the lower parts of the part are more dense than the upper parts. The reason for this is that the porosity in the lower parts is filled first with the effect of gravity during partial melting.

Finally, full melting method can be used for high density and strong interlayer bonding. It is generally preferred in engineering alloys and semi-crystalline polymers. Regardless of the joining mechanics used, sintering has important side effects in production. The first of these is the sintering and agglomeration of unused powder due to high temperature. This situation causes problems such as dimensional accuracy in the reuse of powder. In addition, this sintering situation also takes place around the part, forming a wall outside the part. Thus, the piece grows and the desired size sensitivity can be exceeded. The basic parameters related to production in the powder bed fusion method are laser power, focus size, laser pulse frequency and duration, powder size, layer thickness, scanning speed and pattern, and the temperature of the production chamber.

1.9.4. Material jetting

With this technology, which was started to be developed in the 1980s, polymer, ceramic and metal parts are produced. The first productive studies were made with different types of wax (microcrystalline petroleum wax, candelilla wax). Recently, it has been possible to produce with methacrylate resins and urethane acrylates. In ceramics, on the other hand, alumina and zirconia were worked with, but a large amount of shrinkage was experienced when the binders were removed and sintered to ensure porosity and cohesion. Aluminum, copper and tin are metals developed for the production of parts by spraying material [123].

This method works in the form of creating a layer by spraying the liquid material on the surface in a continuous or intermittent state, and this layer solidifies to form a substrate for the next layer. The first of the main problems of this method is to liquefy the material to be used. This process is done by melting it if it is a metal or polymer, and by preparing a solution if it is ceramic. The second main problem is that the sprayed droplets are in the desired size and shape. Small changes to be made in the material (additives, changing the viscosity, etc.) will directly affect the droplet structure and cause the process to be rearranged. The third main problem is to control the accumulation of these droplets on the surface. For example, when the droplets hit the surface, if the small particles are separated from the original droplet and scattered around, the desired sensitivity may not be achieved. Spraying can be continuous stream or drop-on-demand. In continuous spraying, liquid is fed regularly to the nozzle. In intermittent spraying, drops are created instantly upon request. For this, heater or piezoceramic material can be used [117].

1.9.5. Binder jetting

In this method, the first layer of the model is printed by spraying binder on the powder on the production table. Then, with the help of a feeding hopper and roller, powder is filled on the first layer with the desired layer thickness. The next layer is printed by spraying the binder. This process repeats until the piece is complete. Generally, after the part is completed, it is kept on the production table for a while to ensure that the binder strengthens its effect and gives strength to the model. In addition, after the part is removed and cleaned, a second binder can be impregnated to further increase the strength.

Generally, materials developed based on gypsum are used. The materials used as binders are water-based. Although the produced parts are more rigid than general thermoplastics, their strength is low. In addition, bronze and 420 stainless steel can be produced using polymer binders [124]. After production, a 3-stage heat treatment is applied to the part. First, the polymer binder is removed at low temperature and then sintered. Thus, the part has a density of about 60%. Finally, bronze infiltration is carried out to reach 90-95% density. Parts produced with Inconel 625 (Ni alloy containing 20% Cr, 5% Fe, 10% Mo, 4% Nb+Ta) can reach 99% density by sintering [125]. In addition, studies are carried out on ceramic materials.

The main advantages of this method are that it provides color production and the production speed can be increased by increasing the number of nozzles in the print head. However, the

material that can be used is limited due to the binder-material compatibility. And the strength values of the materials used today are quite low.

1.9.6. Sheet lamination method

The basis of this method is the creation of the sliced layers of the 3D model separately and bonding them to each other with adhesive, thermal or different ways. This method was commercialized in 1991, an earlier date than many AM methods. The method can use plastic, metal, ceramic and paper as materials. Butcher paper was used when the method was first developed. In the first developed method, the layer material was adhered to a substrate and then cut from the lines of the layer with a laser or mechanical knife. The remaining part was left on the production table as support material. In the following years, material diversity was increased with PVC sheets and today it has a much wider range of materials, including metal and ceramics [35]. In general, the advantages of this method are low residual stress, little warping and shrinkage in the final product, a large variety of materials used, and relatively low initial investment cost. However, the unevenness of the layer thickness in each layer, low dimensional accuracy, and inhomogeneity of the mechanical and thermal properties due to the adhesive are disadvantages [126].

Especially due to the difficulties experienced in the production of parts with interior details or gaps, production studies were carried out by first cutting the layer and then sticking it. This method also eliminates the risk of cutting a substrate. In particular, more than one method has been developed for the adhesion of layers to each other. The main ones are thermal bonding, screw tightening, ultrasonic sewing methods. In addition, production is made with belts containing ceramic and/or metal particles, and then the final part is obtained by sintering.

1.9.7. Direct energy deposition process

The point that distinguishes this method from other AM methods is that the material is not ready on the production table, but is transferred to the table with a feeder at the time of production. The method is based on the principle of melting and depositing the material to be used by providing the necessary energy. Although plastic, ceramic and metal materials can be used, metals are mostly preferred. Usually laser or electron beams are used as the heat source to melt the material. The material is added to the medium in the form of powder or wire.

The method is technically the same as laser coating and plasma welding. However, in this method, a completely new part is produced. Today, many companies in the AM sector have developed their own methods using this technology [127 – 129]. Although they all use the same basic structure, there are differences in laser characteristics, nozzle movement systems, powder and inert gas supply systems. The microstructure of the parts produced with this technology is similar to the microstructure of the parts produced by the processes using laser in powder bed technology. The density of the part is high as full melting is done during the process. In addition, the microstructure can be changed by changing the laser properties (intensity, depth, focal diameter, etc.). Again, by changing the scanning angle, the properties of the material can be made as isotropic as possible. Changing the scan angle also reduces the build up of residual stresses. The high thermal conductivity of the material used and the low ability to reflect light facilitate production. Therefore, gold and some Cu and Al alloys cannot be used for production. Ceramics, on the other hand, are not preferred because their melting temperatures are too high and they crack during sudden cooling. Instead, production in composite form such as Ti/TiC is preferred. At the same time, material changes can be made within the part by changing the powder ratios sent from different materials during production.

1.9.8. Extrusion – based systems

Extrusion-based systems are the most preferred among AM methods. The common point of these methods is that the raw material of the part to be produced is not found on the production table, it is transferred to the production table through the nozzle while the part is produced. One of the important details here is that the material coming out of the nozzle is solid in other methods, while it is semi-solid or liquid in extrusion-based systems. After the material comes out of the nozzle, it is printed on the production table and completely solidifies in that way. It also bonds with a substrate during cooling. After the relevant layer is completed, either the production table goes down one layer or the nozzle goes up one layer thickness. The extrusion process usually takes place by heating the material. Thus, the material can be kept in the desired phase. Although the method is similar to the classical polymer extrusion method, the main difference is that the extruder (nozzle) is in a movable and vertical position. The method applied for another phase change (solidification from semi-solid state) is chemical change. For this, materials that dry or react with air are used. This method is preferred especially in biomaterials.

1.10. Literature Review

As it is known, the subject of this thesis study is the production of composite materials with robotic new approaches using 3D printing method. Currently, there are not many studies on this subject in the literature. We tried to include the ones related to the subject, especially the innovative and original ones. In this context, the studies exemplified here are accompanied by a brief summary of the literature.

Sugiyama et al. investigated carbon fiber reinforced composite structures, which are made of light material with high tensile and compression strength on the outside and high shear rigidity on the inside, which are used in the construction of modern aircraft parts. During the production of these parts by conventional methods, complex and expensive joining processes are used. In this study, which was carried out to simplify this process and reduce the cost, production was achieved using honeycomb, rhombus, rectangular and circle internal structures by using a 3D printer that uses continuous carbon fiber [130]. In the continuation of the study, the functional properties, shape evaluations and properties of the produced composite structures were determined according to the 3-point-bending test. As a result of the 3-point bending test, it was observed that the maximum loading and bending modulus increased as the microstructure density increased in all microstructure pattern types. Since the mechanical properties vary with the shape of the internal structure, it was concluded that the desired strength and toughness can be achieved by using the desired internal structure design with a 3D printer that uses carbon fiber continuously. In addition, during the production of these prototypes, since the inner structure will be completely covered by the plates on the lower and upper sides, no support material was used and only the internal tension of the fiber yarns was used while the upper plate was printed. And looking at the prototype surface roughness obtained, it was observed that carbon fiber reinforced thermoplastics have a lower surface roughness than PLA sandwich structures [130].

Tekinalp et al., on the other hand, investigated the machinability, microstructure and mechanical properties of short fiber reinforced ABS composite material in their study. The length of the short fiber used is 0.2 – 0.4 m. The parts produced in the 3D printer were compared with the parts produced with the traditional compression method. Accordingly, the parts produced in 3D printers increased 115% in tensile strength and 700% in tensile modulus compared to parts produced from pure ABS [131].

While the fiber orientation is seen at a rate of 91.5% in the printing direction in the samples printed on the 3D printer, this rate is much lower in the samples produced with the traditional compression method. When the microstructure-mechanical property relationship was examined, a higher rate of porosity was observed in 3D printed samples compared to conventional compression. In addition, while there was visible porosity in the samples produced in the FDM device with ABS containing carbon fiber, this situation was not observed in the samples produced with the traditional compression method. As the fiber content increased, the porosity in the FDM seam (the line left by the nozzle on the table with the melted material) increased, but the spacing between the seams decreased. When the samples produced by both methods are examined, the samples consisting of pure ABS have higher strength. It has been observed that the strength values of the parts produced with the traditional compression method have higher strength values than the parts produced with FDM. From this result, it was understood that the effect of the porous structure was more than the effect of fiber orientation. In addition, when the images were examined in the scanning electron microscope, it was noticed that the fibers came out of the matrix surface, and in this case, it was concluded that the adhesion between the fiber-matrix surfaces was not good enough. As a result of the study, it was concluded that the full potential of the FDM method can be revealed by reducing the porosity, increasing the adhesion between the surfaces and preventing the fiber breakage [131].

Caminero et al., on the other hand, investigated the effects of layer thickness, compression direction and fiber ratio in carbon, glass and kevlar continuous fiber reinforced nylon composites. It was observed that glass fiber reinforced samples had the highest impact strength, while carbon fiber reinforced samples had the lowest impact strength [132].

Khan et al. evaluated the tensile deformation behavior of these two resin types with increasing compressive stress rate in a study they conducted on polyester and vinylester resins used as matrix in glass fiber reinforced composite materials. In order to explain the effect of resin properties in composites, the strength of the resins was compared with the strength of composites containing 42% by weight short fiber reinforcement. Pressure tests were carried out on samples prepared in the form of 10 mm cubes from resin plates molded with a curing time of more than 10 weeks. They determined that the stress strain behavior increased in the linear elasticity region depending on the increasing stress rate and there was a significant difference between the two resins in the flow stress beyond the maximum stress value. In the case of polyester resin, they found that while the flow stress drops significantly

and rapidly from the maximum stress, especially at high strain ratios, a non-significant gradual decrease occurs in the samples of vinylester resin. When the tensile and maximum stress values in the linear elasticity region were compared for both resins, it was seen that both strength values of polyester resin were significantly higher than those of vinylester resin. Likewise, the average modulus value of polyester resin was found to be 18% higher than vinylester resin. When the results are evaluated, it is seen that vinylester resin tends to remain compatible even at high strain rates; On the other hand, it has been observed that polyester resin is brittle and tends to be less compatible at high strain rates, and increasing compressive stress rate affects the mechanical properties of polyester and vinylester thermoset resins. When the strength and modulus estimations of short fiber reinforced composites are evaluated, it is not correct to decide only according to the mixing rule; It has been observed that factors such as interface strength, fiber directions, and voids affect the results [133, 134].

Hawa et al., in their study to investigate the effects of aging and impact loads on epoxy resin composite pipes reinforced with E-glass fiber, produced pipes by filament wrapping method with a wrapping angle of $\pm 55^\circ$. Test samples were taken from these pipes. After immersing the samples in tap water at 80 °C, they were aged for 500, 1000, and 1500 hours time intervals. The same samples were subsequently subjected to burst tests by applying impact loads at three different energy levels (5 J, 7.5 J and 10 J). The images of the test samples were taken with a scanning electron microscope and they determined the correlation between the aging time and the impact energy level on the burst strength of the pipes. The test results showed that the maximum force and displacement increased as the impact energy increased. Burst test results revealed that aged samples gave lower burst strength with higher energy. They observed seepage and eruption defects depending on the applied impact energies [135].

Vinay et al., in their study to experimentally analyze the developing defect process when polymer-based hybrid composites are exposed to tensile and bending loads; Kevlar/carbon fiber vinylester resin and glass/carbon fiber vinylester resin hybrids were produced by hand lay-up method in different combinations with fiber and matrix weight ratios of 60% and 40% and fiber directions as 0° and 90°. Glass and carbon fiber are impregnated with vinylester resin as a single matte fabric, and kevlar and carbon fiber each as a single matte fabric. Cobalt naphtanate was used as an accelerator and methyl ethyl ketone peroxide was used as an initiator in the curing of vinyl ester resin. They conditioned the laminate they

prepared at 30 °C for 3 hours. When the tensile strength is compared, they have seen that the sample composite using glass fiber 0° and carbon fiber 90° showed better improvement. They interpreted the reason for this as surface reform, which improves the adhesion between resin and fiber. When the bending strength was examined, the strength value of the same sample composite was found to be higher. In the Shore D hardness test, it was determined that the composite in which glass and carbon fiber 0° and kevlar and carbon fiber 90° had the highest value. They concluded that the adhesion at the fiber-matrix interface is very excellent for these sample composites [136].

In their study, Okabe and Takeda investigated the effects of stress applied to unidirectional CFRP composites experimentally and analytically. The aim of this study is to present a new micro-mechanical model for internal damage in the composite internal structure. With this model, he revealed the statistical determination of the breaks in the fiber by overlapping with the experimental data [137].

Changliang et al. investigated the damage caused by impact in cylindrical materials produced by fiber winding technology under internal pressure conditions by finite element method. In the study, it was observed that the damage occurred in the tubes, which are exposed to internal pressure and produced by the fiber winding method, are more than the tubes without internal pressure. This study shows that the exposure of the continuous fiber to damage during winding has a great importance in the working performance of the manufactured product [138].

In Cohen's study, the effect of the parameters during the fiber winding process of the tubes on the product was statistically discussed. The most important of these parameters is the magnitude and duration of the prestress. These two variables revealed that the produced pressure vessel plays an important role in terms of strength and quality [139].

Mili and Necip investigated the low velocity impact behavior of glass/epoxy laminated composite plates with three different arrays using aluminum percussion. During the experiments, the acceleration of the impactor, the displacement of the impactor and the collapse values at the impact center were measured, and the effect of the arrangement of the laminated composite plates and the impact velocity on the composite plates was investigated. The Hertzian contact law was used to verify the experimental results, and results consistent with the experimental data and the theoretical model were obtained. However, it was observed that the compatibility between the experimental and theoretical

models decreased with the increase of the impact velocity. It has been explained in the related study that the reason for this is friction losses [140].

Belingardi and Vadori conducted impact tests at different low speeds with carbon fiber reinforced laminated composite plates with two different stacking shapes and three different thicknesses. Using the force-displacement curves obtained from the experiments, they investigated the energy absorption capacity of the plates [141].

Mitrevski et al. investigated the impact damage resistance of hemispherical, ogive and conical strikers and carbon/epoxy layered composite plates and the effect of striker shape. At the end of his experimental studies; showed that the highest energy absorption and impact penetration were in the conical strikers, the highest peak force value and the lowest contact time were in the hemispherical strikers, the damage initiation load was the highest in the hemispherical tipped, then pointed and then conical strikers [142].

In recent studies, the prominent methods in the production of polymer matrix composite materials reinforced with reinforcement elements by AM methods; Stereolithography (SLA), Laminated Object Manufacturing (LOM), Fused Deposition Modeling (FDM), Selective Laser Sintering (SLS) and Extrusion. The production of composite materials in AM technologies is of great interest despite the need for very complex systems. It is one of the newest subjects of AM technologies. At the same time, it offers us the possible improvements that can be achieved with many different combinations in terms of mechanical properties.

During the production of parts, 3D printer development studies that can produce composite parts by adding additives such as nano-particles, carbon nanotubes, graphene, fiber, and powder have increased in recent years [143]. The produced parts exhibit different advanced properties depending on the additive. Desired electrical, thermal and mechanical properties can be obtained with these additives [144]. It is necessary to develop new methods in order to produce composite products with AM methods [145].

The use of fiber as a reinforcement material in reinforcing polymers seems to be attractive for researchers. Premixed materials using particles (short fibers) as additives are an area of intense research as a viable alternative to multi-head printers with complex and costly designs. Polymer matrix composites have been the focus of attention in the production of AM methods, especially due to their ease of production and usability.

Various forms of thermoset and thermoplastic polymers are used as matrix materials in the

AM field. These improvements with fiber reinforcements offer positive combinations for the future development of AM technology [146, 147]. In addition, most current AM methods can utilize fiber reinforcement applications.

Although fiber-reinforced 3D printers are promising [148], there are many problems that need to be solved according to their usage patterns. Some of these can be counted as the negative effect of fibers on solubility, agglomeration problem, heterogeneous fiber distribution, shadow effect, hollow structure, non-adhesion between fiber bundles, and curing time [143].

The method used in the production of polymer matrix composite materials by AM methods is related to the chemical properties of the matrix material and the shape of the reinforcement material. Thermoset and thermoplastics can be used as matrix. Thermoplastics require the matrix to be melted and solidified, whereas thermosets require a catalyst, temperature or UV light, or combinations thereof. Reinforcement materials can be nanotube, powder, particle (short fiber), fiber or fabric.

The melt stacking process is one of the AM methods that has been used in recent times and on which R&D studies have been carried out. Thermoplastic materials are used in this process. The molten thermoplastic material is laid on the layer from the nozzle along the paths obtained by slicing programs. Thermoplastic materials, which solidify by cooling in the relevant layer, are arranged side by side along the cross-section to form layers. The next layer is written by lowering the table as much as the layer thickness in the z-axis. At the end of the layers written one after another, the part is obtained. The melt accumulating process is one of the most widely used AM methods in practice. The most important reason for this is that the material used can be supplied cheaply in terms of its shape and the process is very simple, and there are many manufacturers. A melt stacking AM device basically consists of CNC, feed mechanism, melter, nozzle, table and electronic control card with X, Y and Z directions [149]. In this method, there are important parameters such as the scanning path of the nozzle in the layer, the filling rate, the scanning speed, the table temperature, the nozzle temperature. Various studies have been carried out on the ways the nozzle deposits the melt on the layer, and its effect on compressive and tensile stresses has been studied in detail [150]. In another study, the temperature distribution on the part during part production was examined with a thermal camera, and the effect of temperature differences on part geometry was examined [151]. The surface hardness and cross-sectional shape of the parts produced by these processes are still being studied intensively. The bonding of layers and

stacks to each other in parts formed by molten agglomeration is shown in Figure 1.18 [152, 153]. Figure 1.18-a shows the formation of bonding between the two piles (1-contact of surfaces, 2-neck development, 3-molecular diffusion and bond formation at the interface). In Figure 1.18-b, the microscope image of the cross-sectional area of a part produced by the melt-stacked process is shown.

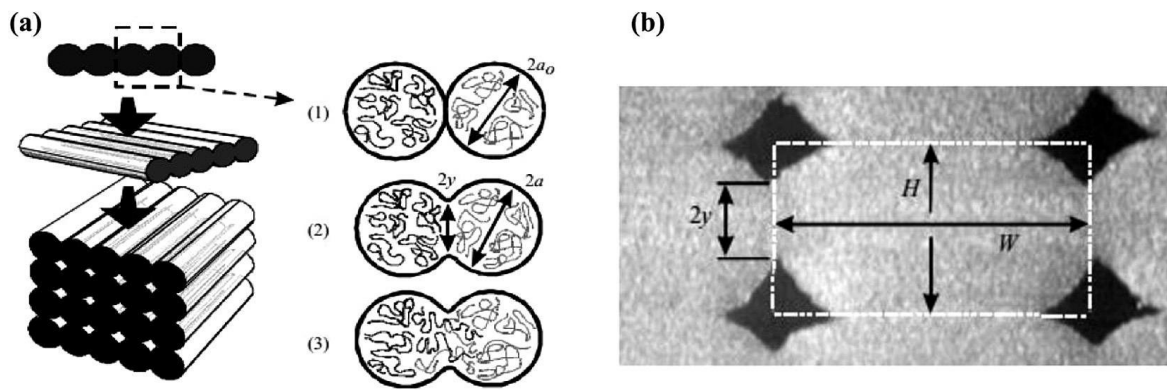


Figure 1.18 a) Bonding formation b) Cross-sectional view of a piece produced by molten agglomeration [152].

Many spelling rules have been proposed to improve the mechanical properties of products. For example, these can be counted as determining writing paths according to the direction of tensile stresses, stress distributions in corners, increasing the filling rate in increasing hardness and strength, using smaller nozzles to increase surface quality, and different orientations in areas where compression and tensile stresses occur [150].

Figure 1.19 shows the SEM images of the fractured cross-sectional area as a result of a piece formed at right angles (two-sided) to each other by pulling it in the tensile test.

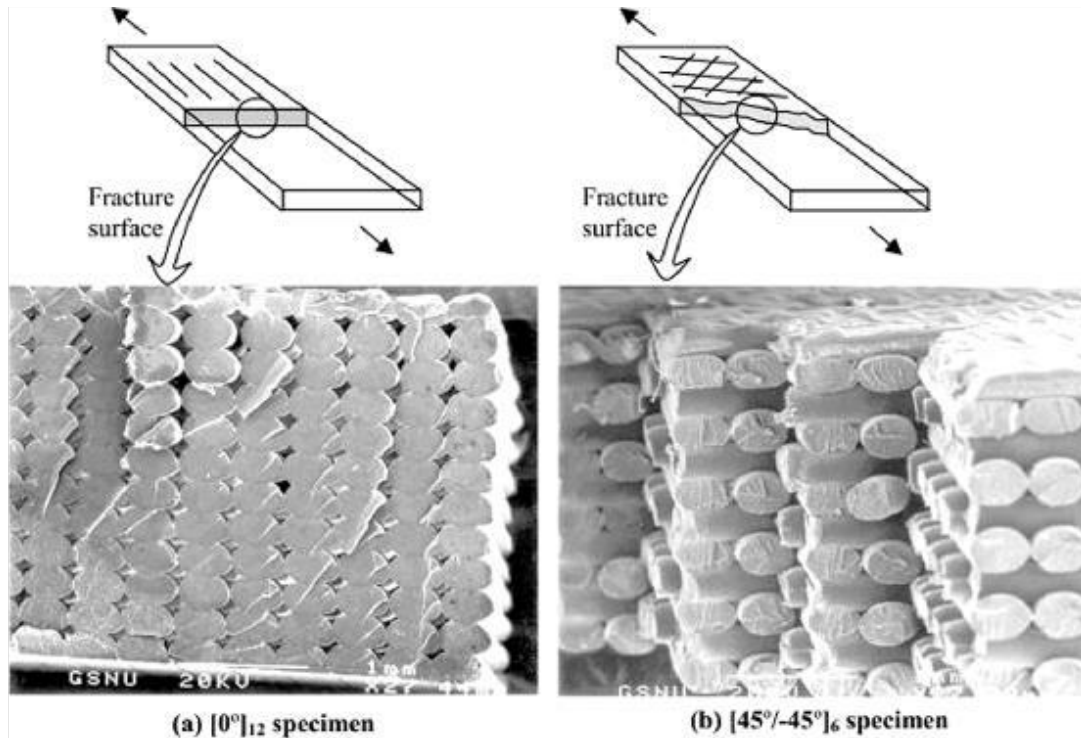


Figure 1.19. SEM images of the fractured surfaces of the samples produced as a) unidirectional $[0^\circ]$, b) bidirectional $[45^\circ/-45^\circ]$ [150].

The melt deposition process is also commonly called FDM in our country as an abbreviation of the English terminology. In the works where continuous fiber is used as a reinforcement element, the part creation process is physically similar to this method, so it is generally called similar to the FDM process in composite works. However, in systems using continuous fiber, melted thermoplastic materials are used as matrix material, as well as thermoset materials that are cured by different methods. The term 'melt' is not correct for applications using these materials. Therefore, from now on, studies using continuous fiber in this study and performed similarly to the FDM method (even if the owner uses it as FDM) will be called fiber stacking because it is more inclusive. Whether the matrix material is thermoset or thermoplastic does not contradict the fiber stacking terminology.

Recently, it has become popular among researchers to use fiber additives in the FDM process. Most of the studies have focused on the production of new filaments by using short fibers in filaments. By adding fibers to the filament, the print quality at the nozzle tip was increased and the product strength was also improved [154]. Carneiro et al., in their study, made investigations by adding glass fiber into polypropylene [155]. In their examination, they achieved an improvement in mechanical properties of the order of 30-40% compared to pure propylene. Steam Produced Carbon Fiber (SPCF) and Single Wall Carbon Nanotube

(SWNT) were mixed with ABS and used in the FDM method. The tensile strengths of the samples with added 5% by weight of SPCF and SWNT were increased by 18% and 31%, respectively, while a serious decrease was observed in their ductility [156]. ABS containing oriented SPCF and SWNT showed up to 93% improvement in strength properties [157]. The SEM image of the composite material produced by fiber routing is shown in Figure 1.20.

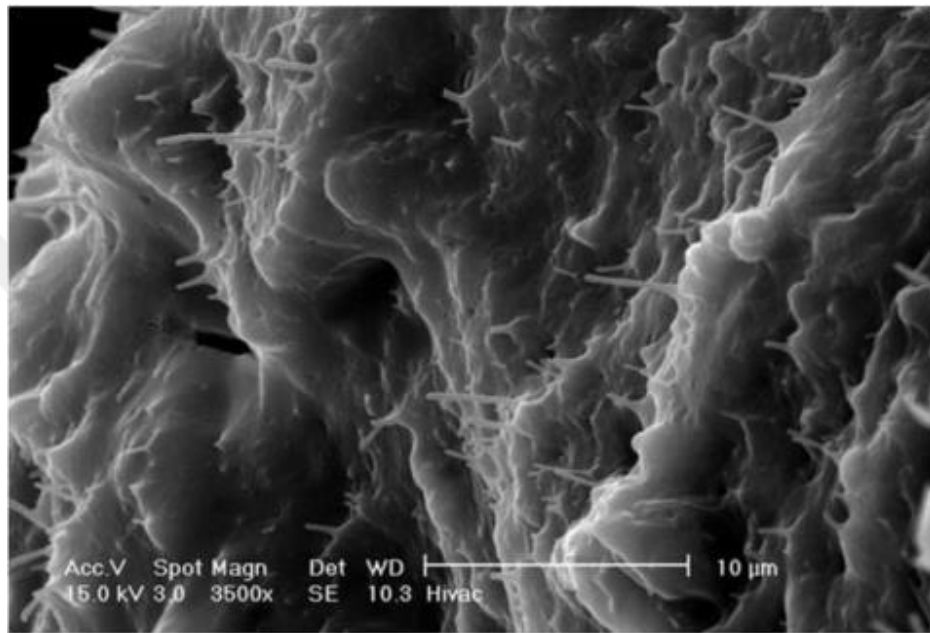


Figure 1.20 SEM image of SPCF / ABS composite material prepared by FDM with aligned SPCF [156].

SEM image of SPCF / ABS composite material prepared by FDM with aligned SPCF [156]. Ning et al. investigated the effect of fiber length and weight ratio on strength in carbon fiber additive to ABS material in FDM process. Carbon fiber ratios of 5% and 7.5% by weight gave the best results in tensile strength and Young's modulus. These researchers concluded that the use of long fibers gave more positive results in terms of tensile strength and Young's modulus. In Figure 1.21, the effect of fiber use on the strength of the parts produced by the melt stacking process is schematized. In the aforementioned study, the use of 30% weight oriented CF–ABS composite material in the melt stacking method increased approximately 115% in strength and 700% in Young's modulus [158].

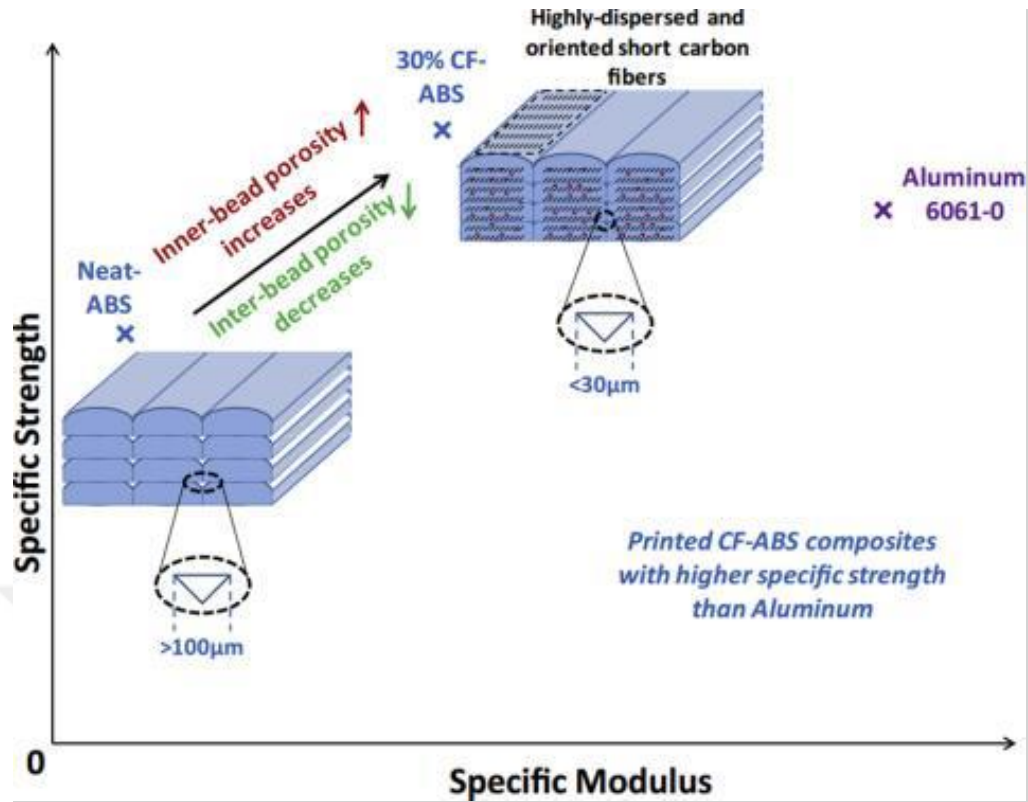


Figure 1.21. Schematic representation of fiber-reinforced composites in parts obtained by melt-stacked modeling [131].

The CF-ABS samples used showed higher strength than aluminum in terms of strength. The triangular channels between the steps are reduced by incorporating carbon fibers into the array. Decrease in mold swelling and increase in thermal permeability are effective in reducing these channels. However, the incorporation of carbon fibers into the feedstock causes stress concentration, and damage can occur at low stresses. The pores formed between the steps during the production in the sample produced with FDM can be seen in Figure 1.22 [131]. In Figure 1.22-a,b, the SEM view of the cross-sectional view is given as a result of the production of pure ABS by melt-burden modeling method. In Figure 1.22-c,d, SEM image of 10% by weight carbon fiber reinforced composite sample is given.

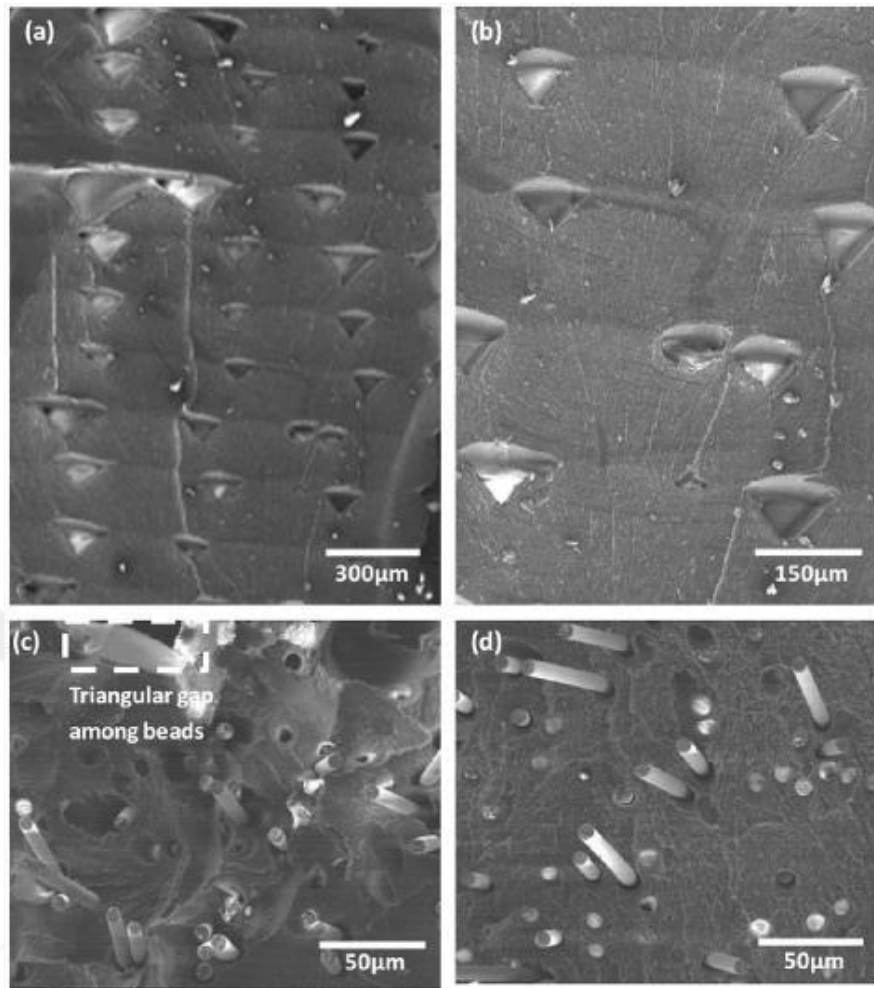


Figure 1.22 SEM images of a,b) pure ABS manufactured with FDM, c) 10% by weight carbon fiber added part, and d) 10% weight carbon fiber reinforced composite produced by compression molding [131].

The biggest challenge facing researchers in the production of polymer composites in 3D printers is currently continuous fiber reinforcement studies. Although it offers us very important improvements in terms of strength compared to the use of discontinuous fiber, there is still no strong and accepted method for the use of continuous fiber. Matsuzaki et al. have developed a new technique for impregnation in the nozzle using a thermoplastic matrix and continuous fiber. In this method, the thermoplastic filament and fiber are fed separately before being heated and mixed at the nozzle. The mixture is then laid out on the tray. In Figure 1.23-a, the impregnation of the thermoplastic matrix to the fiber at the nozzle is shown schematically. Figure 1.23-b shows the fiber bundles used in the process. In Figure 1.23-c, an image recorded during production is seen [159].

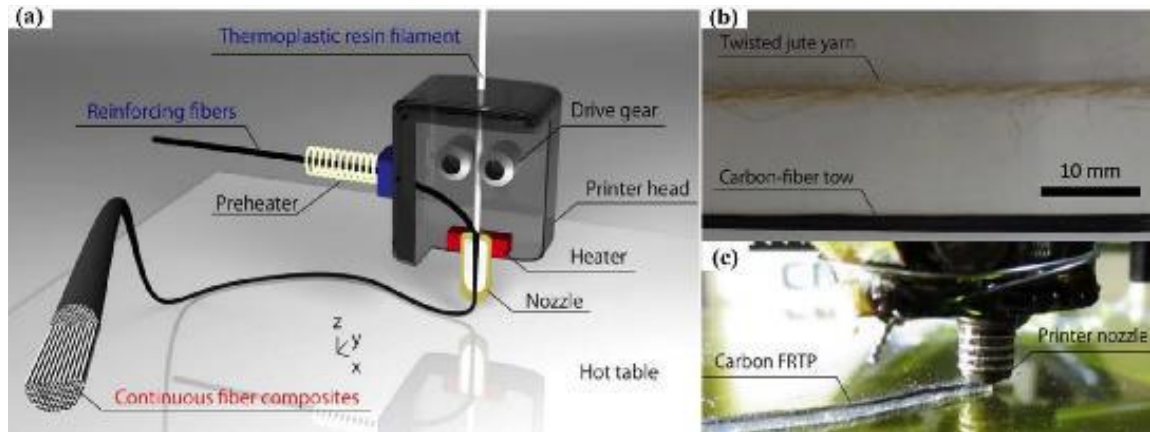


Figure 1.23. Production of continuous carbon fibers by impregnation in the nozzle in the melt stack modeling method a) system diagram; b) the fiber bundle used; c) a view during production [159].

Carbon fiber and twisted jute fiber were used in the reinforcement. Figure 1.24 shows the superiority of continuous fiber use over short fiber and other reinforcement materials and methods. The effect of tensile strength is observed for the samples reinforced with carbon fiber and jute (Cannabis) fiber.

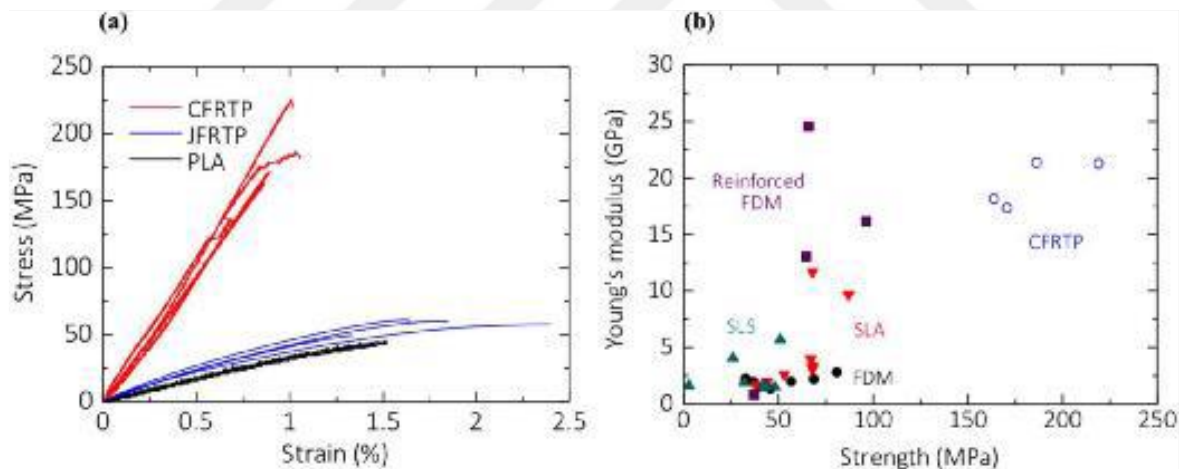


Figure 1.24 a) Stress-Elongation curves of PLA, unidirectional carbon fiber reinforced thermoplastic (CFRTP) and unidirectional jute fiber reinforced thermoplastic (JFRTP); b) Young's modulus and strength comparison according to some methods [159].

Namiki et al applied the same technique for PLA [160]. It has been stated that gaps occur that can be reduced by increasing the resolution. Li et al. observed that the tensile strength of PLA parts reinforced with short fiber was up to 68 MPa, while the tensile strength of up to 91 MPa was obtained in the use of long fiber [161]. The weak bond between PLA and fiber significantly affects the mechanical properties [162]. However, an increase in tensile

and flexural strengths was observed in CF-PLA (carbon fiber reinforced PLA) samples that were surface modified with methylene dichloride in carbon fiber bundles [161]. Figure 1.25 shows the tensile and flexural strengths of pure PLA, CF-PLA, and modified CF-PLA.

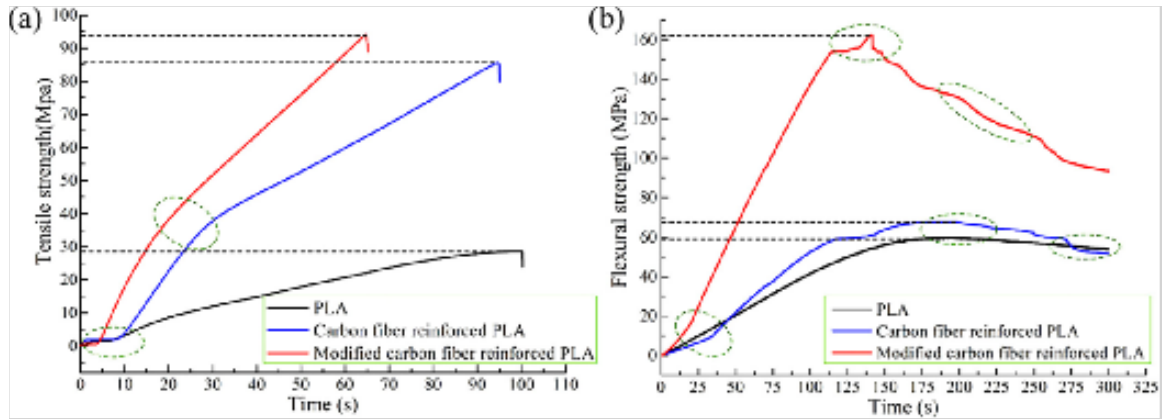


Figure 1.25 Mechanical properties of CF-PLA, CF-PLA and pure PLA modified with Methylene Dichloride a) tensile strength, b) bending strength [161].

The green circles in Figure 1.26 a) show the different phases of the stretching process, i.e. loading of the PLA material between the fixture and the test specimen at the start of the test, and a slight decrease in curve slope due to bonding to the fiber-matrix interface. The circles in Figure 1.26 b) show the load change from resin to fiber at the beginning of the test. As seen in Figure 1.26 b), plastic elongation of PLA polymer chains continued for a while after the carbon fibers were broken. Tian et al. demonstrated the performance of carbon fiber reinforced PLA and the effect of temperature and pressure on the process with a systematic analysis. In Figure 1.26, normal and SEM images of the drawbar cross-section structure and the fibers on the fractured surface are shown, while in Figure 1.27, it is shown in practice that geometries with curved surfaces can be constructed without losing continuity with continuous fibers in 3D printers [163].

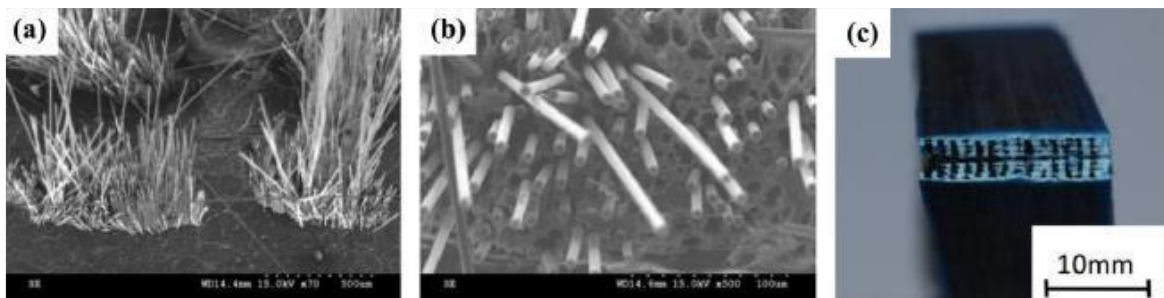


Figure 1.26 a,b) Sem image and c) sectional view of a part based on a continuous carbon reinforced PLA [163].

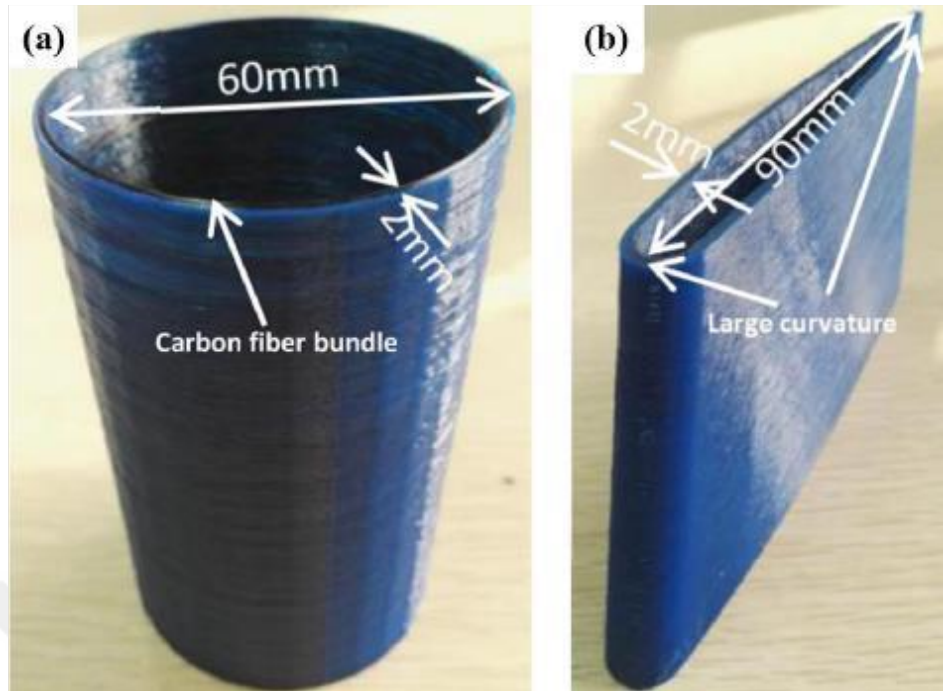


Figure 1.27 High curvatures can be built using carbon fiber reinforced PLA material, continuous carbon fiber [163].

Melenka et al evaluated nylon structures printed on continuous Kevlar fiber reinforced 3D printers using commercial desktop printers to determine their tensile properties [164]. In the study, a significant increase in hardness and strength was obtained with fiber reinforcement. In order to improve the strength and fatigue life, carbon fibers were placed between the polymer layers in 3D printers, while heat treatment was carried out to further increase the mechanical properties [165]. In addition to these, Van Der Klift et al. suggested that as the carbon fiber layers increase, the voids within the part increase, which has a negative effect on the tensile strength [166]. In order for the plastics to be absorbed into the fiber bundle, the process must be between 200 - 230 °C. It was stated that the layer thickness should be 0.4 - 0.6 mm and the line width within the layer should be 0.6 mm. They obtained 335 MPa flexural strength and 30 GPa flexural modulus under these conditions [166].

In this system, which was first developed by the Helisys company, the layer is cut by a laser or cutter in the form of a 2-dimensional cross-section, and each layer is associated with the next. The basic processes of layered object fabrication are shown schematically in Figure 1.28. In this method, paper, metal, plastic, fabric, synthetic materials and composites are used [167, 168].

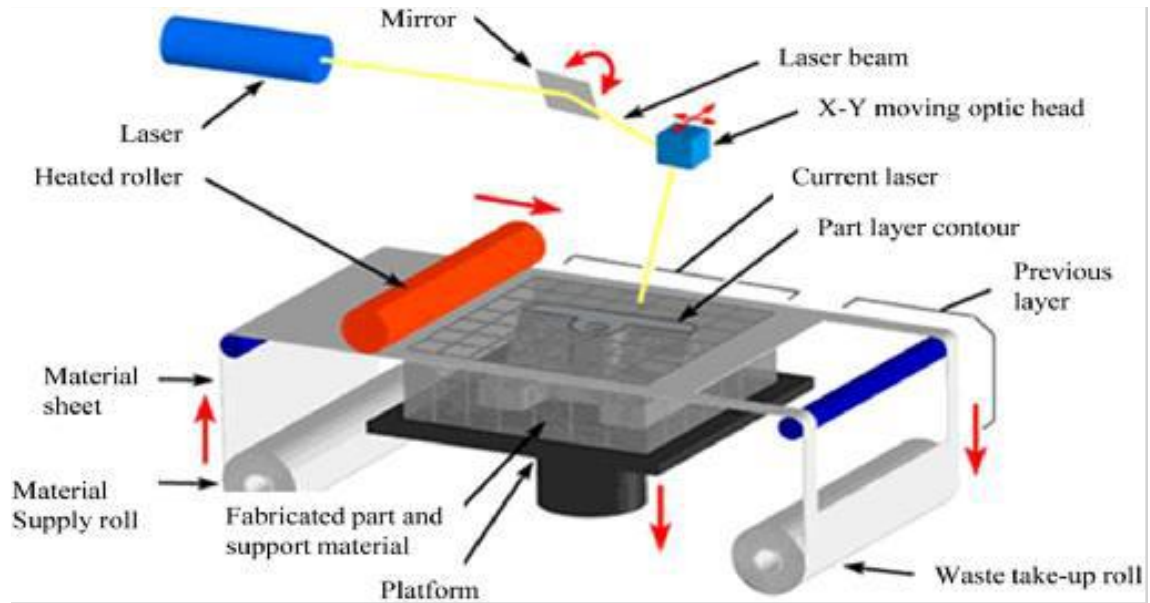


Figure 1.28 Schematic illustration of Layered Object Fabrication [169].

C-shaped polymer matrix composites can be produced directly with a curved LOM. The working principle of the curved LOM and the sample product are shown in Figure 1.29 [170].

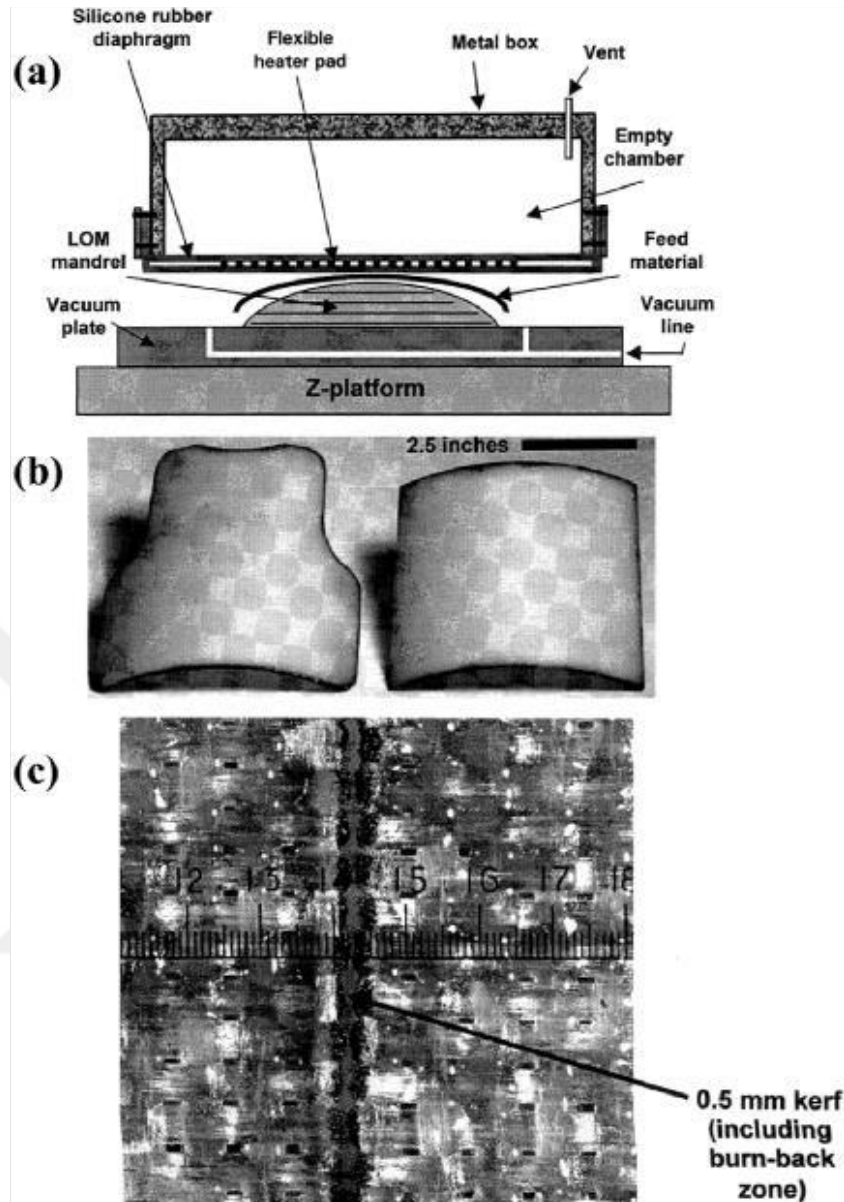


Figure 1.29 a) Operation scheme of curved LOM, b) Cured glass fiber/epoxy composite part made with LOM, and c) Glass fiber/epoxy composite part made with LOM from prepreg fabric and cut with CO₂ [170].

Vacuum is applied to the prepreg fabric with a thermoforming apparatus. The deviation in altitude is up to 7.9%, while accuracy is below 1% in other directions. The shear strength of a produced composite was measured as approximately 24.8 MPa. This value has been accepted by the author as a normal value that can be obtained in a standard process. Figure 1.30 shows the composite part and its internal structure produced with unidirectional continuous glass fiber by the LOM process [171]. When we examine the microstructure of the polymer composite produced with LOM, it is observed that the bonds between the layers are smooth.

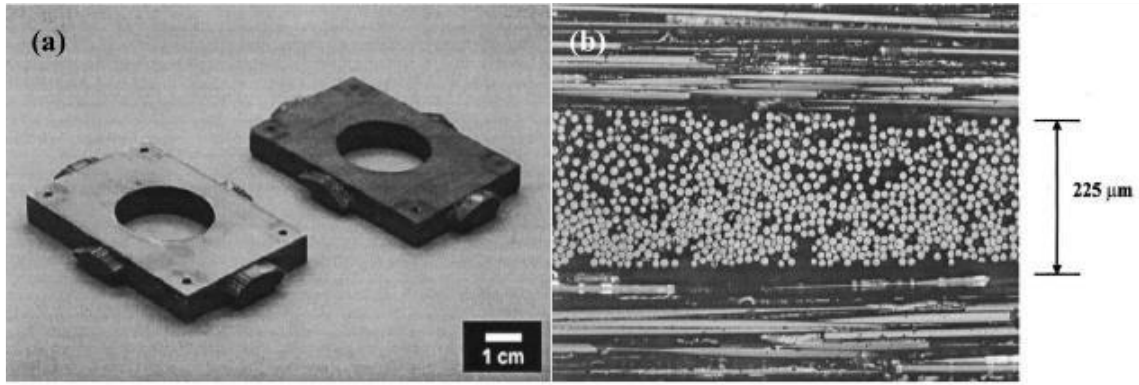


Figure 1.30 a) LOM fabricated glass fiber/epoxy composite piece with unidirectional fabric, right piece cured, and b) section view with $[0^\circ/90^\circ]$ array [171].

The biggest problem encountered in LOM processes is that the heated roller cannot fully cure the layers. This helps to strengthen the bond between the layers and to reduce the internal spaces. The heat transfer during the LOM process was studied to understand the effect of temperature and stress distribution. A new method called Laser-assisted AM using continuous fiber thermoplastic composite material has been developed [172]. In the study, the author suggested using prepreg tapes using continuous fibers instead of prepreg sheets using pre-cut short fibers. While the bands are lined up layer by layer with the help of a cylinder, they are cut with the CO_2 laser beam. The production scheme and the comparison of the sample product with other methods in terms of strength are shown in Figure 1.31.

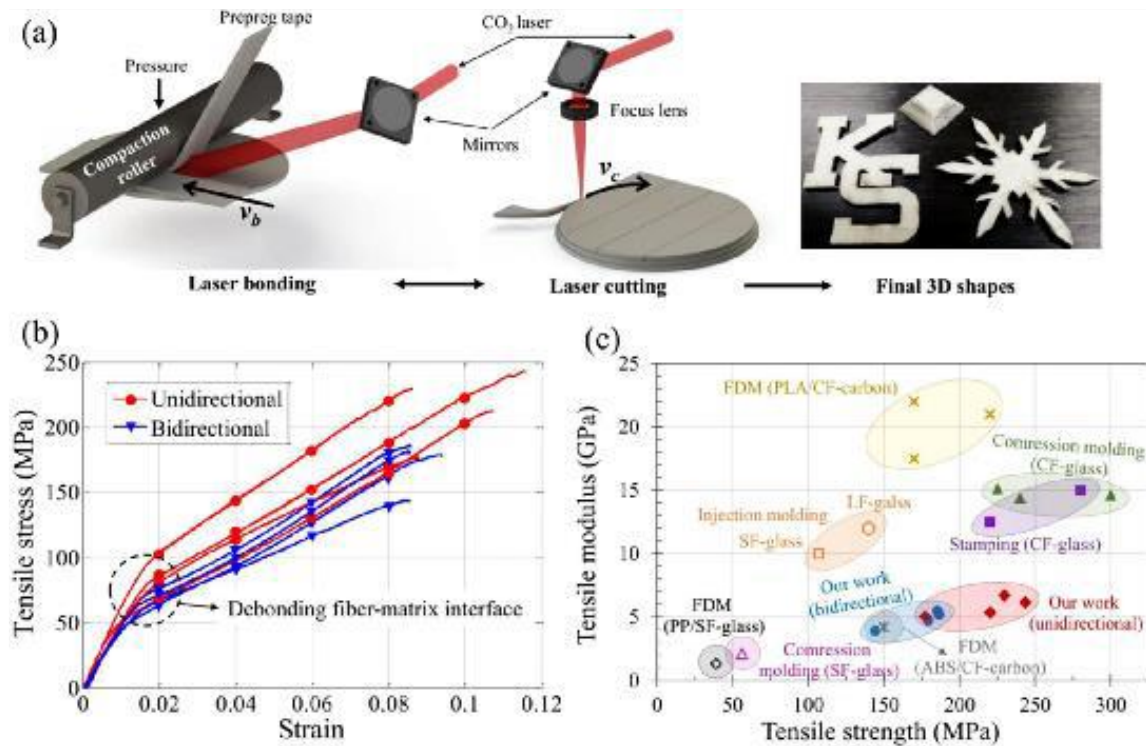


Figure 1.31 a) Schematic representation of the laser-assisted AM process and sample part produced. b) tensile stresses of unidirectional and bidirectional fabrics. c) Comparison with other methods in terms of strength [172].

This method shows significant results in terms of mechanical properties with the use of continuous fiber, high fiber mass ratio, reduction of internal voids.

Parts produced with SLA exhibit poor mechanical properties that prevent their functional use [173]. However, they can be used functionally by strengthening them with fiber. Although the use of continuous fiber seems ideal for reinforcement, the high fiber mass ratio in the use of short fiber makes the use of short fiber comparable, but in the use of short fiber, the breaking of the fibers in mixing with the resin, the random distribution in the material and the fiber fragments of different lengths make the use of short fibers inefficient.

Multi-walled carbon nanotubes have been mixed mechanically and ultrasonically for use in SLA systems [174]. By adding 0.025% carbon nontube by weight, increases of 5.7% and 26% were observed in tensile and bending strengths, respectively. Carbon fiber has been successfully applied to reinforce polymers. But the biggest problem in using carbon fiber is that it is opaque. The resin cannot be cured in the areas blocked by the carbon fiber. Some methods have been developed to overcome this problem. One of them is the use of glass fiber. Glass fiber transmits UV light and reduces the curing problem [175]. Vacuum molding process has been applied to increase the mechanical properties [173, 176]. An increase of

36% in tensile strength and 11% in hardness was observed in polymer glass and nonwoven-polymer sandwich structures obtained by vacuum molding process. The resin viscosity increased significantly [177]. This is important to obtain a high fiber ratio. Laser scanning SLA was used to process acrylic-based photopolymer resin materials containing 20% by volume short glass fiber (length:1.6, diameter:15.8 μm). Figure 1.32 shows the microstructure of samples containing 20% by volume fiber obtained in the experiment [178].

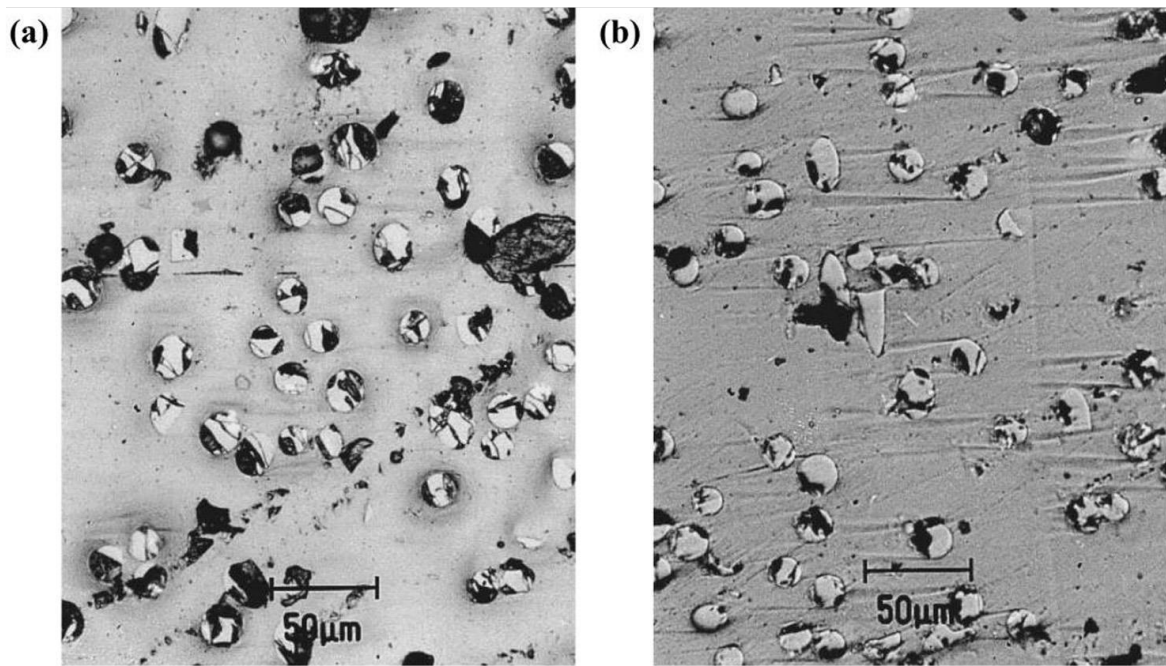


Figure 1.32 SEM image of polymer composite containing 20% fiber by volume produced with SLA, a) Molded sample; b) Sample by laser scanning [178].

Fiber-reinforced polymers offer high elastic modulus and upper tensile strength. In addition, it was observed that the shrinkage / tensile during the production phase is less in fiber reinforced parts. It is used in polymers that cure with double action with UV light and temperature. This solution was considered because the carbon fiber shadows the resin [179]. In particular, the resin remaining between the carbon fibers was estimated to be a quarter of the total. After one hour of heat curing, it was observed that the tensile strength increased by 95%.

The curing method of the resin is also important in terms of mechanical properties. Alpöz et al. investigated the effect of light curing method and light penetration time on the mechanical properties of resin-based dental materials. They used 2 different light sources as the light source. The first is the Optilux501 halogen light source with a wavelength of 400-

515nm and an intensity of 700mW/cm², and the second is the LED bluephase C5 brand LED light source with a wavelength of 430-490nm and an intensity of 500mW/cm². In the study, Vickers hardness value and compression value after curing of the resins by using LED and halogen light source on 3 different resin types (1st type Tetric Ceram, 2nd type Compoglass, 3rd type Fuji II LC) used in dental applications with different penetration times (20s and 40s). strength was measured. As a result of the study, the 1st type resin was cured with 40s LED and 40s halogen light source and no significant compression strength was observed. However, when cured with LED light source for 20s, a significant decrease occurred in compressive strength. The 2nd type resin gave the highest compressive strength at 40s and 20s with LED light source, then 40s with halogen light source, respectively [180].

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The mechanical properties of the photopolymer resin were determined by producing the tensile samples obtained by layering from the edge and surface from photo-cured epoxy using the stereolithography method with different alignment angles. Experiments were carried out in a dark environment in order to eliminate the curing effect of ambient light. Layer thickness of 0.175mm, laser scanning speed of 3200 mm/h, laser spot width of 0.08mm, cross hatching and laser power of 2.5W were chosen as the fixed values used in the experiment. WatershedXC 11122 was used as the photopolymer resin. Tensile specimens were produced as 0°, 45°, 90° with different surfaces and edges. In addition, post-curing was applied to the produced samples for 0, 2, 4, 6, 8 hours. In the test results, the maximum tensile strength was the highest in the sample produced from the edge and having an angle of 0°. The lowest tensile strength value appeared in the sample produced with 0° from the surface. In the post-curing results, 5 samples were produced with the same method and at the same angle, kept for different times, and then tensile test was applied. As a result, the highest tensile strength was obtained in the sample that was post-cured for 8 hours. On the other hand, the lowest tensile strength value was determined in the sample without post-curing [181].

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Jim Lee et al. In their study, they tried to determine the curing depth of the photopolymer experimentally and theoretically. They stated that in the stereolithography method, the curing depth of the photopolymer resin determines the layer thickness, and there is a relationship between the curing depth and the light intensity. In their experiments, photopolymer resin and a laser with a wavelength of 325nm, 250um as a spot width and a laser power of 40mW (He-Cd) were used. To determine the layer thickness, experiments were carried out at 3 different energy densities (0.931 j/cm², 1.732 j/cm², 22.255 j/cm²). As a result of their studies, they stated that as the energy density increases, the curing depth increases exponentially [182].

Marta Invernizzi et al. They worked on UV supported 3D printing of polymer composites obtained by double curing glass and carbon fiber reinforced. They used a new double curable resin formulation in their work, cured with carbon fiber and glass fiber, with UV light and temperature [183].

Llewellyn et al. used an ultrasonic system to disperse micro glass fibers [184]. In this way, they were able to place the fibers in the resin at different angles. This method paved the way for smart material production [185].

Extrusion, as one of the latest developments in 3D printers, has emerged as a method that has expanded the boundaries of the FDM method with its versatility and low cost. In this AM technology, layer-independent free-form production is performed [186]. Lightly porous carbon fiber (10µm diameter and 220µm length) and SiC mixed composite were stacked on the table as shown in Figure 1.33 [187].

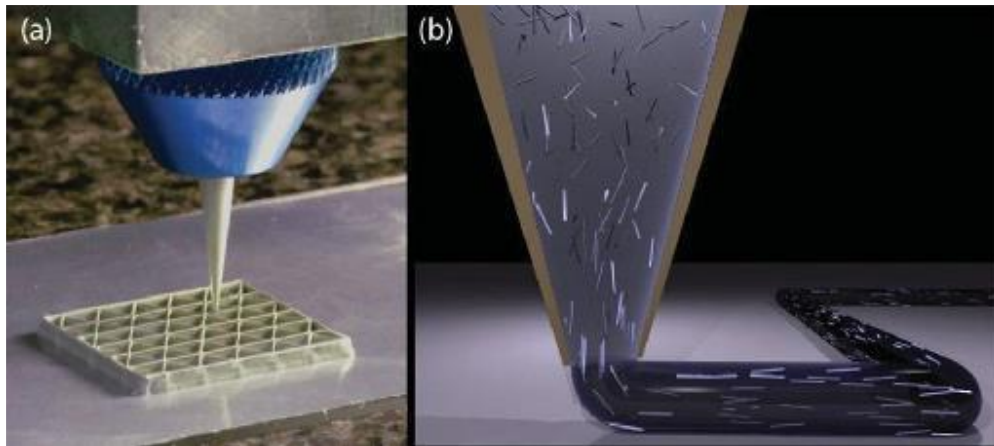


Figure 1.33 a) A 3D rendering of the triangular honeycomb piece. b) schematic view of the process that occurs during composite ink deposition [187].

Epoxy-based ink, which has the desired properties in terms of viscoelasticity and shelf life, is prepared for use. The author suggested that the fiber directions are the same as the production direction. As a result of the experiments, a significant increase was observed in the Young's module. Young's modulus increased from about 3-10 GPa to around 16-25 GPa. PLA/MWNT composite has been used to produce conductive 3D parts by a method called liquid agglomeration modeling [188].

SLS is a powder-based AM method. The laser scans the table where the powders are laid, and during this scanning, a 3-dimensional structure is created layer by layer in the places where the laser passes. The schematic of the method is shown in Figure 1.34. In this method, mainly wax, ceramic, metal and polymers are used. Polymers frequently used in the SLS method can be listed as nylon, polyamide (PA), polyethylene (PE), PEEK and PCL. Composite production in the SLS method was mainly studied by adding carbon nanotubes [39, 189 – 191].

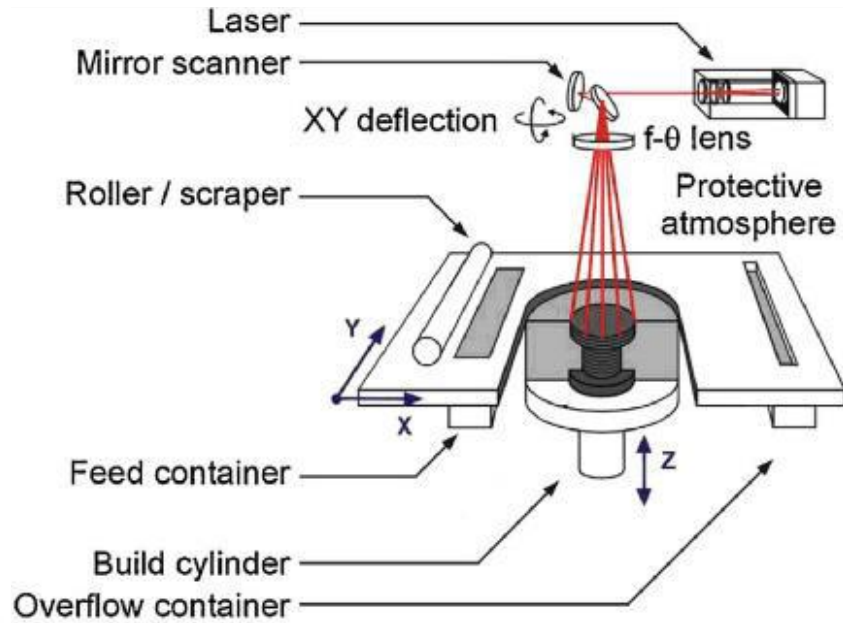


Figure 1.34 Schematic representation of the selective laser sintering method [192].

Wang et al propose a 3-axis computer-controlled filament winding machine to solve the current problems associated with winding composite elbows such as inconsistent quality, low productivity and high costs. In their work, they used the torus and non-geodetic winding equation for the cylindrical sections of the elbow. After the winding model was removed, the composite elbow was produced and tested with a 3-axis filament winding machine [193].

Balasubramanya and Aradhya performed an analysis model for elbows under moment loading to examine the elastic behavior and the effects of internal pressure using the finite element method. They experimented with loadings between 20% more than the material strength and 0% to 40% of the pressure value that will create the yield pressure [194].

Mojarrad et al. investigated the internal pressure behavior of composite elbows molded from knitted fiber material. It shows that the composite elbow is resistant to higher hydrostatic pressure. In addition, the internal compressive behavior of composite elbows is simulated using a multi-scale model. The results showed that the braided composite elbow had higher internal pressure resistance than the non-braided composite elbow. Braided elbows were damaged at 12.5 bar pressure, while non-braided elbows were damaged at 9.5 bar pressure [195].

Fadhel and Omar studied the behavior of pipes with composite curvature under internal pressure. Two groups of materials are used in the manufacture of curved pipes. The first group includes woven carbon composite pipes / epoxy composite, and the second group uses

woven fiber glass composite. Production was carried out with an epoxy fiber mass ratio of 50% by volume. Pipe samples were determined with an inner diameter of 100 mm, radius of curvature (43 degrees) and wall thickness (4 and 3 mm). It has been reported that the circumferential stress for woven carbon composite pipe is about 4.5 times greater than for woven fiber glass composite pipe. The internal pressure utilization in the woven carbon composite pipe was found to be approximately 3 times greater than that of the woven fiber glass composite pipe. It has been reported that the damaged critical area is in the curved inner part of the elbow [196].

Weifeng et al., in their study, designed a robot-based control system that controls the fiber motion trajectory for composite elbow winding. In the traditional elbow winding method, the efficiency and accuracy are low, and the production is manual or semi-automatic. Production flexibility increases in robot-based filament winding [197].

In the Nguyen and Oh studies, a production similar to the injection molding method was carried out by sending liquid polymer composite into the 90° elbow using chopped fiber reinforced polymer composites. They examined the alignment of carbon fiber flowing in polydimethylsiloxane (PDMS) medium by visualizing fiber directions with the help of flow analysis. They reported that fibers close to the convex region are oriented at a greater angle than fibers close to the concave region [198].

In the study of Ellul Grech et al., the compression and in-plane bending tests of e-glass reinforced polyester elbows were experimentally investigated. Glass shredded yarn and weaving mats were used as backing material. The results show that e-glass reinforced polyester elbows can handle industrial loads under bending and internal compressive stresses and create a stiffening effect at the elbow in cyclic bending stresses [199].

Sujith et al. investigated the behavior of E-glass/epoxy and S-glass/epoxy reinforced composite elbows under impact and pressure stresses. In order to measure the impact strength and compressive strength, the composite elbow was subjected to the impact test, followed by the axial compression test. Various impact energy levels of 10, 12.5 and 15 J were tested. The compressive strength generally decreases as the impact strength and the proportion of fiber material used increase [200].

Mahdi Saad et al. investigated the failure of glass fiber reinforced plastic composite (GFRP) elbows before their fatigue life is completed. The life of GFRP composite elbows is calculated as twenty-five; However, the elbows considered in the study were damaged due

to fatigue. The damage-inflicted lifetimes decreased to seven, nine, and ten years, respectively. The GFRP cooling water operates inside the elbows at a pressure of up to 7 bar and at temperatures between 15–36 °C during operation. Visual inspection, analytical, microstructural, mechanical characterizations and chemical analyzes were performed to find the root cause of the failure. In regions with a thickness of less than 15 mm, it is recommended to strengthen using superimposed composites. It is recommended to avoid 45°/–45° fiber orientation and the use of multi-layer chopped strand matte glass fiber [201].

In their study, Xu et al. investigated motion planning for geodesic fiber winding for a six-degree-of-freedom industrial robot with a composite elbow. Different winding parameters, different winding strategies, the winding trajectories of the elbow were calculated with the help of the robot arm and the winding simulation was carried out using ADAMS - MATLAB programs [202].

In this study, Zhang et al., two winding methods for fabricating non-geodetic filament wound composite elbows are discussed. For the cylindrical ends, the torus-shaped mold was closed and geodetic and non-geodetic fiber winding was carried out with this mold. Composite elbows obtained using various initial winding angles were analyzed according to the Tsai-Wu damage theory, and the burst pressure of the elbow was analyzed using the finite element method. The results reveal that for the non-geodetic winding application, the composite elbows lead to better structural performance of the torus tip shape applied for the mold than the non-geodetic winding application [203].

Alexander et al. investigated the use of E-glass/epoxy reinforced composite materials for the reinforcement of large diameter elbows. After determining that composite materials are subjected to bending loads of up to 3.6 million ft-lbs (4.88 million Nm) in scale testing and full-scale applications, it has been reported that the fiber additive can be used to overcome the strain on elbows, 720 psi (4.96 MPa) to 1,440 psi (Variable pressures between 9.93 MPa) affect these elbows in operation as a working condition [204].

Bobba et al. experimentally investigated the effects of seawater absorption on impact behavior on glass/epoxy composite elbows. Using E-glass and S-glass, glass-epoxy composite elbows were manufactured by hand lay-up method. These produced elbows were immersed in water for 0, 3 and 6 months according to operating conditions. The impact strength relationship between unaged and aged samples was examined by calculating the contact force, displacement and absorbed energy values from impact tests. It has been stated

that sea water increases the aging time of both E-glass/epoxy and S-glass/epoxy fiber reinforced composite elbow pipe connections and adversely affects composite elbows. It is suggested that E-glass fiber support should be preferred instead of S-glass fiber for applications that will operate under sea water [205].

In this article, Luu et al describe the development of a six-degree-of-freedom industrial robot by integrating it into a three-dimensional 3D printing system. The robot-based 3D printing system makes it possible to print on inclined planes that cannot be achieved with a conventional 3D printer. Also, by using a knowledge-based strategy to re-plan the Gcode printing method, RAM is enabled to achieve faster and smoother movement compared to its counterpart. Correct execution of the toolpath can be regulated by the robot operating system (ROS) [206].

In their work, Keating and Oxman aimed to combine manufacturing methods using a 6-axis 3D printer extruder, the milling insert as different effectors. New robotic manufacturing processes are being developed and evaluated, such as multi-axis plastic 3D printing, 3D printing from direct recycling [207].

In this paper, Felsch et al. used AM technology with the help of industrial robots for the production of large parts. They developed a three-dimensional additive robotic system to produce large models from any thermoplastic material with a volume of $1.000 \times 1.000 \times 1.000 \text{ mm}^3$ and instead of mold cost-effective productions [208].

In this study, Shembekar et al. studied trajectory planning algorithms for material deposition using non-planar 3D printing using a 6-degree-of-freedom robotic arm. The trajectory parameters have been controlled to avoid collision with the printing surface and exceed the robot limits [209].

In this study, Ishak et al. aimed to use the FDM method in different axes by integrating an extruder system used in typical 3D printing with a 6-DOF robot arm. Here, Motoman SV3X model robot arm is used as the robot arm. A controller is used to control the robot and extruder. MotoCom SDK is used for communication between robot arm and computer interface in a separate controller. As a result of the integration of the robotic arm and the extruder, the use of multi-plane toolpath movements is enabled [210].

In this study, Stevens et al. developed a robotic suite capable of maskless layered photopolymerization on curved surfaces, producing large-area conformal patterns and making free-form objects. The use of the system is divided into phases of freeform creation

of the toolpath, which divides it into curved layers representing the target object to be printed, precision mounting on the robot workspace, and coordinated robotic photopatterning of the target object. Thus, the conditions that need support in the SLA printing method will be overcome [211].

This article by Velazquez et al discusses the basis of a RAM technology based on ultraviolet (UV) curable thermoset polymers. This system is designed to allow composite printing through partial UV curing and fiber reinforcement for structural applications. The proposed system integrates a collaborative robot manipulator and a custom-built extruder end effector designed specifically for printing with UV-curable polymers. The system has been experimented with using various resin compositions, some of which are reinforced with ground glass fiber (GF) or fumed silica (FS). Dimensional stability was analyzed for all formulations and it was reported that resin containing up to 50% by weight fiberglass or at least 2.8% by weight Fumed silica showed dimensional stability [212].

This work Mitropoulou et al enables the flexible and intuitive design of non-planar layered paths for robotic printing. It aimed to overcome the difficulties associated with the realization of single-shell fork structures by adapting the bifurcation zones of the shapes and the behavior of the roads [213].

Many inventors are working on robotic AM and this continuous composite reinforced UV resin curing 3D printing method. These studies include tool design, improvements to improve production quality and to stabilize curing. Recently, more than 250 patents have been obtained in the last few years on this subject, which has been developing rapidly and attracting great attention [214 - 227]

As introduction part, composite materials and their properties and production principles are discussed as the main issue that we try to understand and recognize. These explanations, which are discussed, provide us with motivation for the production of composite elbows without mold, using UV curable photopolymer resin and continuous fiber reinforced composites in production by creating a six axes toolpath with the RAM method. In addition, while producing elbows in this way, RAM parameters such as helical winding method and filling rate were examined by applying helical winding with help of six axes toolpath.

2. MATERIAL AND METHOD

In this thesis, the production of 90° elbows, which is made with molds and has a limited production method, but is needed in many areas as a place of use, is discussed. Since 90° elbows are a complex product due to its geometry, the production here will provide a solution to the production of many complex geometries like this.

Elbows and similar products are widely used in the construction industry, installation and transportation industry, machinery and manufacturing industry, especially in the construction machinery sectors including hydraulics and equipment. Although the materials they are produced in vary in general, the production of elbows made of steel and metal today leaves its place to composite materials due to both strength and weight and difficulties in casting and production. The method used for the production of composite elbows is the filament winding method. Of course, this production method also needs a mold for production.

As in every field, with the developing technology, AM is promising in composite products in some constraints that traditional production methods cannot overcome. However, there are still issues that need to be developed in AM. At this point, in our thesis, we focus on the manufacturing of 90° composite elbows for the production of complex geometries innovatively by blending improvements with the AM method for traditional composite manufacturing and current developing technologies.

AM has overcome the constraints of traditional production such as material waste or mold requirement. However, the materials used in the AM method and the positioning of the layers are insufficient in many applications in terms of issues such as strength. For these reasons, if we prefer the materials used in traditional composite production for the production of composite materials in AM, the desired properties can be obtained from the product. In addition, if we parametrically arrange the slicing process required for 3D printing not only in layers on a single axis, but also parametrically, we will not only improve the strength and geometric limitations of AM, but also turn traditional composite production into moldless and full automation. The stages of the study are given schematically in Figure 2.1.

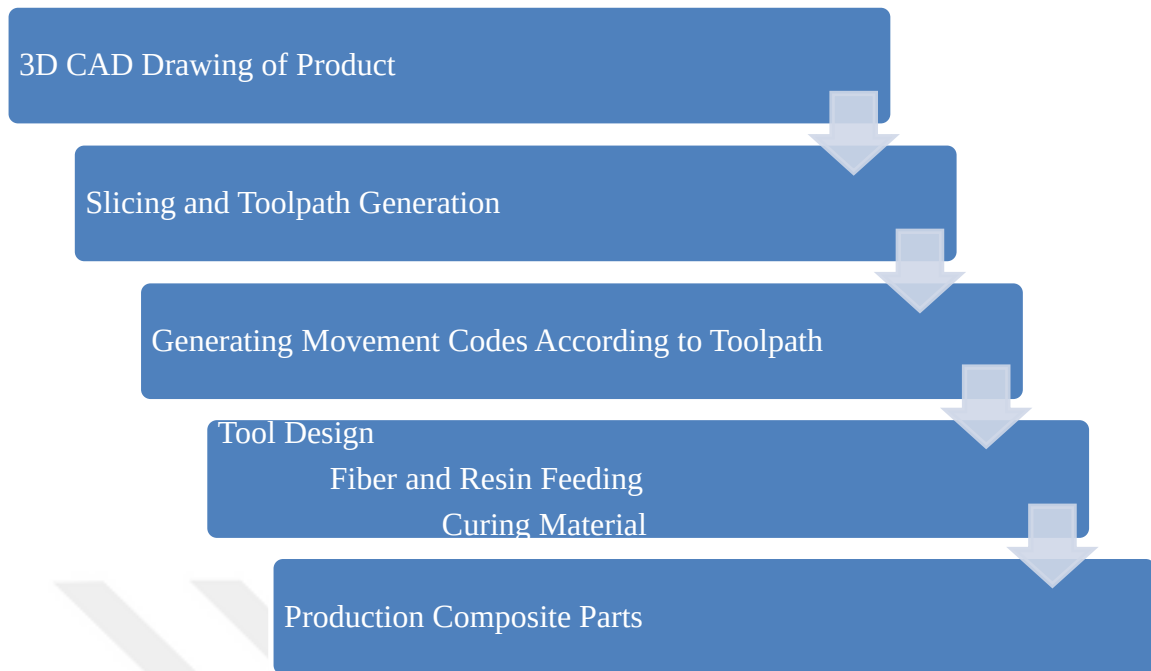


Figure 2.1 The stages of the composite production with additive manufacturing.

If we briefly explain the mentioned stages in the study, 3D design comes as the first step. The product to be produced must first be drawn in the computer environment. At this stage, many different applications are available in the market. Among these programs, we chose the Rhinoceros 3D drawing program, which is powerful and can be used parametrically, which is preferred in architecture and many fields. We performed the product design parametrically in this program. Next comes the slicing and toolpath generation part required for 3D printing. For this stage, the Grasshopper plugin of the Rhinoceros 3D drawing program was chosen. The reason for choosing this plugin is that it is compatible with drawings and there is no software on the market that slices more than 3 axes and generates non-gcode code. The Grasshopper plugin is not a slicing or toolpath creation program. However, with the help of the possibilities it offers, parametric programs can be created for the desired operations by programming. In addition, with this prepared slicing and toolpath program, the motion codes required for the manipulator can be programmed and motion simulations can be made.

Another important issue is design and production of tool that will product the composite material. Before proceeding to the tool design, the materials to be used and the solidification method must be determined.

As it is known, a matrix and reinforce material are required in composite materials. In this study, thermoset matrix material was preferred instead of thermoplastic matrix material. As

stated in the introduction of the study, thermoset matrices exhibit higher strength properties than thermoplastic matrices. Thermoset materials are preferred because of better bond structure and penetration into fibers [228, 229].

Photopolymer resin is a type of polymer that changes its physical properties when exposed to UV light and consists of monomer resin and photoinitiator as raw material. Featuring high precision and low shrinkage, the resin contains methacrylate monomers to reduce volume shrinkage during the photocuring process, this ensures high precision in 3D printing. Wash the products with 95% or higher ethanol alcohol for at least 30 seconds after the completion of the post-production. Afterwards, the product was kept in sunlight until it dries completely in order to fully develop the physical properties. The properties of the preferred resin are given in Table 2.1. The brand of resin used in this thesis is ESUN and its picture is given in Figure 2.2.



Figure 2.2 Photopolymer resin

Table 2.1 Properties of photopolymer resin [230].

Features	Values
Viscosity (25°C, MPa.s)	100-150
Wavelength (nm)	395-405
Density (g/cm ³)	1.07-1.12
Tensile Strength (MPa)	46-67
Elongation at Break (%)	11-20
Flexural Strength (MPa)	46-72
Flexural Modulus (MPa)	1000-1400
Hardness (Shore D)	80-82
Izod Impact Strength (J/m)	18-40
Shrinkage (%)	3.72-4.24

Glass fiber fiber material was preferred as additive material. The reason why this was preferred was determined in relation to the solidification method. The solidification method in our study is the photo curing method. This curing method is one of the ideal methods for fast bond formation in thermoset materials. Therefore, it is preferred in harmony with glass fiber reinforcement [231]. The selected glass fiber is not selected as chopped. Chopped fibers do not provide homogeneous distribution and provide a much lower increase in strength compared to continuous fibers. Because, when the continuous fibers are placed in the direction of the loads, the product strength increases very high. Due to the continuous fiber tool tip path, it is very suitable for use in 3D printing method, since it has a continuous line movement. The properties of the selected fiber material are given in Table 2.2. In addition, the selected fiber tex density was selected as 300 tex. The reason for this is that by adding as desired, instead of purchasing fibers in different tex density separately, they can be obtained and tested as multi-end. The picture of the fiber material used is given in Figure 2.3.



Figure 2.3 Image of the fiber material used.

Table 2.2 Properties of fiber glass [232].

Features	Values
Glass Type	E
Rowing Tex (g/1000m)	300
Filament diameter (μ)	Nominal 14
Tensile Strength (MPa)	2306
Elasticity Modulus (GPa)	81.5
Density (g/cm^3)	2.48-2.60
Elongation at Break (%)	2.97

This method is actually the solidification method used in printers known as regular SLA or DLP. However, in our study, resin and fiber are mixed and deposited from a FDM-like nozzle. Solidification will be carried out with the help of Ultraviolet (UV) light, which is used after the material is stored out of the nozzle. UV light emitted diode (LED) light was preferred as the UV light source. The reason for this is that it consumes less energy and does not emit much heat. The properties of the UV light selected for the curing process are given in Table 2.3. The picture of UV led lights used in this thesis is given in Figure 2.4.



Figure 2.4 UV LED lights used in the study.

Table 2.3 Specification of chosen UV light source.

Features	Values
Wavelength (nm)	400-405
Color	Purple UV
Current (mA)	700
Voltage (V)	3.2-3.4
Viewing angle (°)	120
Power (W)	3
Lumen (Lm)	10-15
Energy	80-110

After the solidification method and the materials to be used are determined, appropriate tool design and production will be carried out. In addition to these, an industrial robot arm was preferred as the manipulator to move the tool. One of the main criteria when choosing here is the ability to move in 6 axes. The robot arm used in the thesis study is a Nachi brand MZ07L model industrial robot arm. A picture of the robot arm and dimensions of robot arm are given in Figure 2.5. Table 2.4 contains a list of the main features of the robot arm.

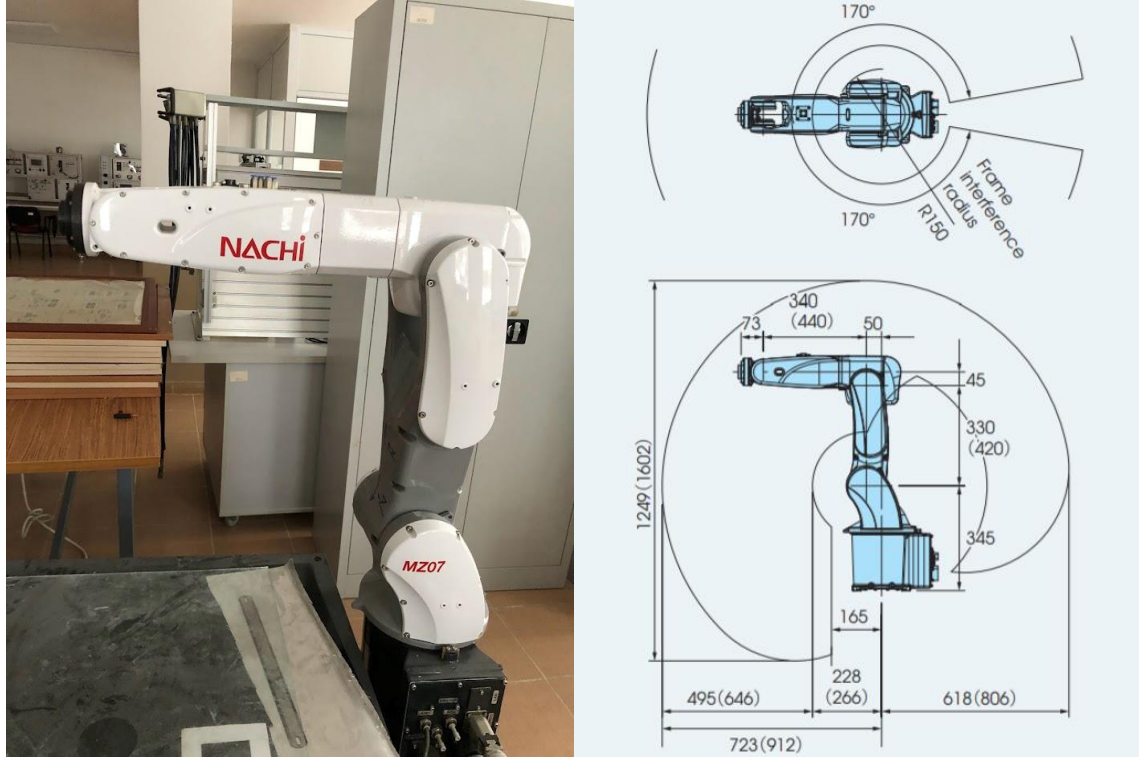


Figure 2.5 Robot arm used as manipulator in the study - robot dimensions and working envelope [233].

Table 2.4 Basic specification of robot arm [233].

Item	Specification
Robot model	Nachi MZ07L
Number of axis	6 axis
Drive system	AC servo drive
Max. Payload (kg)	7
Allowable static load (Nm)	16.6
Loading torque (Nm)	9.4
Max. reach (mm)	912
Position repeatability (mm)	± 0.03
Ambient condition (°C)	0 – 45
Installation	Floor/Wall/Tilted/Invert mount
Dust proof	IP67
Robot mass (kg)	38

2.1. Tool Design and Manufacturing

In our thesis, after choosing the fiber and matrix material and the curing method to be used, the design and production of the tool that will perform this process is required. The tool design was carried out for the FDM-like production of UV-curable composite materials with

a continuous glass fiber reinforced thermoset matrix. This design and production process has been carried out iteratively and has been finalized with continuous improvements as a result of trials. As a working principle, there are two main issues here. The first is the mixing of fiber and resin. The other main issue is that this mixture is removed from the nozzle and solidified. For this, the first design made by considering basic composite production and 3D printing method is given in Figure 2.6.

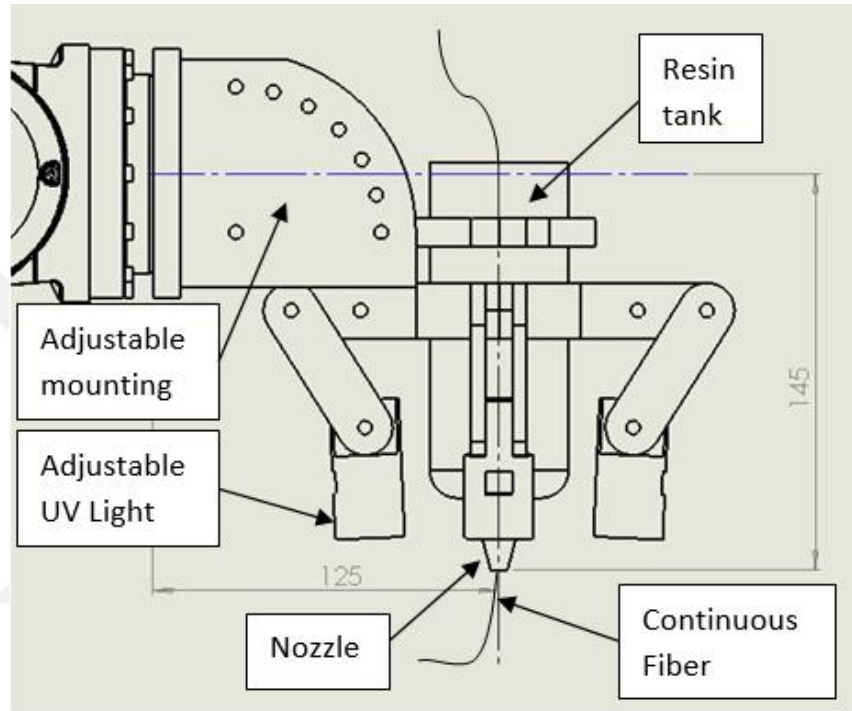


Figure 2.6 First designed iteration of 3D printing tool.

After this design is realized, the stage of material and method selection for production comes. For material selection, metal-based material was chosen in order not to react with thermoset resin. Other parts are produced by 3D printing method. In Figure 2.7, there is a picture of the tool that was produced and attached to the robot arm.

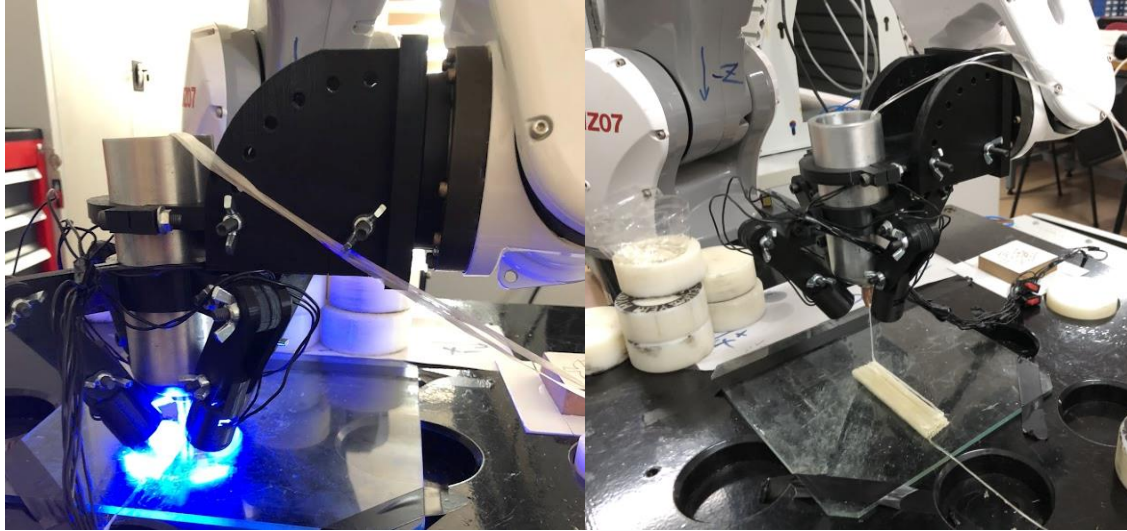


Figure 2.7 Produced first tool.

Afterwards, the adjustable robot connection part and UV LED lights were determined and positioned at fixed distances after the trials. In addition, the robot connection is rounded in accordance with the robot in order to increase its mobility. The state of the team after these arrangements is given in Figure 2.8.



Figure 2.8 Fixed position of the adjustable parts of the tool.

After the trials, the need for a feeding system for the fibers emerged. Because setting up a special fiber for each production of a certain length poses difficulties. Therefore, it will be used by winding on fiber spools. Special spools have been designed and produced to wind the fiber. In addition, a hand drill connection piece has been designed and produced to wind the fiber onto spools. These fiber spools are fixed and then transferred to the resin in the fiber chamber and then delivered to the nozzle. Figure 2.9 shows the designed and

manufactured fiber spool and the process of winding the fiber onto the spool.

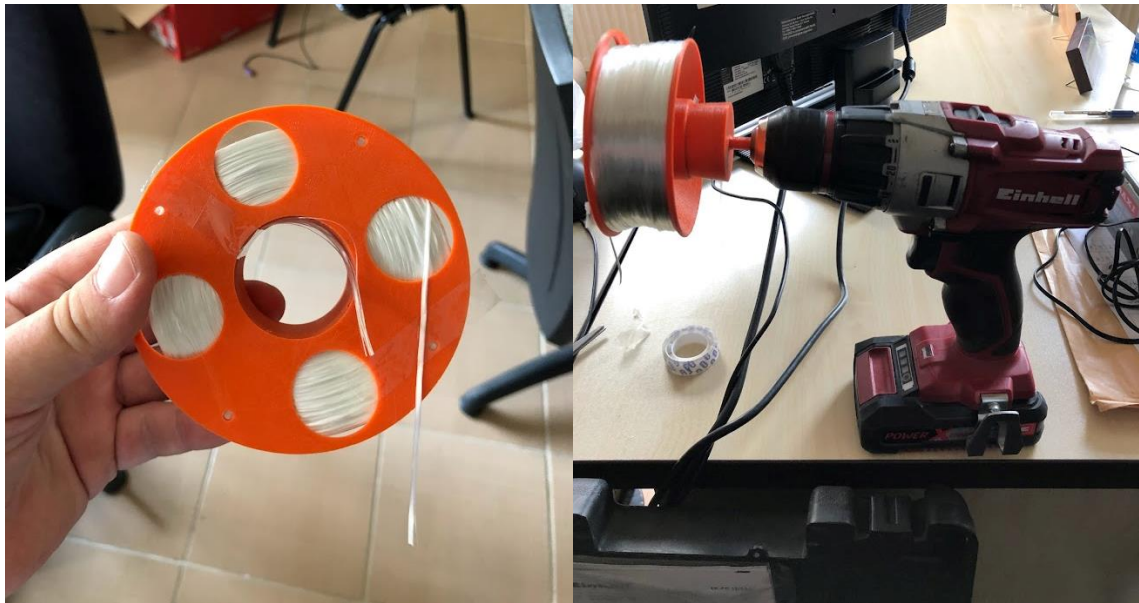


Figure 2.9 Spool and spool winding process.

Another improvement is that the lights are added just at the end of the chamber, preventing the nozzle from approaching the part at an angle, and it is desirable to connect the light system as close to the nozzle as possible. For this, UV LED lights are carried up from the nozzle to carry the light with a fiber optic cable and extended between the nozzle and the chamber. Figure 2.10 shows the set with fiber feeding and light transmission system designed and manufactured.

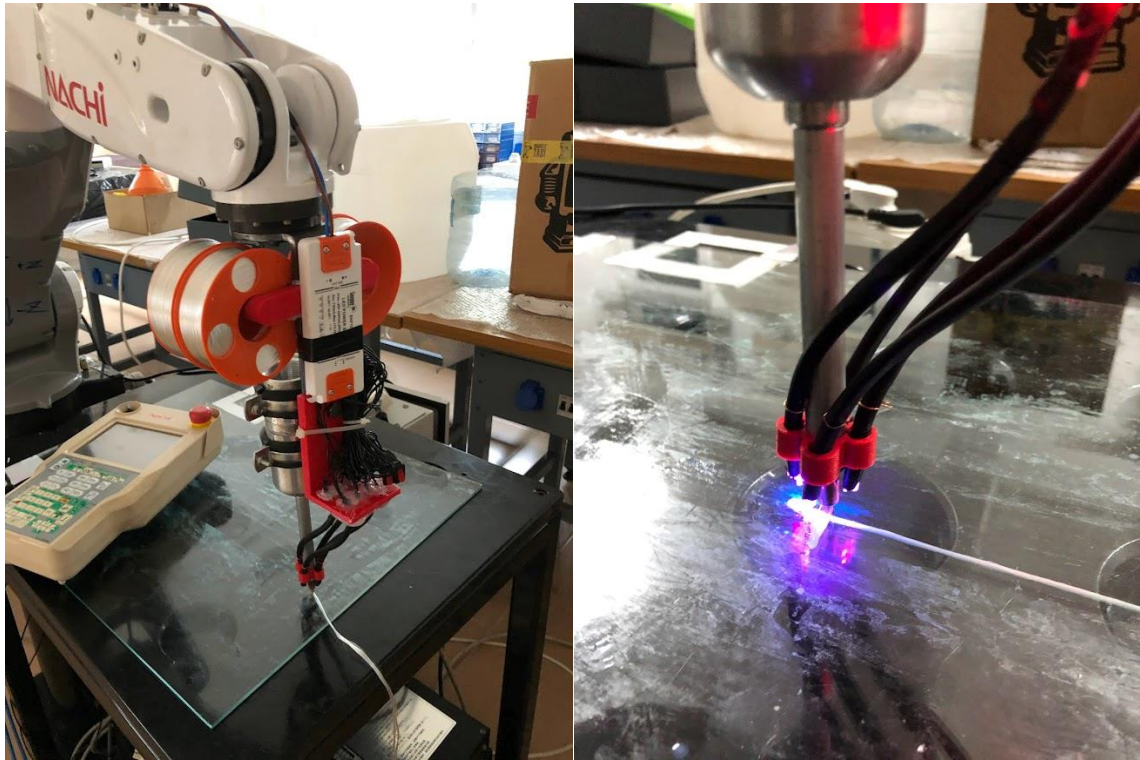


Figure 2.10 Revised tool with fiber feed and light transmission system.

Since the light transport of the UV LED light with the help of fiber optic affects the curing negatively, the position of the lights has been revised again near the nozzle. However, since it cannot be brought very close to the nozzle, the light directly reaches the tip of the nozzle from a certain distance. Since this reaching light initiates curing without spreading the resin coming out of the nozzle into the layers, it creates problems of non-adhesion between the layers and hinders the production. For this reason, it is produced by designing a cylindrical shade nozzle to shade the tip of the nozzle. This type of light connection and the state of the canopy can be seen in Figure 2.11.

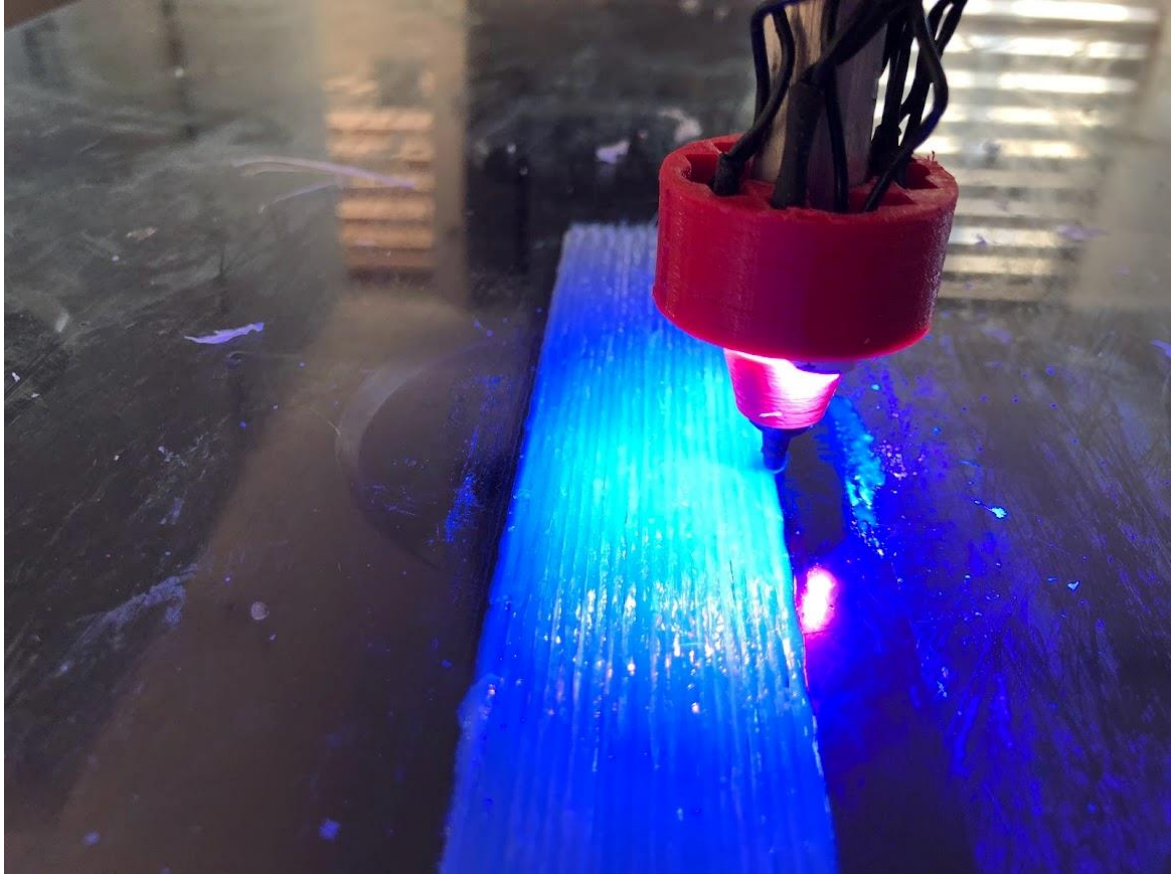


Figure 2.11 Light connection to the nozzle and shade of the nozzle tip.

Afterwards, this system can work stable for three axes operation as cartesian. Production quality and precision are equivalent to other composite manufacturing methods. However, this system has been a long total length with fiber feeding and nozzle tip length and problems occur in angled productions. The robot position cannot be adjusted angularly at every angle. Another issue is that when the resin chamber rotates with the nozzle tip during movement, negative effects may occur in the fiber and resin combination. For these reasons, fiber feed and resin chamber are separated from the nozzle tip and fiber and resin are fed to the nozzle from two separate inlets and a mixture is made inside the nozzle. In addition, the collected fibers are oriented by means of bearings to prevent uneven pulling force. The revised set is given in Figure 2.12.

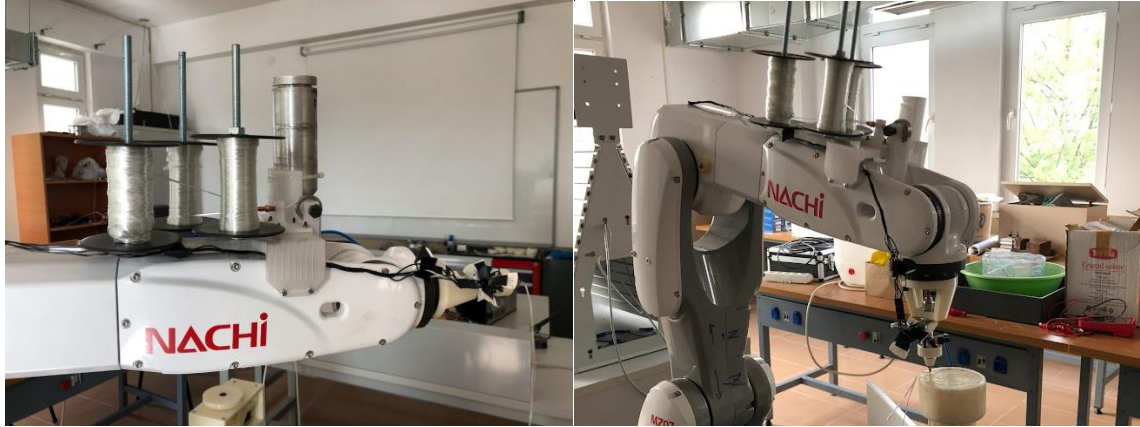


Figure 2.12 Tool with separated fiber and resin feeding system.

In addition to all these, in the production of 90 degree elbows, a turntable is required since it is not possible for the robot arm to rotate around the elbow while helical winding from the outside. In order to perform this operation, an electronic turntable that can rotate at the desired angle has been designed and produced. In Figure 2.13, there is the turntable and the electronic box of this table.

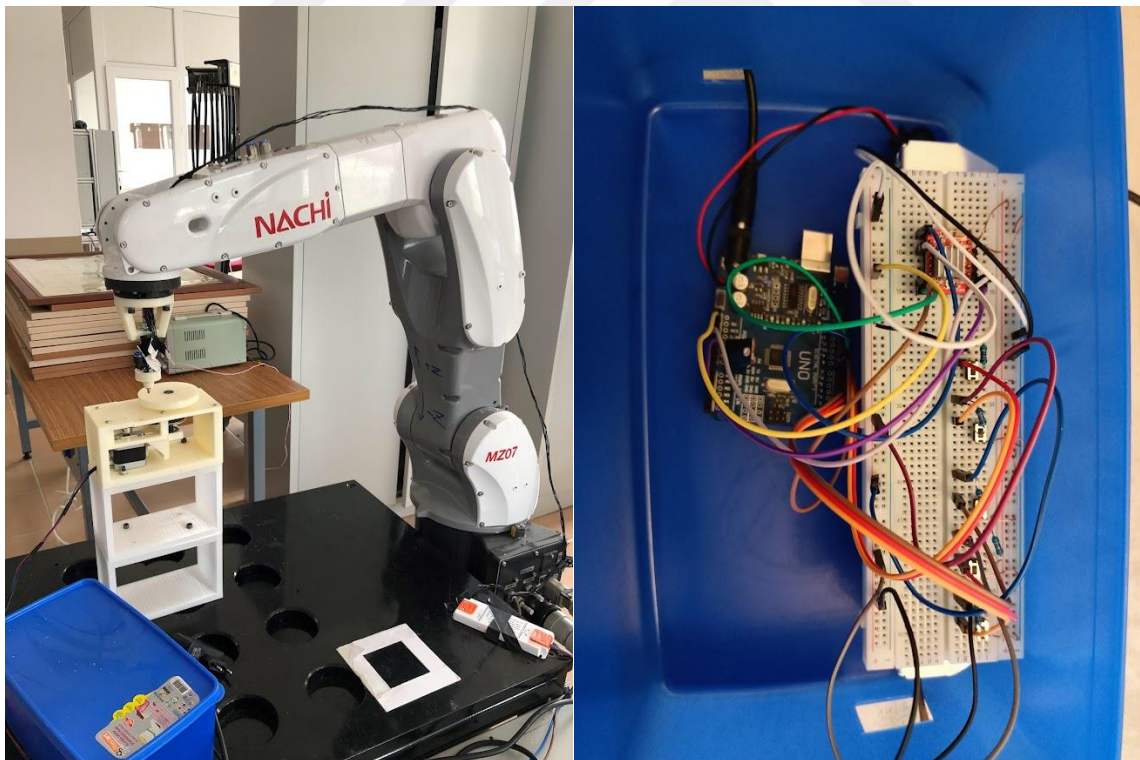


Figure 2.13 Turntable and electronics box.

Since the resin chamber we connected to the fourth joint could be positioned below the nozzle during production, the fiber resin mixture was negatively affected. For this reason, a fixed connection has been made to the third joint, which will not turn upside down at all for

the resin tank. In addition, the bearing system and pulley system were revised as the desired smooth fiber movement could not be achieved in the system in which we transport the fibers. The revised system is given in Figure 2.14.

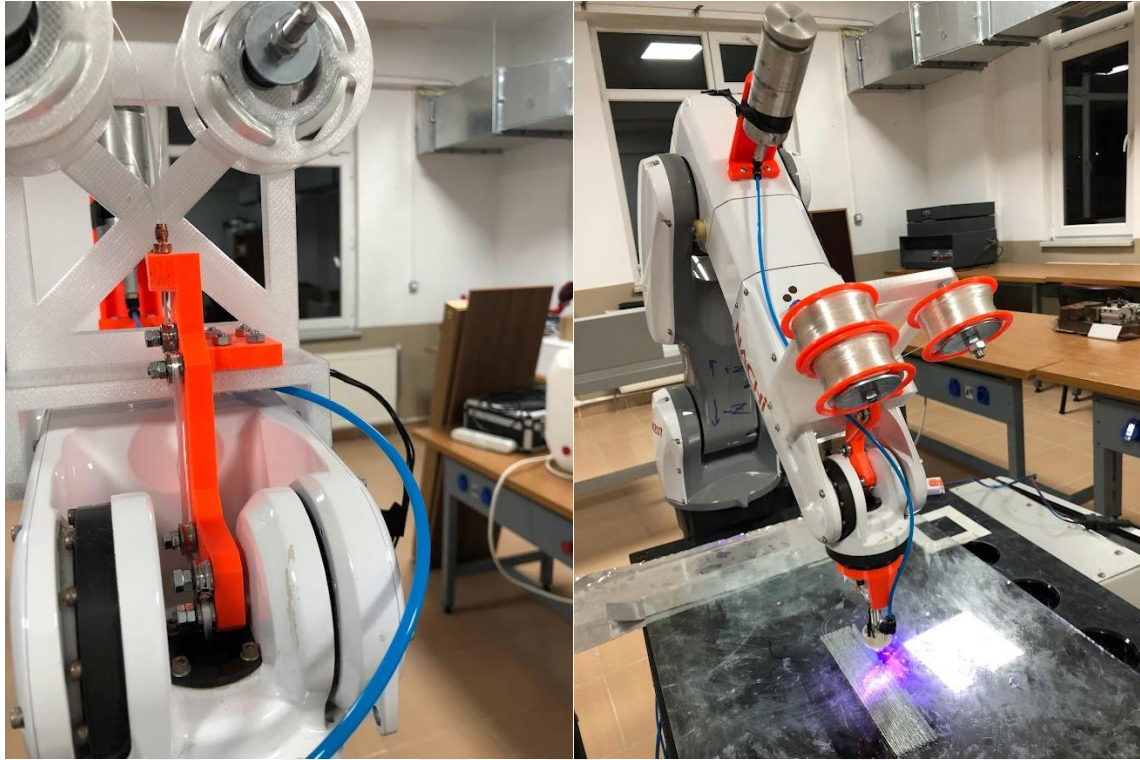


Figure 2.14 Set of separately positioned fiber and resin feeding systems.

Since the turntable is made of plastic, it impairs the position accuracy and creates stretches, so the turntable is made of metal for more precise and quality production. The hollow pipe and the heavy and fixing plate are welded to the bottom. The upper part consists of two cylindrical plates and the center pin is firmly inserted into the outer plate. There is a swivel connection to the lower plate. A NEMA 17 stepper motor is connected to this plate from the inside and rotates the plate to which it is connected by a tight-fitting with the center pin. Thus, the produced elbow can be rotated at the desired angle and the productions can be made and completely surrounded. The metal turntable is shown in Figure 2.15.



Figure 2.15 Metal turntable.

Finally, along with our turntable, which took its final shape as a result of iterations, as the last improvements in our tool, the fiber feeding system has been made even smaller and parallel to the robot arm, as it causes difficulties during the movements of the robot arm. Another important change is that the part where the robot is connected with the nozzle is very important for the precision of the nozzle and the production precision. For this reason, this connection piece is made of Aluminum alloy material in order to be both light and rigid and not stretch. thus, tool tip precision has decreased to micron levels. Figure 2.16 shows the final state of the tool.



Figure 2.16 Final version of the revised tool for composite elbow production.

As a final step in tool design and improvement, it is necessary to examine the temperature increase caused by the heat caused by curing and the operation of UV lights in a long time during production. For this reason, temperature control was carried out at certain intervals with a thermal camera during the studies. It has been observed that the resulting temperatures do not create an external cooling requirement and do not have a negative effect on material production. An example of thermal camera images is given in Figure 2.17.



Figure 2.17 Thermal camera images of RAM composite material.

2.2. Slicing and Creating Toolpath

There is not yet a standardized operation or program for AM with an industrial robot arm. Especially AM of composites is a very new and open subject. In addition, slicing operations and programs only offer three axes solutions. Robotic simulation programs cannot generate

toolpaths, they only help convert some drawn toolpaths into code. There are no extrusion speed and similar parameters specific to AM in these generated codes. In this context, a simulation program has been developed for the RAM of continuous fiber reinforced composites in different approaches by considering the programming of industrial robots, slicing processes for RAM and six axes toolpath strategies.

2.2.1. Robot programming

The key point underlying the use and widespread use of industrial robots is that people can do the things they have to do and are forced to do without error and quickly. For this reason, it is common to use robot arms in work done by people rather than manufacturing. Take - put, put - remove, hold - release and similar sequential operations can be given as examples of these works. The coding of such operations is also programmed through teaching. In addition to these, there are special commands for some operations and these are added between the teaching operations and many additional options are added to the programs. Another important point here is that each industrial robot arm company develops a unique programming structure and logic. One of the reasons why the programming in these industrial robots is planned in this way is that the controllers are realized through the Programmable Logic Controller (PLC). In addition, robot programming language has been created by companies for programming robot arms in manufacturing and similar works. In this part, we will talk about the programming and programming language of Nachi brand industrial robots for manufacturing that we used in our thesis.

Robot language is a programming language that is customized to tell the robot what to do. In this language, specific commands, coordinates or formulations that perform calculations for certain jobs can be used in a single program where necessary.

Nachi robot language is organized according to JIS B9439 standard and is based on Standard Language for Industrial Manipulator (SLIM) logic.

While defining the position for movement in the robot arms, many different postures can be defined to a desired position due to the flexibility of the robot's movement. In this regard, there is a fixed definition that represents the arm and angle of the robot for the robot to take the desired pose. This definition is called pose constant. These pose constant definitions are used to define position when writing motion commands. There are three different pose constants in the SLIM robot language.

MOVEX-X expresses the position of the tool tip and the angles of the tool tip with 3 axes separately according to the cartesian coordinate definitions. In the form of (X, Y, Z, r, p, y), the positions in the 3 axes according to the robot's coordinates, respectively, and then the angles made by the tool tip with the Z, Y and X axes are expressed respectively. This recognition is called a pose. This is the most appropriate and widely used definition for the manufacturing sector, and this pose definition will be used in our thesis.

MOVEX-J represents the definition of the 6 joints of the robot arm, respectively, at which angles they should be in pose definition.

MOVEX-E represents pose definition where encoder data on each axis is defined respectively.

Figure 2.18 shows the coordinates used when defining poses on robot arms.

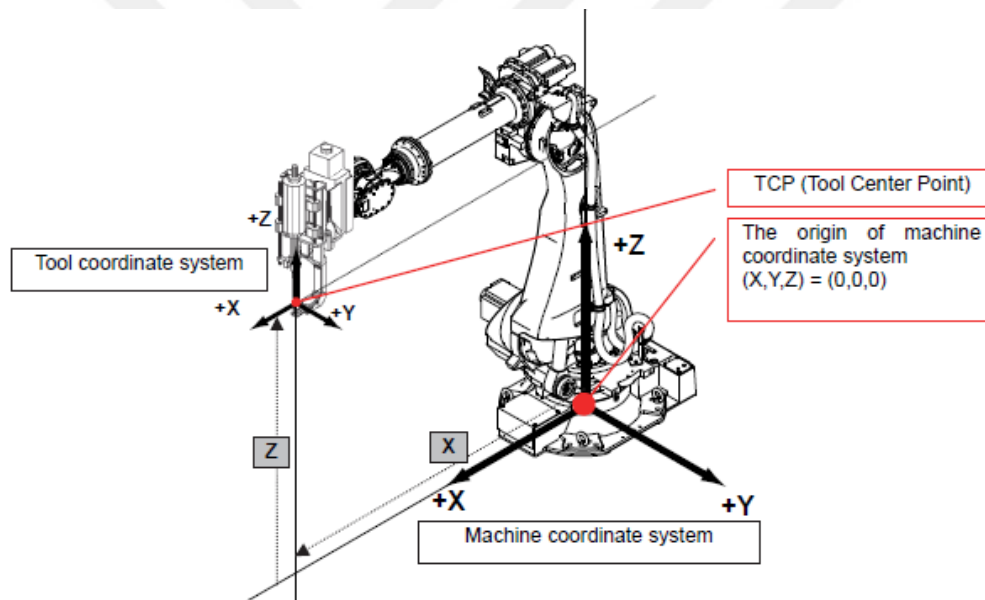


Figure 2.18 Machine and tool coordinate systems [234].

A sample code line written with SLIM coding for the 6 axis industrial robot arm is given below. In addition, the components used for the relevant coding and their explanation are given in Table 2.5.

MOVEX A=1,AC=1,SM=1,F,M1X,C1,(250,100,75,0,0,90),S=10,H=32,MS,CONF=0000

Table 2.5 Definitions used in the NACHI SLIM robot programming language [234].

Mark	Description	Value
A	Accuracy	1 – 8
AC	Acceleration	0 – 3
SM	Smoothness	0 – 3
F	Fine motion	-
HM	Synchromotion	-
M1X M1J M1E	Mechanism of pose constant format	-
P L C1 C2	Joint interpolation Linear interpolation Circular interpolation (middle point) Circular interpolation (end point)	-
S T R D	Linear speed (mm/s) Movement time (s) Speed rate (%) Tool angle change speed (deg/s)	-
H	Tool definition number	1-32
MS	Speed standard	-
CONF	Wrist unit FLIP / NON-FLIP Elbow above / below Left side arm / right side arm Flange axis rotation direction	0000 - 1112

2.2.2. 3D printing slicing process and Gcode

A 3D model slicer is software that runs in a computer environment. It acts as a translator for your 3D printer. These slicing software are generally; They read 3D file formats that describe three-dimensional coordinates, such as Standard Triangle Language (STL), 3MF, or OBJ.

The STL file format is an industry standard file type for 3D printers. It uses a series of triangles to represent the surfaces of a solid model. All modern CAD software allows you to export native file formats to STL. The 3D model is then converted into machine language (G-Code) through a process called "slicing" and is ready for printing. Slicing software slices the three-dimensional object into multiple horizontal layers and creates paths through which a 3D print head (extruder) can cast line by line, layer by layer.

Correct 3D slicing software settings are critical to the difference between a successful print and a failed print. For this reason, it is extremely important to know how slicing software works and how each different setting will affect its results.

3D printing slicing parameters can be listed as follows;

- **Layer Height**

You can think of the layer height setting as the resolution of the model. This setting specifies the height of each filament layer in the print. Prints made with thinner layers have a smooth surface where it is difficult to see individual filament layers. Printing with thinner layers will take longer to print a model because the more layers make up your model.

- **Shell Thickness**

The shell thickness specifies how many shells the outer walls of the design will consist of by the 3D printer before starting the hollow parts of the design. This defines the thickness of the sidewalls and is one of the biggest factors in the strength of the print. Increasing this number will create thicker walls and increase the strength of the print.

- **Retraction**

This feature allows the 3D printer to pull the filament back from the nozzle and stop the flow of the filament when there are discontinuous surfaces in the print, as in the model in the picture below.

- **Fill Density**

Infill refers to the density of the cavity in a model's outer shell. You will notice that this is set in % instead of mm like the layer height. If a model is printed with 100% infill, its interior will be completely solid. The higher the fill percentage, the stronger and heavier the object. It takes more time and filament to print. If you are printing with 100% fill every time, this can be expensive and time consuming.

- **Print Speed**

Print speed refers to the speed at which the extruder moves as it pushes the filament. The optimal speed setting depends on which model you are printing, the type of filament you are using, the capabilities of your 3D printer, and the layer height.

In order to produce 3D Model files used in 3D Printers with .stl or .obj extensions, they must first be converted to g-code in slicer programs called Slicer (CURA, Simplfy3D). G-code

transmits a lot of information to the 3D Printer, such as which route and speed to follow in the coordinate plane. So Gcode converts our 3D Model into a language that the machine can understand for 3D Printing.

G-code is the abbreviation of geometric code. G-code does not only include the route that the 3D printer will follow in the coordinate plane, but also includes what rate of material should be flowed from the extruder or what the table temperature should be. G-code contains hundreds of lines of code blocks. All of these code blocks contain a task. The 3D Printer, on the other hand, carries out the tasks by following these lines starting from the first line.

A block of G-code is seen as in the code block below. This block of code sends a task to the 3D Printer to follow a straight line. X=27, Y=-3.7 and Z=3.6 indicate the distance it will travel in the coordinate plane. Here, G-codes are generally divided into two. Either before starting, the 3D Printer resets itself at the origin point and proceeds to the coordinate points it receives from the code blocks, or it receives the correct information to follow by taking distance information, as in the example above. While only positive values are used in the first method, the second method and the negative (-) values that we will go over today are included in the G-code.

```
G1 X27 Y-3.7 Z3.6 F2600 E0.0845
```

The letter F in the code block is the abbreviation of Feeder and contains information on how many mm to feed per minute. The letter E in the code block is the abbreviation of Extruder and contains the information about how much material will flow from the extruder. G1 at the beginning of the code block conveys the information that it will be drawn correctly. The letter G stands for the head of the 3D printer. There are different G commands for different tasks. However, the G command is not sufficient to control the entire 3D Printer. Different commands are used for commands such as start the fan or heat the tray. For example, the M140 is used to determine the table temperature, while the M190 tells the 3D Printer to wait until the target temperature is reached.

Important Gcode commands can be given as follows;

Since it will be a very long article to examine all the commands, the commands that I think will be enough for you to know at the beginning are as follows:

- **G0 – Quick Action**

This command is used when the 3D Printer head needs to move fast. For example, before

3D printing, this command can be used when moving from one point to another, while the extruder is not yet flowing a material.

- **G1 – Controlled Movement**

G1, which is the command you will see most when you examine a G-Code, contains the information about how the 3D Printer head will move during 3D printing.

- **G20 / G21 – Units**

While G20 is used to express the inch unit, G21 is also used to express the millimeter unit.

- **G28 – Return to Origin**

As in the explanation part, this command is used to return the 3D Printer head to the starting point.

- **G90 – Absolute Mode**

The G90 command is used to specify the origin point if the g-code contains the point where the 3D Printer head will go in the coordinate plane rather than the distance.

- **G2 – Clockwise**
- **G3 – Counter-Clockwise**
- **; – It is used to annotate the code block.**

2.2.3. Rhinoceros 3D drawing program and Grasshopper add-in

Digital media, which was initially used as a representation tool, has been used in design and manufacturing in different ways in the last 20 years and has affected many sectors. The developing computer and informatics sector has become a new tool for conceptual design. On the one hand, the design was inspired by the various possibilities of digital technology. On the other hand, many subjects from different fields also affected the design. Mathematical and geometric algorithms that could not be modeled before, and forms that could not be drawn have now become more understandable and accessible models for design.

Before introducing parametric design, it is necessary to explain the concepts of parameter and parametric. A parameter can be defined as a quantity that can change and be changed for a situation. The number of parameters may vary depending on the situation. Parameters are at the core of algorithmic thinking and are used within the algorithm. The situation

involving one or more quantity concepts can be described as parametric.

The parameters and equation values, which are generally used to define relationships between forms, shape the parametric design. Thus, it is possible to establish a connection between the forms and the behavior of the forms under transformation (mathematically and geometrically) can be defined. Since 1990, parametric design has influenced the development of digital design in two different ways [235]

- **Conceptual parametric design**

Conceptual parametric design is based on specific design parameters that are explained outside of the design form. By assigning different values to the parameters, different objects or their configurations can be easily created. This design method, which consists of mathematical algorithms where interactive design is not possible, requires programming or scripting knowledge [236].

- **Constructive parametric design**

Constructive parametric design is associated with data embedded in predetermined 3D objects. Instead of drawing lines, circles, curves, and the like, designers can add pre-made components to their drawings. The mentioned parametric concept is realized through various computer aided software. However, some limitations have been identified in these software tools. First, it is not possible to standardize the materials and components of the building for all manufacturers and to consider a wide range of different building materials in order to provide a smart model. Second, these software tools designed for standard structural elements (machine elements and similar elements) are not applied for non-standard elements of contemporary digital design [237].

Within the scope of this thesis, computer aided design programs that allow parametric design have been examined. Rhinoceros and Grasshopper software, which are mostly preferred by engineers, are discussed.

To understand the generative algorithm concept, it is necessary to remember the traditional method of numerical design. Numerical modeling covers the description of transformation and modification of two or three-dimensional elements. Each change in design is directly interconnected with other elements and leads to geometric changes that become complex. Since these changes change the size, shape and scale of each element, it makes it necessary to review the elements again [238].

Generally, two basic principles can be mentioned in the design process. The first is virtual structure modeling based on the hierarchical functioning of interrelated objects. The second is the principle of generative modeling, in which the most suitable 3D configurations are selected for a solution. These configuration selection criteria can be technical and aesthetic. Computer-aided design programs, which are generally used by engineers, do not require programming or coding knowledge, allow users to create impressive forms, and allow constructive parametric design, which are best known by users, can be listed as SolidWorks, Catia, AutoCAD, Sketchup Rhinoceros 3D and the like.

- **Rhinoceros and Grasshopper**

The method using the generative modeling relationship is the generative algorithm modeling method. As the name indicates, there is an algorithm term in this process. Because in this design type, objects are produced using algorithms; The output of the objects for the other stages of the design is also created with algorithms. When it comes to design, one of the most widely used generative design programs is Grasshopper. Grasshopper provides a set of mathematical tools for generative modeling based on Rhinoceros' 3D objects, such as operators, conditional tables, functions, and trigonometric curves [239].

Rhinoceros is a Nurbs-based modeling program and CAD software specifically designed for 3D modeling and prototyping, widely used in engineering and construction. Although it was intended as an add-on for the AutoCAD program, it was later developed by Robert McNeel & Associates as an original software for its own name. It provides information exchange between various programs with its import and export feature. It speeds up the inter-program workflow by enabling files in many different formats [240].

There are many utilities that can be added to the Rhinoceros program. Built in Rhinoceros and working together, Grasshopper, which provides algorithmic modeling to the user by using Rhinoceros knowledge, is the most widely used and known plugin today. Grasshopper can also be used without any programming knowledge. Algorithmic modeling is done using modeling tools in Grasshopper and the model can be rebuilt by changing the settings of each or a part of the created parametric models. In this modeling phase, the commands of the Rhinoceros program are not used. However, Rhinoceros' user interface is used to visualize the model. The operations applied in Grasshopper are mathematical. At the same time, logical links can be created. These operations are independent of the parametric model, that is, they can be changed or removed. The advantages provided by Grasshopper software to

users using the Rhinoceros interface can be listed as follows [239].

Transformation is the basic process of modeling and manufacturing geometry. It helps to scale and orient (copy, reverse copy, move) the desired model or object.

Datasets and Maths, Grasshopper works with a simple and understandable algorithm system. Infinite geometric combinations can be created by using numbers and objects used in algorithms and simple mathematical functions.

Parametric Space, Grasshopper enables the numerical representation of forms and tectonics (relationship between forms), different articulations of elements, multiple processes of lineages, Nurbs far from the classical idea of symmetry, and a continuous curvature design model. It is divided into 3 groups as 1-dimensional curves, 2-dimensional surfaces and 3-dimensional objects.

Nurbs Surface and Meshes, Grasshopper has multiple surface components. Edges and planes, the final product of the design, can be generated and modeled as point and spline data to create surface geometries.

Fabrication; today, there is an intense interest in fabrication, material application and production with computer aided production. It is certain that new design processes and algorithms cannot be explained by traditional construction processes. By providing data exchange between Grasshopper and 3D printers, it is possible for designers to produce their own design products.

Deformation and Morphing is among the powerful functions of freeform design. In Grasshopper, geometries can be bent, cut, and fused by deformation, and deformed by deformation.

2.2.4. Created toolpaths and simulation program

In this thesis, since there is no commercial slicing or toolpath program for RAM, these processes will be used with programs for 3D printers and simulations we have prepared ourselves. In this context, the slicing and toolpath extraction processes required for RAM were performed with the help of Simplfiy3D, Rhinoceros and Grasshopppe programs. In addition to these, conversions to SLIM robot coding language for NACHI robots were also carried out with text editor programs as a final operation when necessary.

As the first step, the drawing of the geometry desired to be produced is required. Then, in order to create a slicing and tool path for this product to be produced, the processes on which

axis the slicing will be made and the path and similar production parameters that the tool will draw are determined. As a result of these choices, if a 3D printing program can already be used, production codes are derived by converting to SLIM robot coding language after slicing and Gcode extraction processes. However, since there is no slicing program available for elbow production and six axis toolpath creation, the parametric design program Rhinoceros was used for our own parting and toolpath extraction processes and Grasshopper plugin was used for simulation and coding.

First of all, a toolpath was created for the experiments to test the parameters required for the AM of the continuous glass fiber reinforced photo-curable material with a thermoset resin matrix and to examine the curing quality. The tool path required here includes L-shaped movement in two axes, which first moves in the Y axis and then goes up in the Z axis. Since this toolpath is not a 3D drawing, the requirements for direct SLIM robot coding, not slicing, were realized with the help of Rhinoceros and Grasshopper programs. First, the L shape was obtained by determining the coordinates at the corner points of the road to be followed. Afterwards, the required SLIM coding for these points was created. The software and picture of this generated code are given in Figure 2.19.

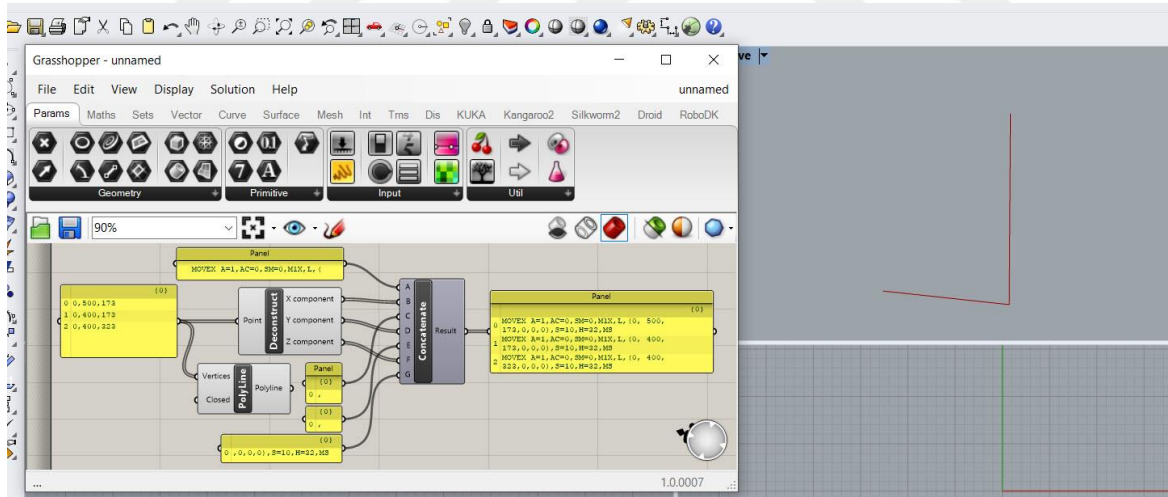


Figure 2.19 Rhinoceros and Grasshopper coding for L-shaped toolpath.

Next, the toolpath is required to produce a rectangular test specimen in a straight row. This toolpath is also realized with the help of Rhinoceros and Grasshopper drawing program. Here, first of all, the corner coordinates of the rectangle were determined, and row lines were created to scan this area with equal spacing, and these points were divided into corner points and these points were converted into SLIM robot codes. This process was repeated by adding the required number of layers in the Z axis and sorting the coordinate list in

reverse order. This sequentially generated slicing and coding process is given in Figure 2.20
Figure 2.21 shows how the layer has a toolpath in this slicing.

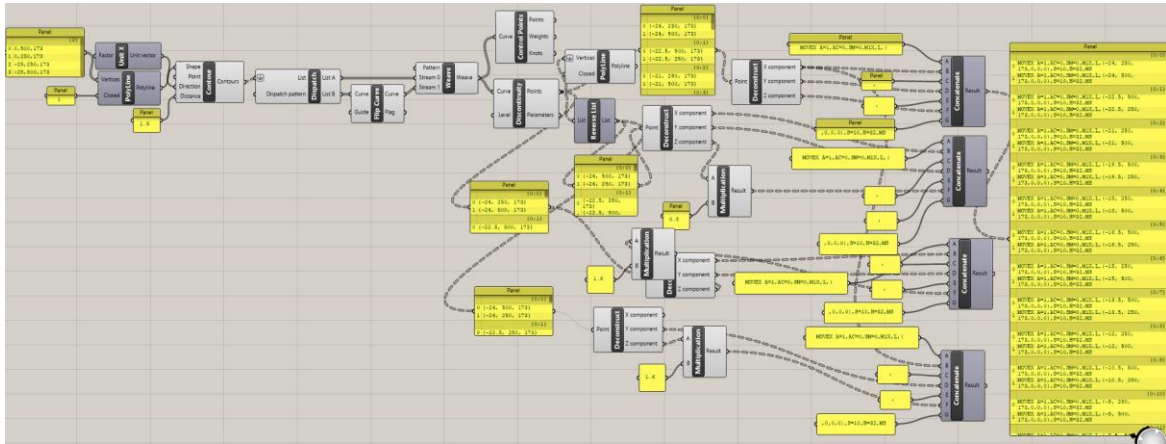


Figure 2.20 Slicing and SLIM robot coding of rectangular test specimen with Rhinoceros and Grasshopper drawing program.

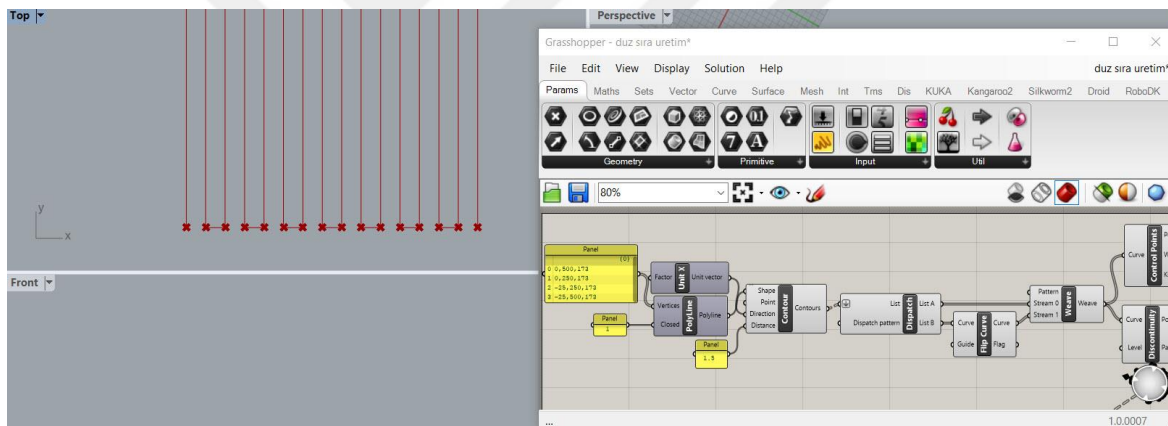


Figure 2.21 Toolpath in layer of rectangular test specimen.

Then, in order to examine the mechanical properties of the products for RAM with this material and curing system, slicing and toolpath at different fiber angles are required to produce rectangular test specimens. For this purpose, toolpaths with 0° , $0^\circ/90^\circ$, $\pm 45^\circ$ fiber directions were extracted and Gcode was created with the help of Simplfify3D slicing program for convenience, since it has no difference with 3D printing. These created Gcodes were converted into SLIM robot coding language with the help of text editor. Figure 2.22, Figure 2.23 and Figure 2.24 shows toolpaths with fiber directions 0° , $0^\circ/90^\circ$, $\pm 45^\circ$, respectively.

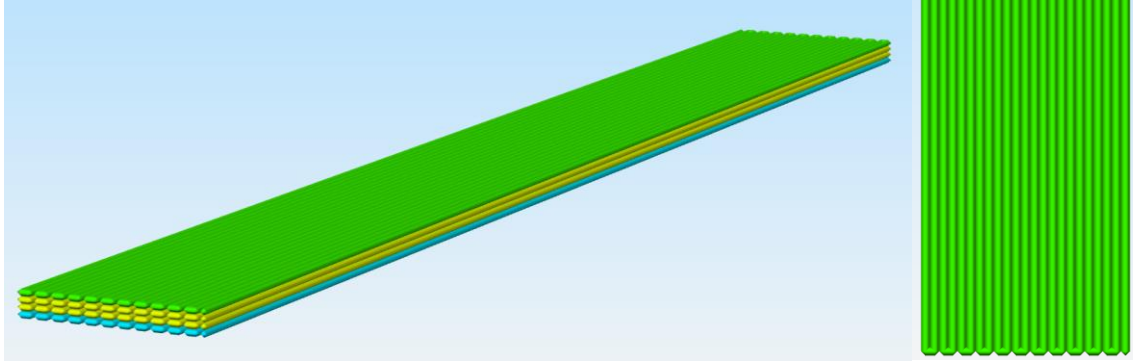


Figure 2.22 Toolpath with 0° fiber orientation.

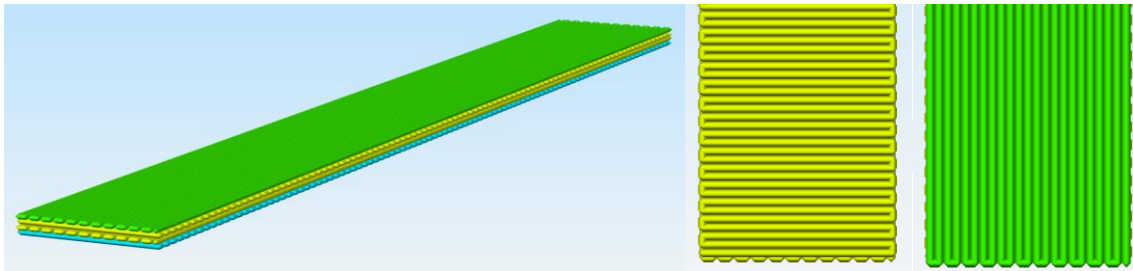


Figure 2.23 Toolpath with 0°/90° fiber orientation.

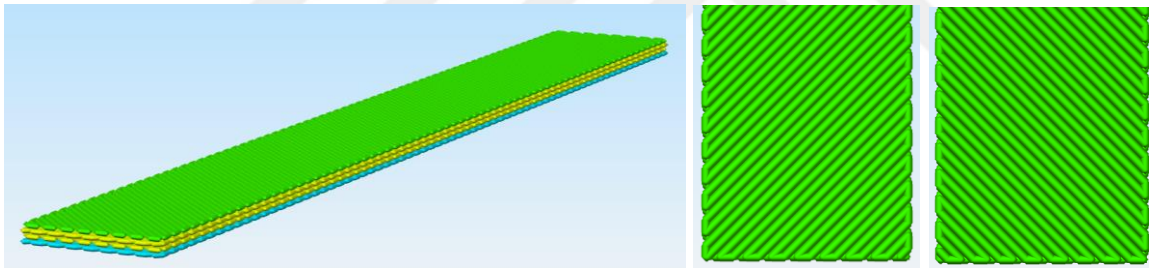


Figure 2.24 Toolpath with $\pm 45^\circ$ fiber orientation.

Finally, a parametric simulation program was created with the help of the Rhinoceros drawing program and the Grasshopper plugin to extract the production codes required for the production of 90 degree composite elbows. This simulation program consists of three different stages.

The first layer, which is the inner layer, is created first. For this first layer, circles are formed by angularly dividing the number of layers to match the minimum and maximum layer thickness determined on the principal axis in the form of a 90-degree quarter circle passing through the center of our elbow. Afterwards, these circles were divided into points and the SLIM robot movement codes required for production were created according to these points. The codes created for the first layer are given in Figure 2.25 and its simulation image is given in Figure 2.26.

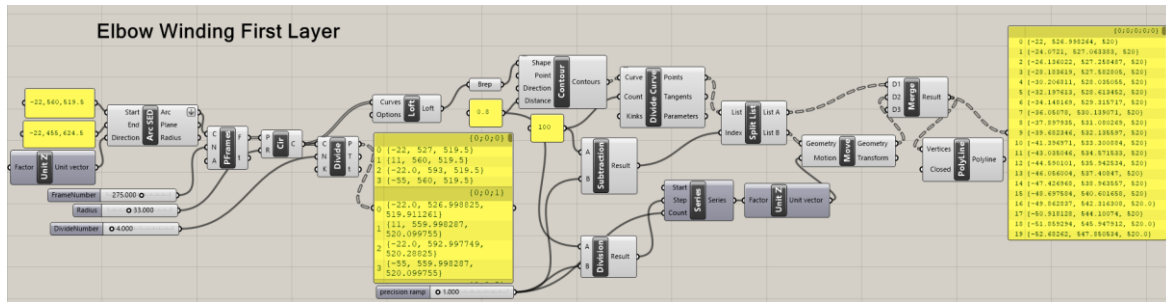


Figure 2.25 First layer coding program created for angular slicing.

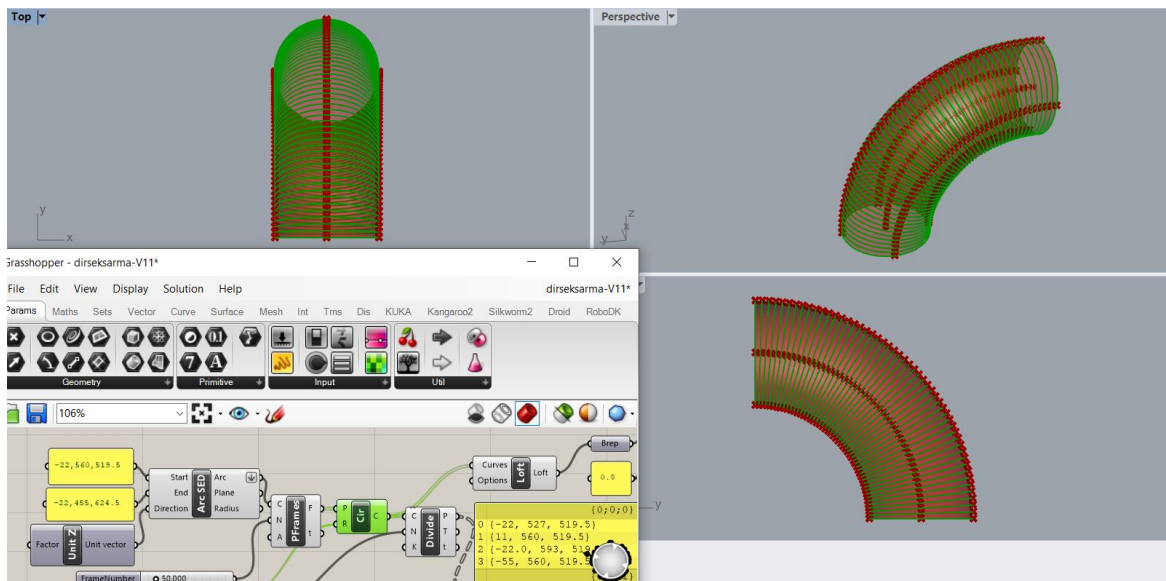


Figure 2.26 Visual simulation for generated first layer codes.

Later, coding and simulation were carried out on this first layer, which will perform the winding with the help of angular curves that can be changed helically from the outside. The most important point here is that the strength increases as you approach the right angle. For this reason, a program has been created that allows winding at vertical and variable angles. However, by creating opposite angles for each layer in the helical shape, a helical filling pattern and variable filling rate can be determined similar to the rectilinear filling pattern. The coding created for this created helical winding and helical filling rate consists of three parts in itself. Here, as the first part, the geometry of the desired dimensions, that is, the 90 degree elbow in our study, was drawn and angular slicing was applied to create the helical winding, as in the first layer. At these sliced angles, reference points on the circles and a slicing for the helical 3D winding are created by rotating these points in the relevant circle. In the second part of the coding, the order and coordinates of the points for this path are listed. In the third and last code part, the reference angles of the tool tip are extracted perpendicular to the center in addition to the coordinates. Here, the reference is the tangent

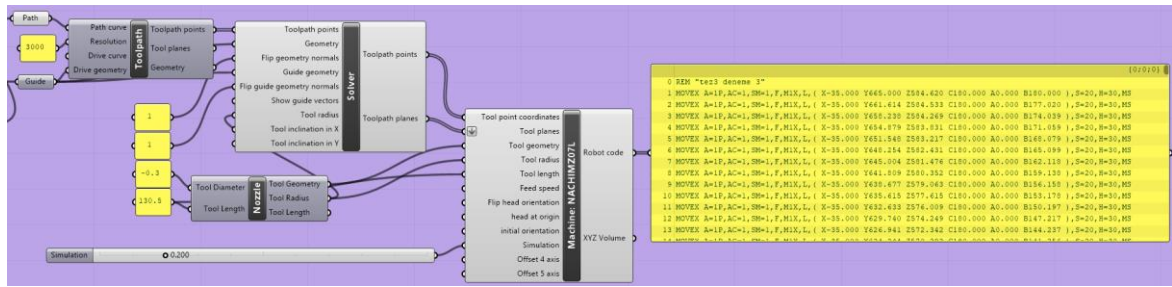


Figure 2.29 Generating SLIM robot codes for middleware.

Figure 2.30 and Figure 2.31 show the simulation of the tool path created by the helical parting off process.

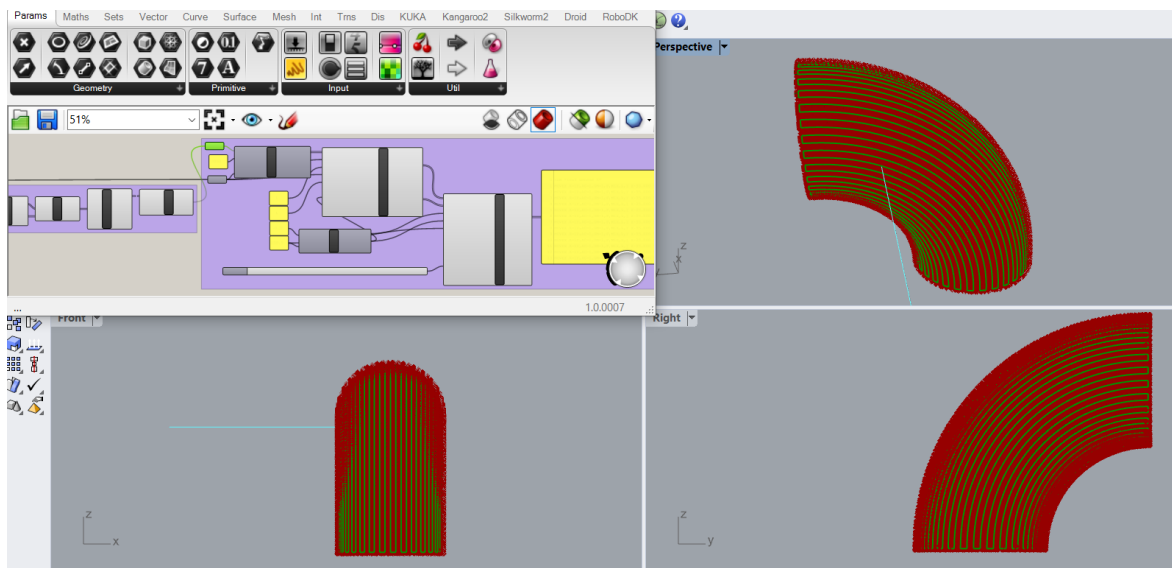


Figure 2.30 Simulation of the toolpath followed for winding at right angles.

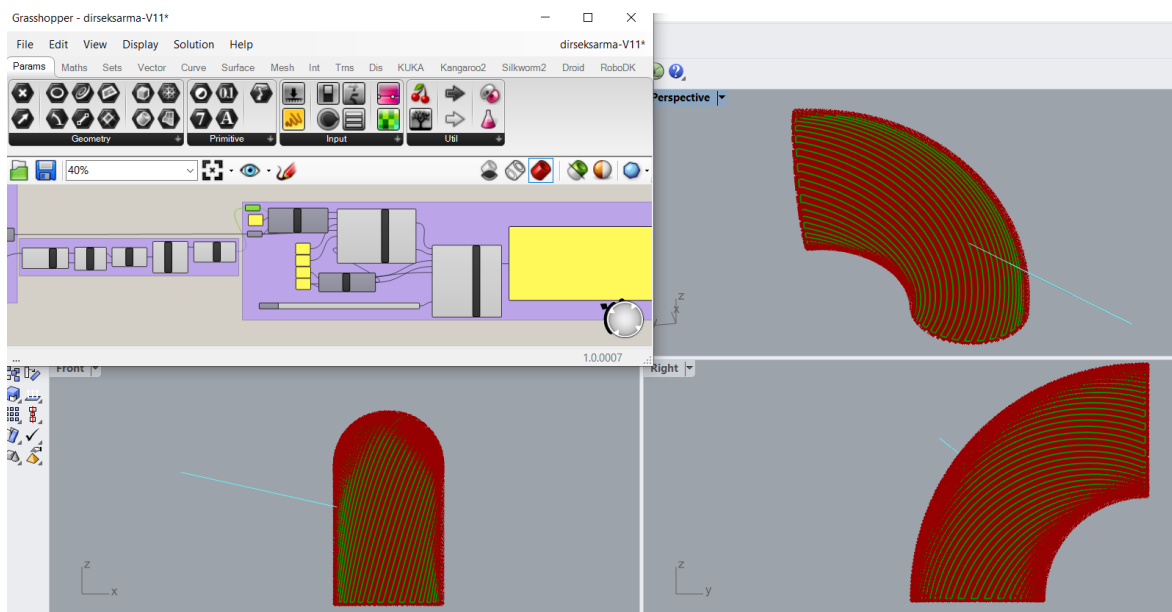


Figure 2.31 Simulation of the toolpath followed for helical winding.

For the outer layer winding, a single helix curve has been drawn to wrap around the elbow in order to adjust the position of the tool tip around the elbow synchronously by rotating the elbow with the help of the rotary table. The coordinates of the tool tip according to the rotation speed of this drawn single helix curve are listed as synchronous. Figure 2.32 shows the coding of the single helix curve created for the outer layer. In Figure 2.33, the simulation of the single helical winding created for the outermost layer is given.

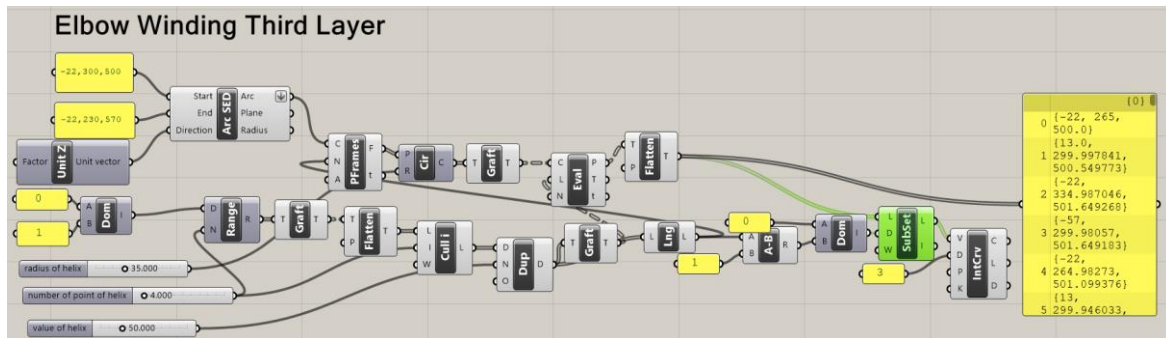


Figure 2.32 Generating SLIM robot coordinates for outer layer.

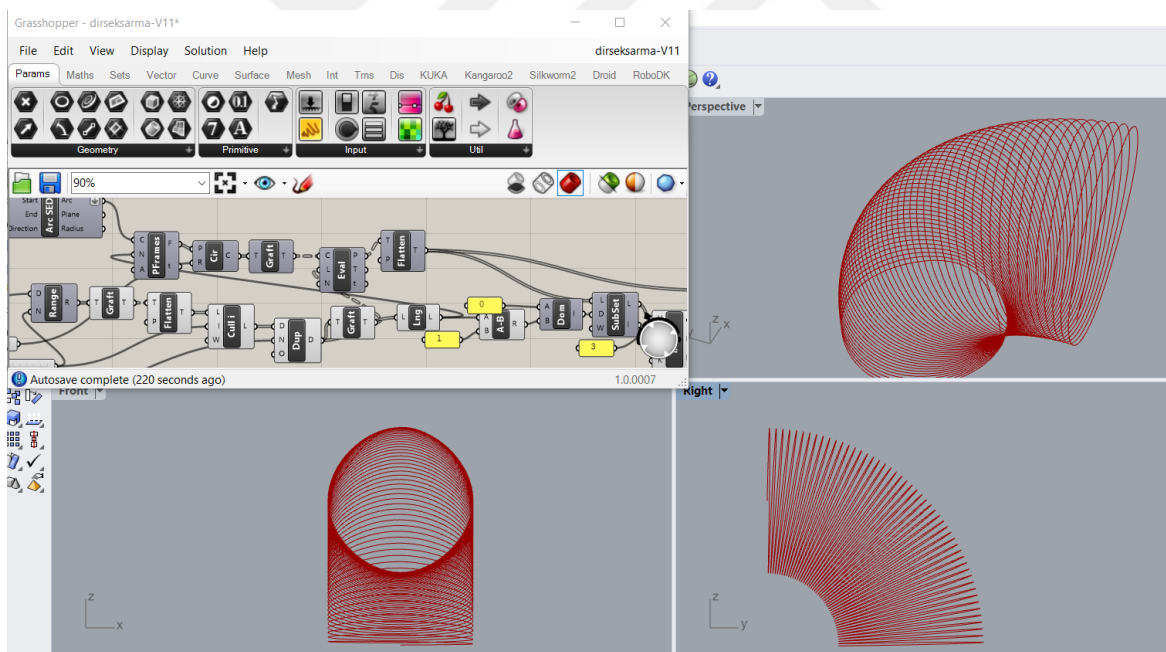


Figure 2.33 Simulation of the toolpath followed for outer layer.

2.3. Examination of Process Parameters

After the production method is determined, the production parameters need to be determined. For this, the most important issue is that the curing process takes place properly and that the resin penetrates the fiber. In order for the production to be smooth, productions were made with different production parameters and these were examined. For these

investigations, some calculations and theories should be given first.

The materials obtained by combining two or more materials that do not dissolve in each other in a macro structure to obtain better properties are called composite materials. Composite materials consist of filling or reinforcing elements. Obtaining the mechanical properties of the materials used in stratified structures allows us to have information about the production parameters, the selection of the materials to be used and the areas to be used. In this section, the stiffness, strength, thermal and expansion coefficients, fiber volume ratios and theoretical calculations of the constants of the materials used for each component that make up the composite materials are examined.

Before modeling the parameter values of the unidirectional composite, the concept of fiber ratio in the volume must be found. This concept is very important. Because the theoretical formulas used to find the stiffness, strength and hygrothermal properties of a unidirectional lamina depend on the fiber volume ratio. Measurements of components are usually based on their masses. Therefore, the fiber mass ratio should be determined. In addition, in order to determine the fiber volume and void ratio of the composite, it is necessary to determine the fiber composite density. In addition, composite density should be determined within the concepts of specific modulus and strength [24].

2.3.1. Volume ratios

Consider the following symbolic matrices for a composite consisting of fiber and matrix [24].

$v_{c,f,m}$ = volume of composite, fiber and matrix respectively.

$\rho_{c,f,m}$ = density of composite, fiber and matrix respectively.

If the fiber volume ratio is V_f and the matrix volume ratio is V_m ,

$$V_f = \frac{v_f}{v_c} \text{ and } V_m = \frac{v_m}{v_c} \quad (2.1)$$

Total volume ratios;

$$V_f + V_m = 1 \quad (2.2)$$

From Equation 2.2.

$$V_f + V_m = V_c \quad (2.3)$$

2.3.2. Mass ratios

Assuming the following symbolic notations for composite material,

$w_{c,f,m}$ =mass of composite, fiber and matrix, respectively.

If the fiber mass ratio is W_f and the matrix mass ratio is W_m ,

$$W_f = \frac{w_f}{w_c} \text{ and } W_m = \frac{w_m}{w_c} \quad (2.4)$$

Total volume ratios;

$$W_f + W_m = 1 \quad (2.5)$$

From Equation 2.5.

$$w_f + w_m = w_c \quad (2.6)$$

If a single material density definition is considered;

$$w_c = \rho_c * v_c \text{ and } w_f = \rho_f * v_f \text{ and } w_m = \rho_m * v_m \quad (2.7)$$

Equation 2.7. equation 2.4. If it is put in its place, in terms of fiber and matrix volume ratios, mass and volume ratios are specified in the equations below [24].

$$W_f = \frac{\rho_f}{\rho_c} * V_f \text{ and } W_m = \frac{\rho_m}{\rho_c} * V_m \quad (2.8)$$

Mass and volume ratios are shown below in terms of the properties of each component.

$$W_f = \frac{\frac{\rho_f}{\rho_m}}{\frac{\rho_f}{\rho_m} * V_f + V_m} * V_f \text{ and } W_m = \frac{1}{\frac{\rho_f}{\rho_m} * (1 - V_m) + V_m} * V_m \quad (2.9)$$

Knowing the mass and volume ratios in composite material calculations is very important in terms of composite theory. It is seen in Equation 2.8. that the mass and volume ratios are not equal.

2.3.3. Density

The density of composite materials with known volume ratios is found with the following equations [24].

$$w_f + w_m = w_c \quad (2.10)$$

If Equation 2.7 and Equation 2.10 are substituted,

$$\rho_f * v_f + \rho_m * v_m = \rho_c * v_c \text{ and } \rho_f * \frac{v_f}{v_c} + \rho_m * \frac{v_m}{v_c} = \rho_c \quad (2.11)$$

Using the definition of fiber and matrix volume ratios in Equation 2.1,

$$\rho_f * V_f + \rho_m * V_m = \rho_c \quad (2.12)$$

Composite volume is equal to the sum of fiber and matrix volumes.

$$v_c + v_f = v_m \quad (2.13)$$

The density of the composite in terms of mass ratios is found as follows.

$$\frac{1}{\rho_c} = \frac{W_f}{\rho_f} + \frac{W_m}{\rho_m} \quad (2.14)$$

2.3.4. Void amount

During the production of composite material, voids may remain in the composite material. This undesirable situation has a negative effect on the mechanical properties of the composite. In addition, the theoretical composite density is calculated higher than the actual density values.

The voids that may occur in composite structures reduce the values of the properties given below [24].

- Shear strength,
- Compressive strength,
- Transverse tensile strength,
- Fatigue resistance,
- Corrosion resistance.

It causes a strength loss between 2-10% in the 1% void structure that may occur in the composite structure.

The void volume ratio V_v for the composite with void volume v_v is defined as follows.

$$V_v = \frac{v_v}{v_c} \quad (2.15)$$

The total volume of the void composite material (v_c),

$$v_c = v_f + v_m + v_v \quad (2.16)$$

If the experimental density of the composite material is defined as ρ_{ce} , the actual volume of the composite is,

$$v_c = \frac{w_c}{\rho_{ce}} \quad (2.17)$$

If the theoretical density of the composite is defined as ρ_{ct} , the actual volume of the composite is,

$$v_f + v_m = \frac{w_c}{\rho_{ct}} \quad (2.18)$$

If Equation 2.17 and Equation 2.18 are substituted in Equation 2.16,

$$\frac{w_c}{\rho_{ce}} = \frac{w_c}{\rho_{ct}} + v_v \quad (2.19)$$

The void volume is found as follows.

$$v_v = \frac{w_c}{\rho_{ce}} * \left(\frac{\rho_{ct} - \rho_{ce}}{\rho_{ct}} \right) \quad (2.20)$$

2.3.5. Nozzle diameter

Since the material will be transmitted from the nozzle, similar to the production of composite filaments with the pultrusion technique, the nozzle diameter can be calculated according to this method. Therefore, the nozzle diameter must be calculated first. This calculation is done with the following formula [241].

$$D = 2 * \sqrt{\frac{TEX}{10^3 * \rho * \pi}} \quad (2.21)$$

Where,

D, the diameter of the nozzle.

TEX, the linear mass of the fiber, (1200 TEX (g/km)).

ρ , the density of the fiber, (2.48 kg/m³).

If the calculation is made using Equation 2.21, the recommended nozzle diameter is calculated as 0.8 mm. Considering this reference value, we will use 2 nozzle diameters as 0.8 and 1.0 mm in the thesis study.

2.3.6. Layer height and layer width

First, we will try to determine the dimensions of the material to be poured from the nozzle, such as the width and length of the resin that the supplied UV light energy can cure. This process was principally studied by Jacobs and its diagram is given in Figure 2.34.

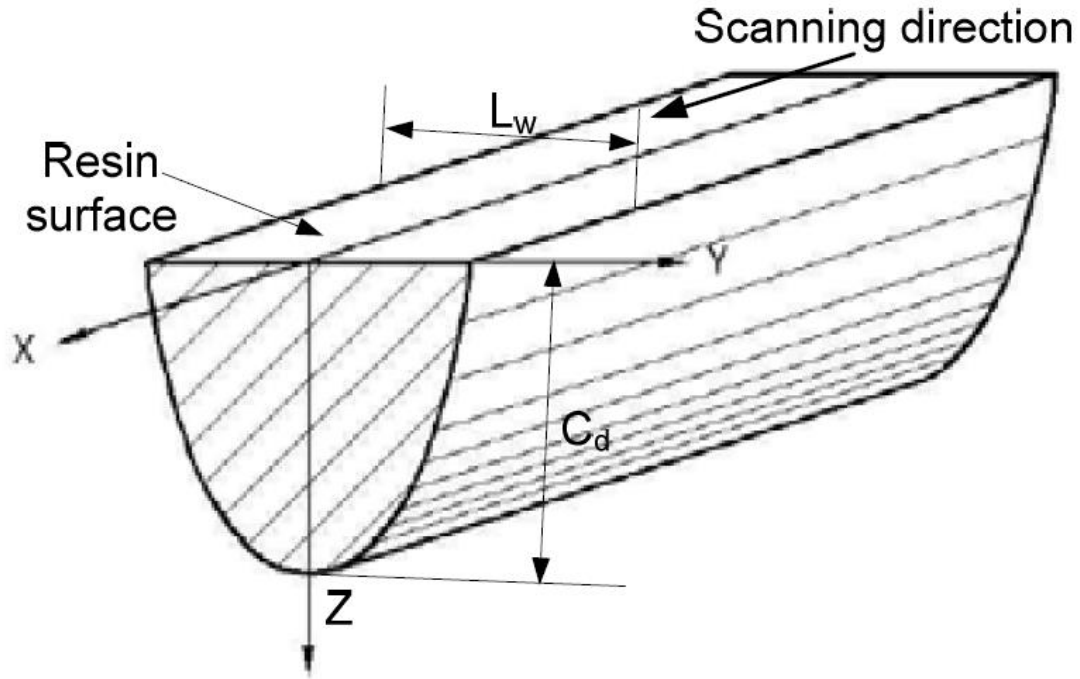


Figure 2.34 Parabolic cylinder of a cured line [242].

Jacobs studied the effects of SLA resin on the curing process with a laser beam. It can be defined as the minimum energy requirement (E_c) for curing a particular type of liquid resin. According to the Beer-Lambert exponential absorption law, laser exposure will decrease exponentially as z depth increases. It can be defined as the depth of penetration of the resin (D_p) and we can express the relationship of the depth of curing (C_d) depending on the maximum exposure on the resin surface with the help of the following equation;

$$C_d = D_p * \ln\left(\frac{E_{max}}{E_c}\right) \quad (2.22)$$

Also, a line that cures in a parabolic cylindrical shape is produced when a UV light scans the P_L resin surface at a constant speed in a straight line. This hardened line is given in Figure 2.33. Accordingly, the hardening width and depth of the section of the hardened line can be found with the help of the parabolic equation. If this mathematical analysis is organized by geometric equations, you can get the following important equation. This equation gives the cured line width and depth.

$$L_w = B * \sqrt{\frac{C_d}{2 * D_p}} \quad (2.23)$$

where L_w is the line width. This equation shows that the cured line width is proportional to

the laser diameter, as well as the square root of the ratio between the curing depth and the resin penetration depth.

This equation alone gives the relationship between curing width and depth. However, since we expose the SLA resin to light when it comes out of the nozzle, similar to the FDM method, we can also think geometrically as calculated in the FDM method. This simulation is given in Figure 2.35.

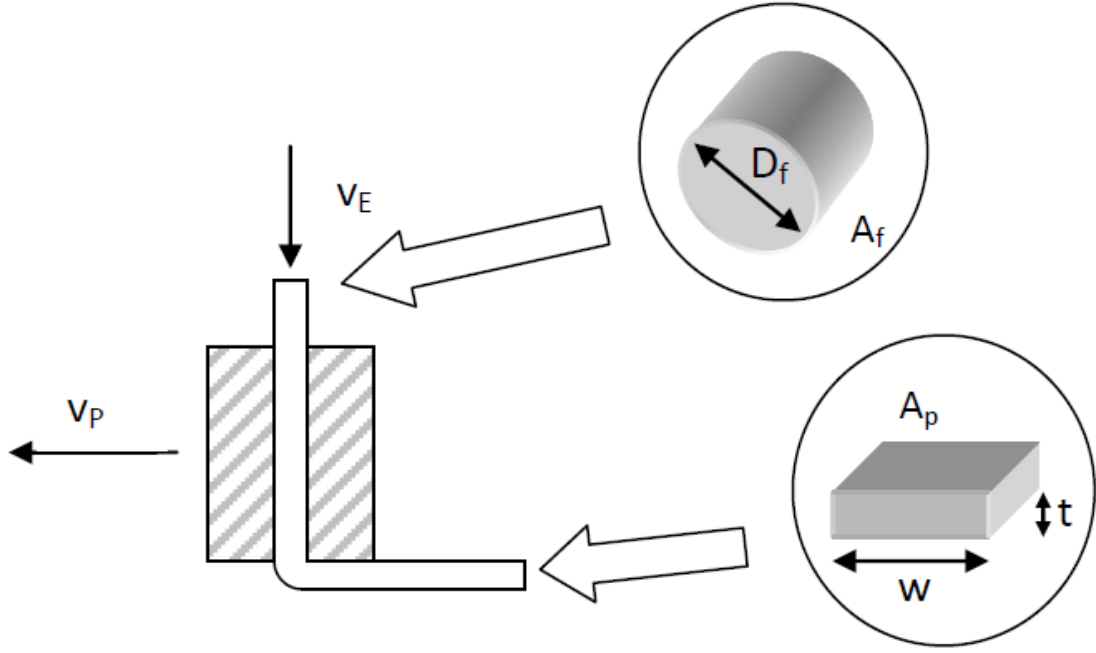


Figure 2.35 Printing process of FDM method [241].

Since the glass fibers in the filament do not stretch during the printing process, motion is achieved with a printing speed V_P equal to the extrusion speed of V_E . This means that the cross-sectional area of the filament entering the nozzle is equal to the cross-sectional area of the printed line. This leads to:

$$A_f = A_p$$

When $w \gg t$, the printed trace is highly flattened and can be considered a regular rectangle.

$$w = \frac{\pi \cdot D_f^2}{4 \cdot t} \quad (2.24)$$

It has been revealed that values between 0.4 mm and 0.8 mm can be given for the layer thickness, together with the calculations and production trials for the nozzle diameters and possible layer thicknesses selected by equation 2.23 and equation 2.24. For the line width was determined that values between 1.0 mm and 2.0 mm could be selected.

In UV-curable RAM, there are important parameters that affect the dimensional accuracy, production time and mechanical properties of the product. Therefore, these parameters should be carefully evaluated. Important parameters are the number of UV LED sources, nozzle diameter, fiber density and printing speed. These parameters directly affect the curing mechanism of composite production. Since the number of UV LEDs directly affects the light intensity and the curing mechanism, it was chosen as the effective parameter. The nozzle diameter is set as 0.8 and 1.0 mm because as the nozzle diameter increases, the possibility of giving details in the produced parts decreases. In addition, the fiber density is adjusted as 300, 600, 900 tex because as the tex rate increases, the curing will be adversely affected and the fiber resin ratio will decrease. In terms of curing stability, the number of UV LEDs was determined from 2 sides and 4 sides. According to these parameters, 3D printing was performed on the horizontal x-y axis (100 mm) and vertical z axis (150 mm). Figure 2.36 shows RAM and the printed L-shaped sample.

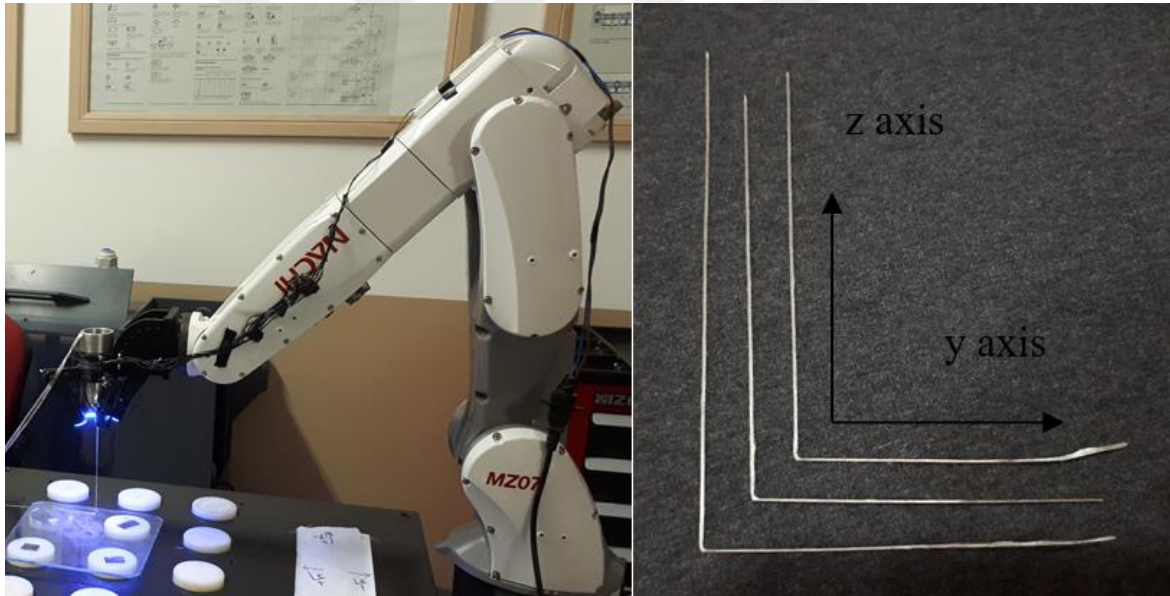


Figure 2.36 RAM composite L shape lines [243].

Nozzle diameter is the most important parameter that determines the fiber mass ratio. This affects all the properties of the final product. Since the printing speed is the movement speed of the tool, the fiber resin combination poured from the nozzle was chosen as the effective parameter that affects the curing time. The parameters selected for the experiments are shown in Table 2.6.

Table 2.6 Process parameters of L shaped lines.

Example No	Nozzle Diameter (mm)	Fiber TEX (g/1000m)	Printing Speed (mm/s)	No of UV LED
1	0.8	300	5	2
2	0.8	300	10	2
3	0.8	300	15	2
4	0.8	300	20	2
5	0.8	600	5	2
6	0.8	600	10	2
7	0.8	600	15	2
8	0.8	600	20	2
9	0.8	900	5	2
10	0.8	900	10	2
11	0.8	900	15	2
12	0.8	900	20	2
13	0.8	300	5	4
14	0.8	300	10	4
15	0.8	300	15	4
16	0.8	300	20	4
17	0.8	600	5	4
18	0.8	600	10	4
19	0.8	600	15	4
20	0.8	600	20	4
21	0.8	900	5	4
22	0.8	900	10	4
23	0.8	900	15	4
24	0.8	900	20	4
25	1.0	300	5	2
26	1.0	300	10	2
27	1.0	300	15	2
28	1.0	300	20	2
29	1.0	600	5	2
30	1.0	600	10	2
31	1.0	600	15	2
32	1.0	600	20	2
33	1.0	900	5	2
34	1.0	900	10	2
35	1.0	900	15	2
36	1.0	900	20	2
37	1.0	300	5	4
38	1.0	300	10	4
39	1.0	300	15	4
40	1.0	300	20	4
41	1.0	600	5	4
42	1.0	600	10	4
43	1.0	600	15	4
44	1.0	600	20	4

45	1.0	900	5	4
46	1.0	900	10	4
47	1.0	900	15	4
48	1.0	900	20	4

Pieces of 50 mm in length were cut from these L-shaped lines and weighed for the tests. In terms of the accuracy of the experiments, each experiment was repeated 3 times under the same conditions and the average of the measured values was taken. Scanning Electron Microscope (SEM) images are taken by FEI brand Quanta FEG 250 model device, which is located within the Scientific and Technological Research Application and Research Center of Duzce University. SEM images were taken from the samples produced at 20 mm/s speed for each tex density and fiber and resin combinations were observed. In Figure 2.37, SEM device and a weighing device is given which has precision of 0.001 g.



Figure 2.37 SEM device and weighing device [243].

The test sample in rectangular dimensions of 100x15x5 mm was printed with fixed parameters at each individual nozzle diameter and fiber density; Layer thickness (0.5 mm) and extrusion width (1.0 mm) were used as printing parameters, and then the test samples were cut in the middle with a water jet. Thus, SEM images were taken from the cross-sectional regions. It was observed how the internal structure was at each density. Figure 2.38 shows the production of the rectangular test sample.

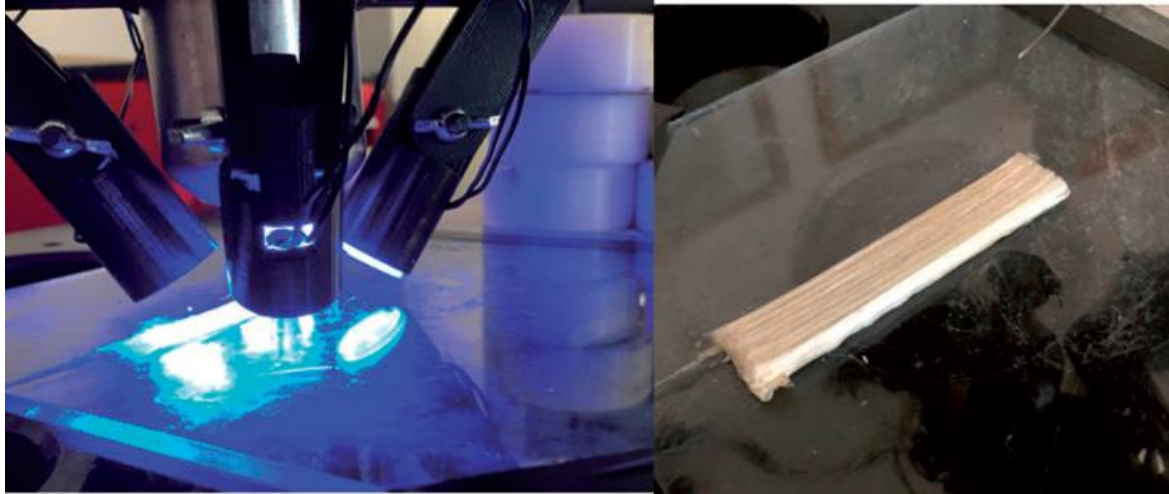


Figure 2.38 3D printed rectangular test samples for SEM crossection images [243].

2.4. Examination of Mechanical Properties

Understanding the mechanical properties of continuous fiber reinforced RAM parts is important to verify that these parts provide the required strength properties in applications. In order to specify whether continuous fiber reinforced FDM printed composite parts can be used functionally, the mechanical properties must be determined. Examining photopolymerized composites and their robotic AM methods motivates our work. In this thesis, 3D CFRP composite parts were printed with a six-axis industrial robotic arm based on FDM technology.

2.4.1. Calculations of mechanical properties of fiber reinforced composite materials

Since fiber reinforced composites show high strength and rigidity in the direction of the fiber long axis, the mechanical properties of the produced composite vary depending on the fiber type, direction and mixing ratio. In the mechanical properties of such materials, the mechanical properties in the 1 direction, that is, in the fiber direction, differ from the mechanical values in the 2 and 3 directions perpendicular to the fiber in Figure 2.39. For this reason, the mechanical properties are not the same in all directions, and calculations are made by calling the fiber-based materials as orthotropic materials [244].

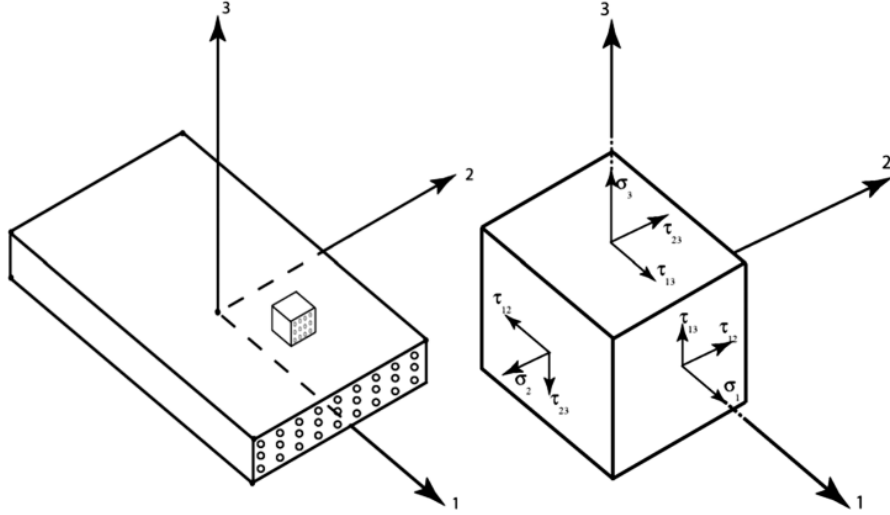


Figure 2.39 Example display of fiber-reinforced composite materials [244].

When we write in matrix form the unit deformations that occur as a result of shear stresses τ_{12} , τ_{23} and τ_{13} , such as normal stresses σ_1 , σ_2 and σ_3 , applied in the above definitions for the composite material;

$$\begin{Bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{Bmatrix} = \begin{bmatrix} 1/E_1 & -\nu_{21}/E_2 & -\nu_{31}/E_3 & 0 & 0 & 0 \\ -\nu_{12}/E_1 & 1/E_2 & -\nu_{32}/E_3 & 0 & 0 & 0 \\ -\nu_{13}/E_1 & -\nu_{23}/E_2 & 1/E_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/G_{23} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/G_{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/G_{12} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{13} \\ \tau_{12} \end{Bmatrix} \quad (2.25)$$

In the simplest and plainest form of Equation (2.25.);

$$\{\varepsilon\} = [S]\{\sigma\} \quad (2.26)$$

By writing Equation 2.26, $\{\varepsilon\}$ and $\{\sigma\}$ are unit strain and stress vectors with 6x1 matrix and $[S]$ is named as elasticity matrix and it is like $S_{11}=1/E_1$, $S_{12}=-\nu_{12}/E_2$, ... $S_{66}=1/G_{12}$. When we arrange it, the matrix is arranged as follows;

$$\begin{Bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{Bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{21} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{31} & S_{32} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{13} \\ \tau_{12} \end{Bmatrix} \quad (2.27)$$

If the matrix form, which is the inverse of the elasticity matrix $[S]$ and called the stiffness matrix $[C]$, is converted into its general structure;

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{13} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{21} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{Bmatrix} \quad (2.28)$$

It is provided to calculate the stresses that occur in the structure of the obtained matrix material as a result of deformation. Equation (2.29) is obtained if this form is simplified.

$$\{\sigma\} = [C]\{\varepsilon\} \quad (2.29)$$

We have previously stated that there are differences in mechanical properties in fiber-reinforced composite materials when three aspects are examined. Although the mechanical properties in the fiber direction differ from other aspects, the properties in the other two directions are the same. For this reason, if we choose the 1 direction in the fiber direction, from the equations $E_2=E_3$, $\nu_{12}=\nu_{13}$ and $G_{12}=G_{13}$;

$$G_{23} = \frac{E_2}{2*(1+\nu_{23})} \quad (2.30)$$

When Equation (2.30.) is obtained, material constants E_1 , E_2 , ν_{12} , ν_{13} , G_{12} are sufficient for strength calculations in fiber reinforced composites [245 – 247].

It is necessary to determine the constants of fiber-reinforced composite materials in the calculations given above in the macro structure. The mechanical properties of such materials vary depending on the incorporation rate of fiber and matrix in the unit cell. This situation can be seen in Figure 2.40. The mechanical properties are determined by the equation in Equation (2.31.) by using the fiber volume ratio (V^f) and matrix volume ratio (V^m) in the unit cell. V^m can be easily calculated by determining the fiber reinforcement ratio between $0 < V^f < 1$ by making use of the cross section or weight while determining the mixing ratios in the materials [248].

$$V^f + V^m = 1 \quad (2.31)$$

By determining this mixing ratio, the "simplification" approach is used to determine the elasticity constants of fiber-reinforced composites. In this method, the elasticity constants of the material are determined depending on the mixing ratios and orientations of the fiber and matrix.

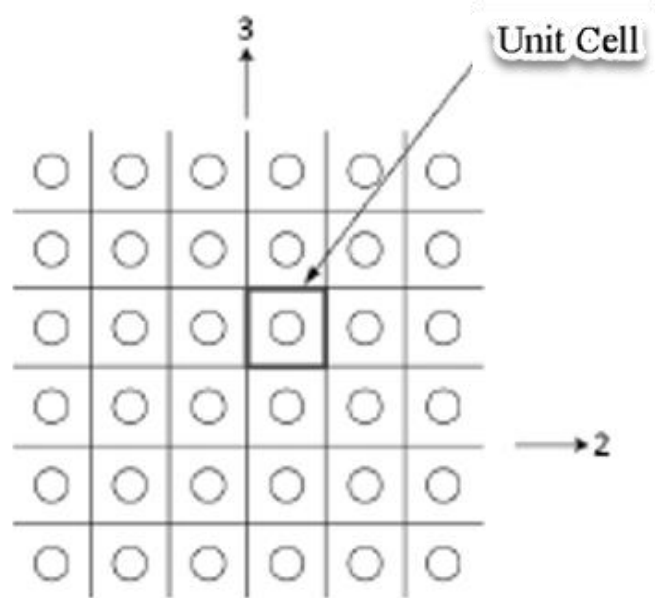


Figure 2.40 Matrix fiber arrangement in the unit cell of fiber reinforced composites [249].

- Modulus of elasticity in the 1 direction (fiber direction) of composite materials;

If the strain in the fiber direction was not the same in the fibrous structures of the composites, a crack would occur between the fiber and the matrix. This is a logical explanation for this approach. Because the strain is the same in matrix and fiber. The above-mentioned approach is also an important approach in beam, plane and shell theories in general material mechanics. Based on this basis, it can be deduced that; assumptions in material mechanics, the properties of unidirectional fiber-reinforced composite materials with orthotropic modulus are mainly E_1 , E_2 , ν_{12} and G_{12} , and every assumption that is the basis of this approach is fixed and not arbitrary. It is calculated by the participation ratios of the mechanical properties of the fiber and the resin in determining the initial modulus in the 1 direction (which is the fiber direction) of the composite materials. Unit volume element loaded as 1 direction and under stress situations are also given in Figure 2.41, Figure 2.42 and Figure 2.43.

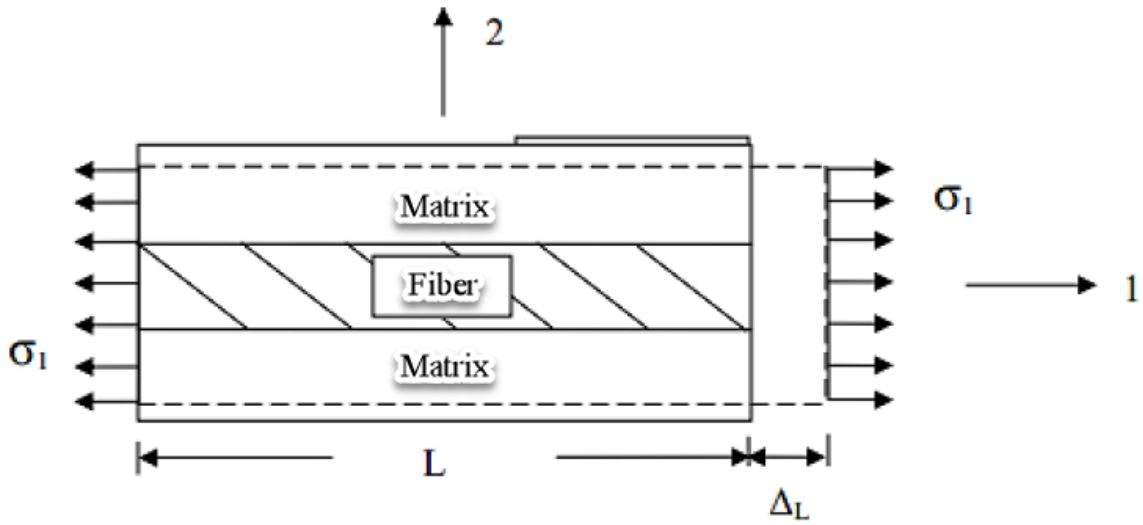


Figure 2.41 Unit volume element loaded in the 1 direction [248].

$$V^f = \frac{A^f}{A} \quad (2.32)$$

$$V^m = \frac{A^m}{A} \quad (2.33)$$

$$E_1 = E^m * V^m + E_1^f * V^f \quad (2.34)$$

- Modulus of elasticity in the 2 direction of composite materials;

However, since the obtained Equation (2.34) did not give very good results in practice, Equation (2.35) was developed by adding the correction factor (η) to this formula. This factor is a value between $0 < \eta < 1$ and the coefficient between 0.4 and 0.6 is used more in practice [250].

$$\frac{1}{E_2} = \frac{V^f}{E_2^f} + \frac{V^m}{E^m} \quad (2.35)$$

$$\frac{1}{E_2} = \frac{\frac{V^f}{E_2^f} + \frac{\eta * V^m}{E^m}}{V^f + \eta * V^m} \quad (2.36)$$

- Determination of G_{12} for composite materials;

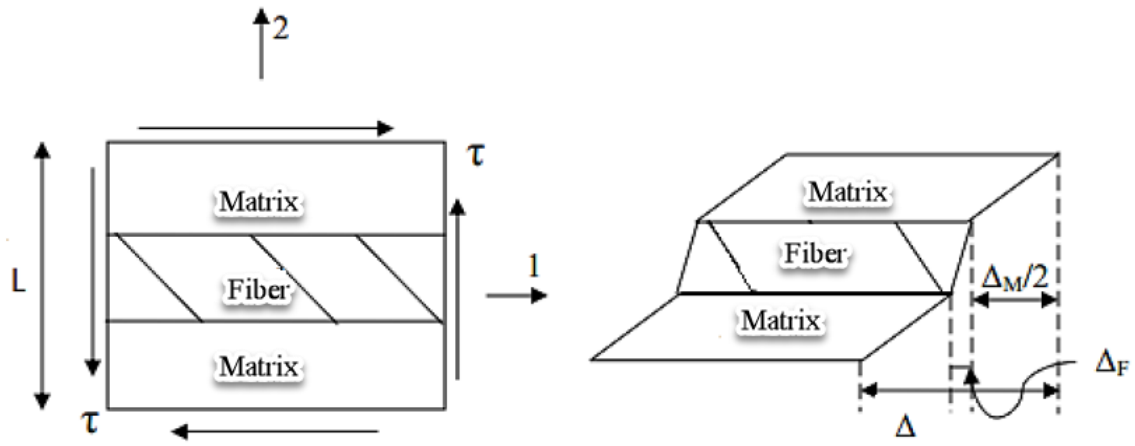


Figure 2.42 Unit volume element under stress [245].

$$\frac{1}{G_{12}} = \frac{v^f}{G_{12}^f} + \frac{v^m}{G_{12}^m} \quad (2.37)$$

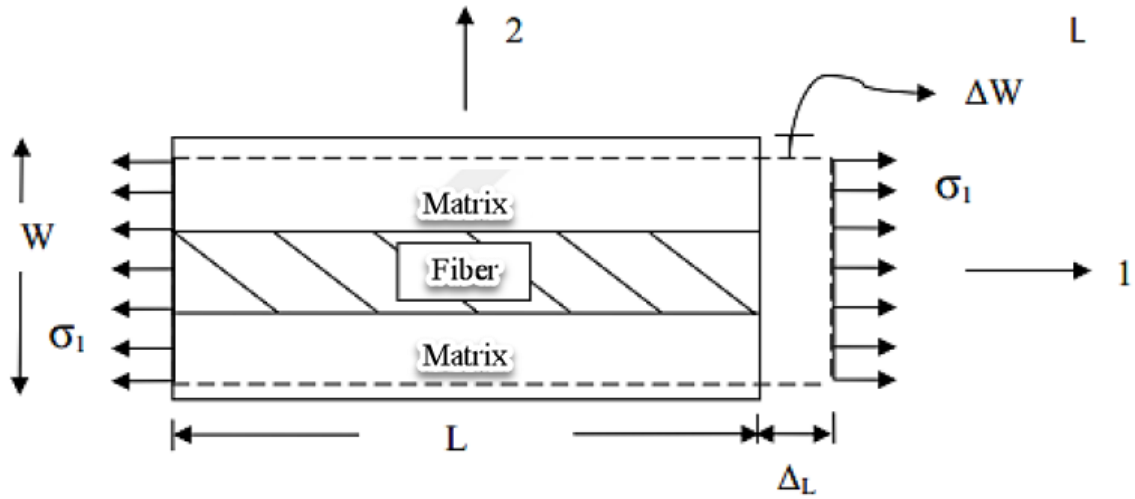


Figure 2.43 Unit volume element loaded in 1 direction [248].

$$v_{12} = V^m * v^m + V^f * v^f \quad (2.38)$$

$$v_{21} = \frac{E_2}{E_1} * v_{12} \quad (2.39)$$

According to the equations expressed above, fiber and matrix material ratios in composite materials and strength calculations on fiber orientation were investigated. In addition, as mentioned before, the light exposure time due to the light curing method is directly related to the production speed. Based on these basic principles, products with different fiber densities, different fiber directions and different printing speeds were produced and tested for the examination of mechanical properties.

2.4.2. Experimental set up for mechanical properties

As the production coding for the test samples to be produced provides convenience, as explained in Section 2.2. the samples were drawn in the SolidWorks program and the Gcodes produced in the Simplify3D program were converted into SLIM robot motion codes. For the 3D printing process of the photopolymer matrix fiberglass reinforced robotic composite, the manufacturing parameters have as much effect on the mechanical properties as the material. Therefore, the most effective parameters on the mechanical properties were selected. These parameters are; print speed, fiber density and fiber orientation. These parameters and their levels are given in Table 2.7.

Table 2.7 Printing process parameters.

Features	Values
Printing speed (mm/s)	10, 20, 30
Fiber density (%)	45, 55, 65
Fiber orientation (°)	0, 0/90, ± 45
Layer height (mm)	0.8
Extrusion width (mm)	1.8

The fiber density parameter, one of the parameters given in Table 2.7, is a fixed parameter and is obtained with the nozzle diameter and the fiber TEX value used. It is detailed in the section examining the process parameters in Section 2.3. To put it briefly, the resin gets uncontrolled below 40% fiber density. In the case of fiber density higher than 65%, the amount of resin is insufficient. It becomes difficult to achieve uniform solidification [251]. The selected nozzle diameter and fiber TEX values for the fiber density used are given in Table 2.8.

Table 2.8 Parameters determining fiber density.

Fiber density (%)	Nozzle diameter (mm)	Fiber TEX
45	1.0	600
55	0.8	600
65	1.0	900

Examples of productions for mechanical properties are shown in Figure 2.44. It can also be observed how different fiber orientations are produced.

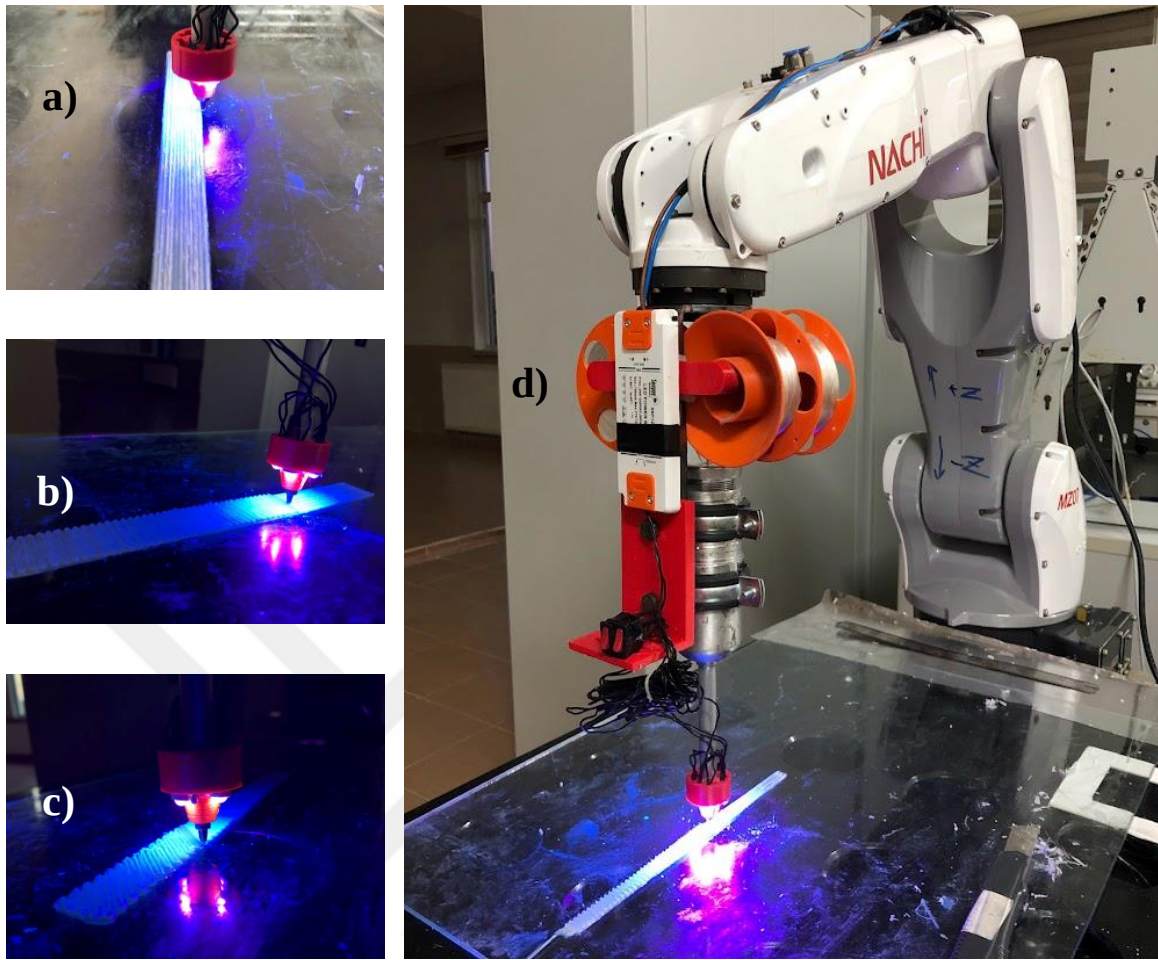


Figure 2.44 Fiber orientations; a) 0° , b) $0^\circ/90^\circ$, c) $\pm 45^\circ$, and d) RAM composite material.

In Table 2.9, the experimental setup determined to examine the mechanical properties is listed in full. Three samples were produced and tested for each parameter under identical conditions with the parameters given here.

Table 2.9 Experimental setup for the examination of mechanical properties.

Experiment No	Fiber density (%)	Printing speed (mm/s)	Fiber orientation (°)
1	45	10	0
2	45	20	0
3	45	30	0
4	45	10	0/90
5	45	20	0/90
6	45	30	0/90
7	45	10	±45
8	45	20	±45
9	45	30	±45
10	55	10	0
11	55	20	0
12	55	30	0
13	55	10	0/90
14	55	20	0/90
15	55	30	0/90
16	55	10	±45
17	55	20	±45
18	55	30	±45
19	65	10	0
20	65	20	0
21	65	30	0
22	65	10	0/90
23	65	20	0/90
24	65	30	0/90
25	65	10	±45
26	65	20	±45
27	65	30	±45

2.4.3. Testing of mechanical properties

Being able to determine the mechanical properties of materials is very important in order to use these materials structurally. The mechanical properties of the materials are determined by producing samples according to the determined standards and performing tests under the conditions determined according to the standards. Tensile test, bending test, izod impact tests and hardness measurement tests are most commonly applied to determine the mechanical properties. All of these tests are performed according to separate standards. The devices for tensile and bending tests are the 10 kN capacity tensile test device.

For the tensile test ASTM D3039 [252] describes the tensile test test for composite materials. Rectangular specimens measuring 250x25x2.5 mm were produced according to this standard. Tests were carried out under normal conditions at a constant speed of 5 mm/s.

The average of the values found was taken. It was drawn during the tensile test in Figure 2.45.



Figure 2.45 Tensile test process.

For the bending test, the ASTM D7264 [253] test standard was taken as reference. A test sample measuring 130x13x4 mm was produced according to this standard. These produced samples were bent in the tensile device with the help of a three-point bending device and the damage stress was removed. It was taken during the bending test in Figure 2.46.

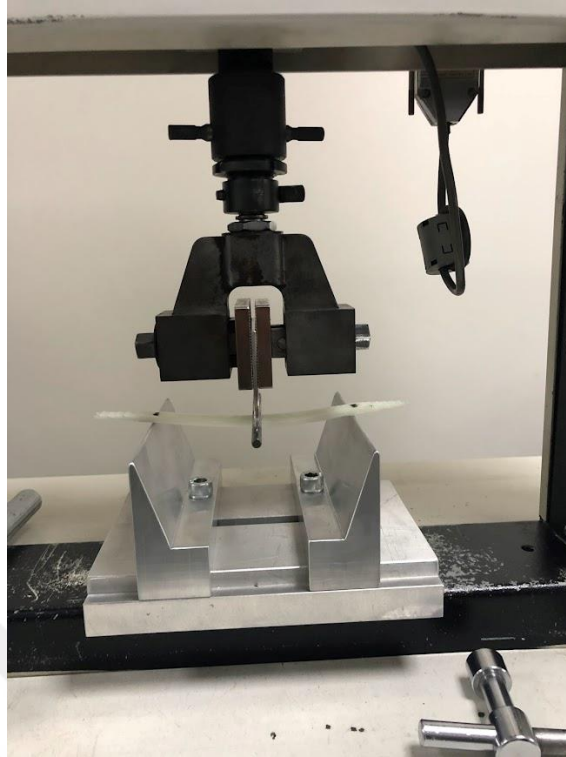


Figure 2.46 Flexural test process.

Izod impact test was performed by producing test specimens with dimensions of 63.5x12x7x3.24 mm according to ASTM D256 [254] test standard. As in all other tests, all tests were repeated three times and the average of the measured values was taken. The pendulum energy of the Izod impact tester is 7.5 Joules and the impact speed is 2.9 m/s. A picture taken during the izod impact test is given in Figure 2.47.

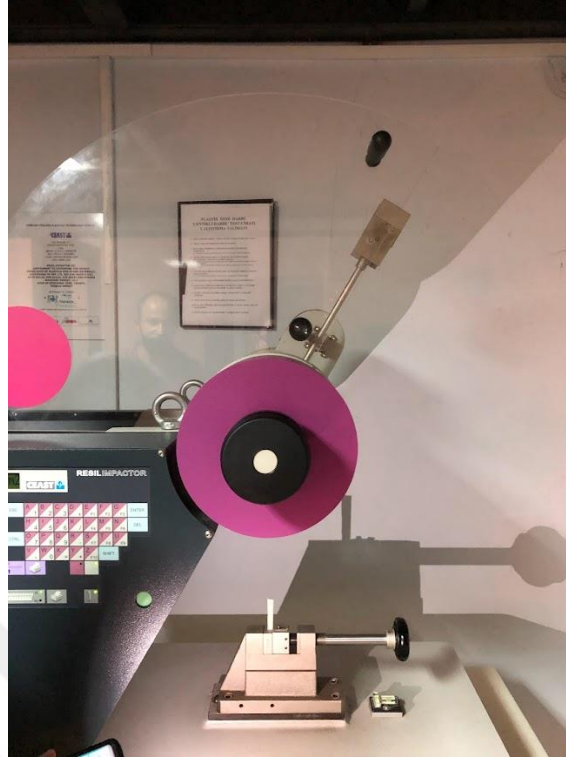


Figure 2.47 Izod impact test process.

Hardness is the resistance of the material to the object pressed from the surface, which is harder than the material itself. Hardness values are of great importance as they are directly related to the strength of the materials. In composite materials, the part that affects the hardness is mostly formed by the full curing of the resin. In addition, the hardness of plastic-based composites has similar properties to the hardness of the matrix material and is measured with the same methods. Shore D hardness measurement method is generally preferred for hardness measurement of plastics and composites. In order to determine the mechanical properties, we performed the hardness measurements as Shore D. Figure 2.48 shows a picture taken during hardness measurement.



Figure 2.48 Shore D hardness test process.

2.5. Production and Examination of Composite 90° Elbow

Pressure vessels are tanks and tanks that provide high sealing properties. According to TSE, pressure vessels are vessels closed to the atmosphere, consisting of a combination of spherical, cylindrical sphere, cylindrical or cone-shaped volumes used for the transport or storage of $0.49 \times 10^5 \text{ Pa}$ (0.5 bar) and higher pressure liquids and gases [255]. In other words, it can be defined as a container that is forced by internal and external pressure. Since pressure vessels contain dangers that will greatly affect the health and safety of living things, problems that may occur in use must be determined and resolved in advance. For this reason, detailed analyzes should be made in the design of pressure vessels and their production should be carried out as a result of accurate engineering calculations [256].

2.5.1. Calculations of interval pressure of composite 90° elbow

The pressurized fluid in the pressure vessels transmits the pressure to the vessel walls at the same rate from all directions and exposes it to stresses on the wall. Cylindrical pressure vessels are divided into two groups in the literature as thin-walled and thick-walled. In pressure vessels, it is accepted whether the vessel is thin-walled or not according to the ratio of $\frac{r}{t} \geq 10$ between the inner diameter of the cylinder (r) and the wall thickness (t) [257]. In

thin-walled cylinders, axial, radial and circumferential stresses occur due to the internal pressure (P) and this is seen in Figure 2.49.

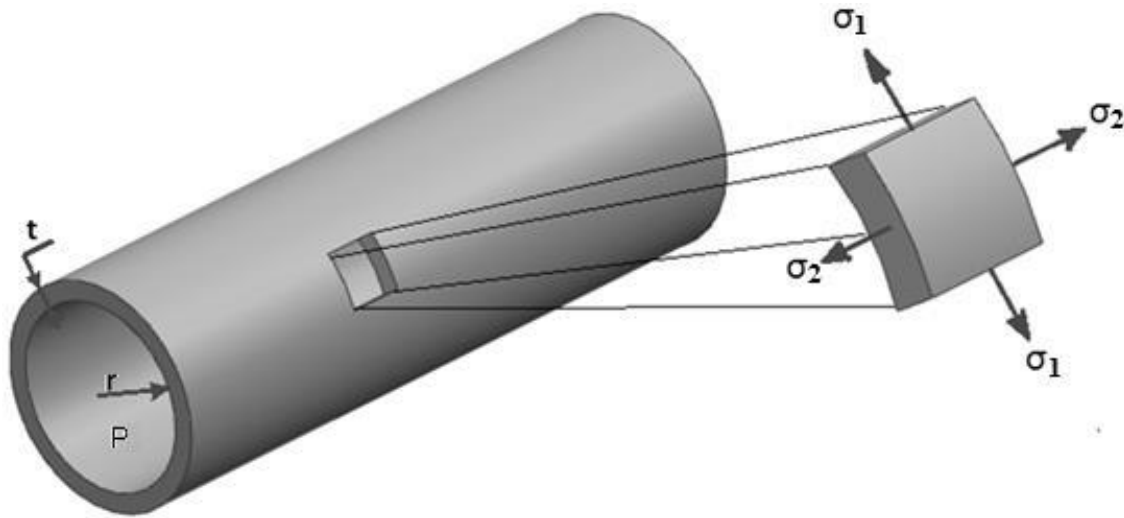


Figure 2.49 Pressure vessels and stresses in cross section under internal pressure [249].

In thin-walled vessels, radial stresses are neglected because they are much lower than other stresses on the wall surface [258]. The circumferential (σ_1) and axial stress (σ_2) that occur due to pressure in thin-walled cylinders are given in Equations 2.40 and 2.41 when the figure given in Figure 2.50 is examined.

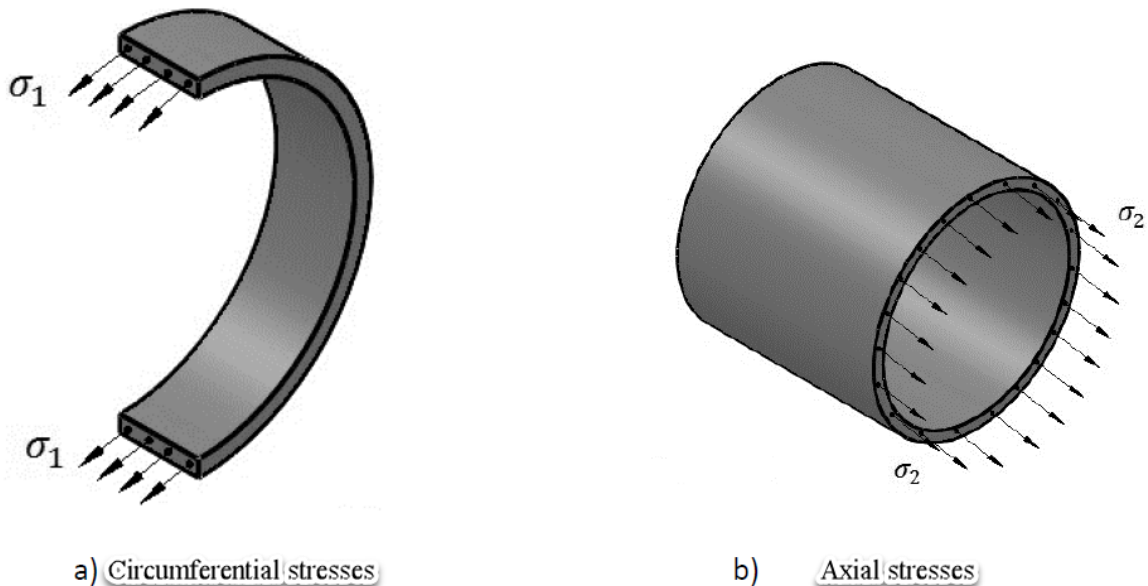


Figure 2.50 Stresses in pressure vessels [249].

$$\sigma_1 = \frac{P \cdot r}{t} \quad (2.40)$$

$$\sigma_2 = \frac{P*r}{2*t} \quad (2.41)$$

In cylindrical parts, there is a relationship between the circumferential and axial stress that occurs on the cylinder surface under internal pressure. Since the circumferential stress is twice the axial stress under the same pressure, it is the most important parameter in the calculations during the design process of pressure vessels. When Figure 2.51 is examined, the matrix form forming the two stresses is given in Equation 2.42.

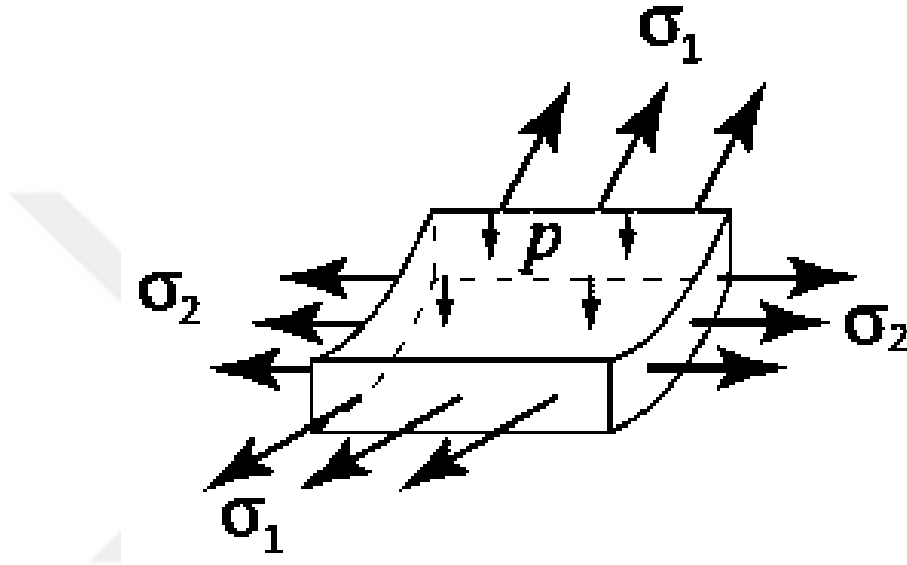


Figure 2.51 Peripheral and axial stresses on the pressure vessel wall [249].

$$\begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \frac{P*r}{2*t} * \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2.42)$$

2.5.2. Experimental set up for interval pressure of composite 90° elbow

For the production of composite elbows, it is important to determine the dimensions first. While determining the reference dimensions for the composite elbow here, since there is no reference measurement for the internal pressure strength test, the commonly used dimensions in the market were preferred. For this reason, it has been produced with a diameter of 63.5 mm (2.5 inches) and a radius of curvature of 95.25 mm (3.75 inches), as indicated in Figure 2.52, with reference to the dimensions. These selected dimensions are in accordance with the EN 10253 [259] steel fittings standard and the AWWA C950 [260] fiberglass pressure pipe standard.

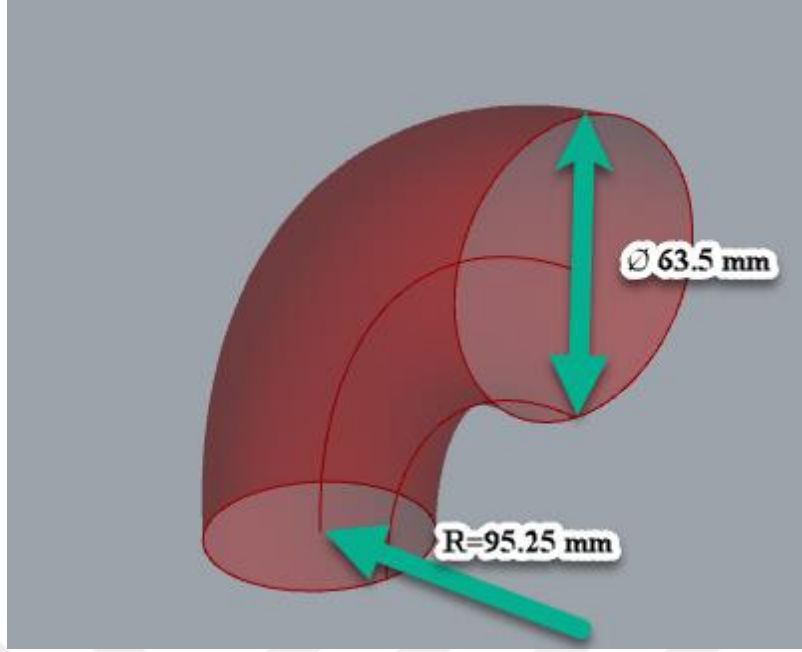


Figure 2.52 Dimensions of composite 90° degree elbow.

After determining the dimensions of our composite elbow as a test sample, the drawing and slicing processes of this elbow in computer environment were carried out with the help of Rhinoceros 3D drawing program and Grasshopper plugin. These slicing operations and steps are given in Section 2.3. In addition, while performing these slicing operations, it was used in the results of the experiments we made while determining the production parameters in the first parts. In addition, the effective parameters selected in Section 2.3 were taken into account while determining the production parameters. The most important point is that there are parameters specially arranged due to the geometry of the 90° composite elbow. winding angle, fiber density and filling rate were determined as effective parameters selected for the production of 90° composite elbows. The effective parameters along with other fixed parameters are given in Table 2.10.

Table 2.10 Printing process parameters for 90° composite elbow.

Features	Values
Printing speed (mm/s)	10
Fiber density (%)	45, 55, 65
Winding angle (revolution)	0, 0.125
Filling rate (%)	50, 75, 100
Layer height (mm)	0.4 - 0.8
Extrusion width (mm)	2.0 - 1.8

The printing speed is fixed at 10 mm/s as given in Table 2.10. The reason for this is to keep the dimensional stability and shape tolerances in balance while producing circularly.

Another important detail is that since the first layer of the elbow is sliced angularly, the layer thickness in the inner part of the radius of curvature of the slices varies as 0.4 mm and the layer thickness in the outer radius of the curvature as 0.8 mm. This variable layer thickness has been selected within the maximum and minimum values determined in the section where the printing parameters are determined. Since the fiber density among these parameters is determined together with the nozzle diameter and fiber TEX value, these values corresponding to the fiber density are given in Table 2.11.

Table 2.11 Parameters determining fiber density.

Fiber density (%)	Nozzle diameter (mm)	Fiber TEX
45	1.0	600
55	0.8	600
65	1.0	900

After determining all these printing parameters, the experimental setup for composite elbows is given in Table 2.12.

Table 2.12 Experimental setup for the internal pressure test of 90° composite elbow.

Experiment No	Winding angle (revolution)	Fiber density (%)	Filling rate (%)
1	0	45	50
2	0	45	75
3	0	45	100
4	0	55	50
5	0	55	75
6	0	55	100
7	0	65	50
8	0	65	75
9	0	65	100
10	0.125	45	50
11	0.125	45	75
12	0.125	45	100
13	0.125	55	50
14	0.125	55	75
15	0.125	55	100
16	0.125	65	50
17	0.125	65	75
18	0.125	65	100

After the experimental setup and all parameters were determined, the production stages were determined. This part is mostly related to slicing and robot motion coding. Here, in the RAM process, the first layer is made in the form of angular slicing. In Figure 2.53 the production of the first layer of 90° composite elbows is given.



Figure 2.53 Production of the first layer of the 90° composite elbow.

Then, as the second layer, six axes winding was carried out from the outside. Here, a total of six different toolpaths have been created, with two different winding shapes as straight winding and angled winding, and three different filling rates. These toolpaths are produced in 3 different fiber densities. In all these 18 different experiments, three of each were manufactured and tested. In order to avoid erroneous measurements, the found values were averaged. Figure 2.54 shows an image during straight winding for the middle layers.



Figure 2.54 Straight fiber winding for the second layer.

Another important step applied during the windings for the second layer was a 180° table piece that was turned upside down. However, the toolpath was revised 180° and production

continued. The reason for this is that the robot arm we use cannot reach everywhere around the elbow. In this case, 180° of winding was done, the table was rotated and the other part was wrapped again. In Figure 2.55 a picture of the continued production as rotated for straight winding is given.



Figure 2.55 Continued production as rotated for straight winding is given.

In all productions for the second floor, a table was rotated at 180° and production continued. Then, filling rate were applied for straight winding. In Figure 2.56, the application of the filling rate for flat winding is given as a picture.



Figure 2.56 RAM with 75% filling rate in straight winding.

Figure 2.57 shows 1/8 turn helical winding application with 100% filling rate. Here, the reason for choosing a low helix winding angle is that the winding angle is kept small because the mechanical properties of the elbow are improved as it approaches the right angle.

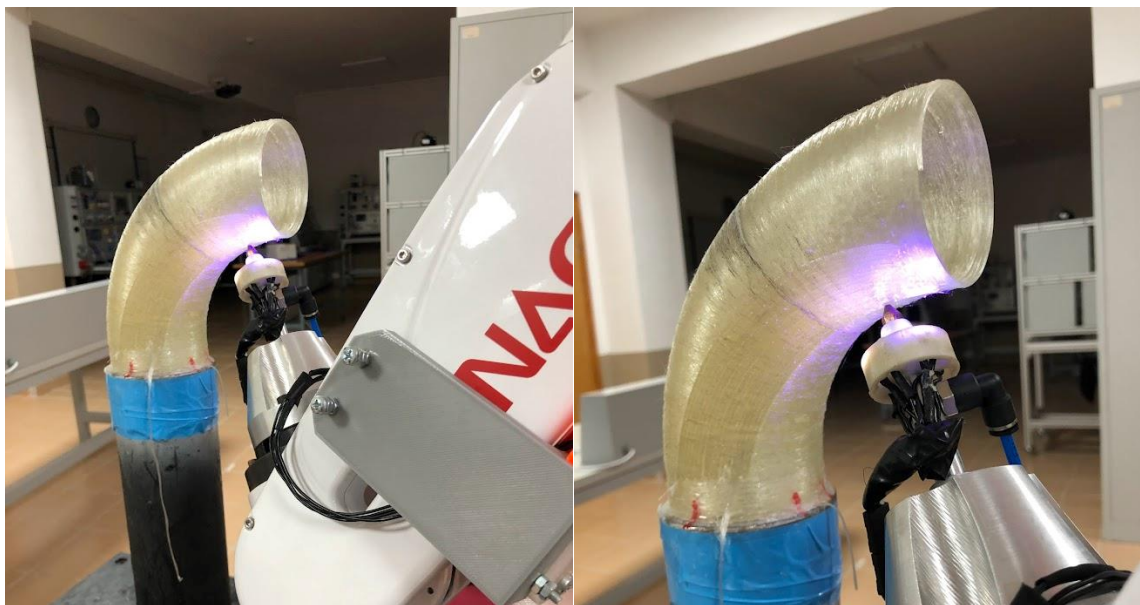


Figure 2.57 1/8 turn helical winding application with 100% filling rate.

The application of the filling rate with the 1/8 turn angled helical winding is given in Figure 2.58.



Figure 2.58 75% filling rate with the 1/8 turn angled helical winding.

After the second layer as angled winding, the third layer was wound with a helical winding angle in the opposite direction. As an example of this winding, 1/8 turn helical winding angle is given in Figure 2.59 with 50% filling rate.



Figure 2.59 Winding of the reverse angled third layer.

The third layer for straight winding and the fourth and last layer for helical winding are provided by the circular motion of the table from the outside of the elbow. For this, the rotation of the elbow from the outside with the table movement is given in Figure 2.60.

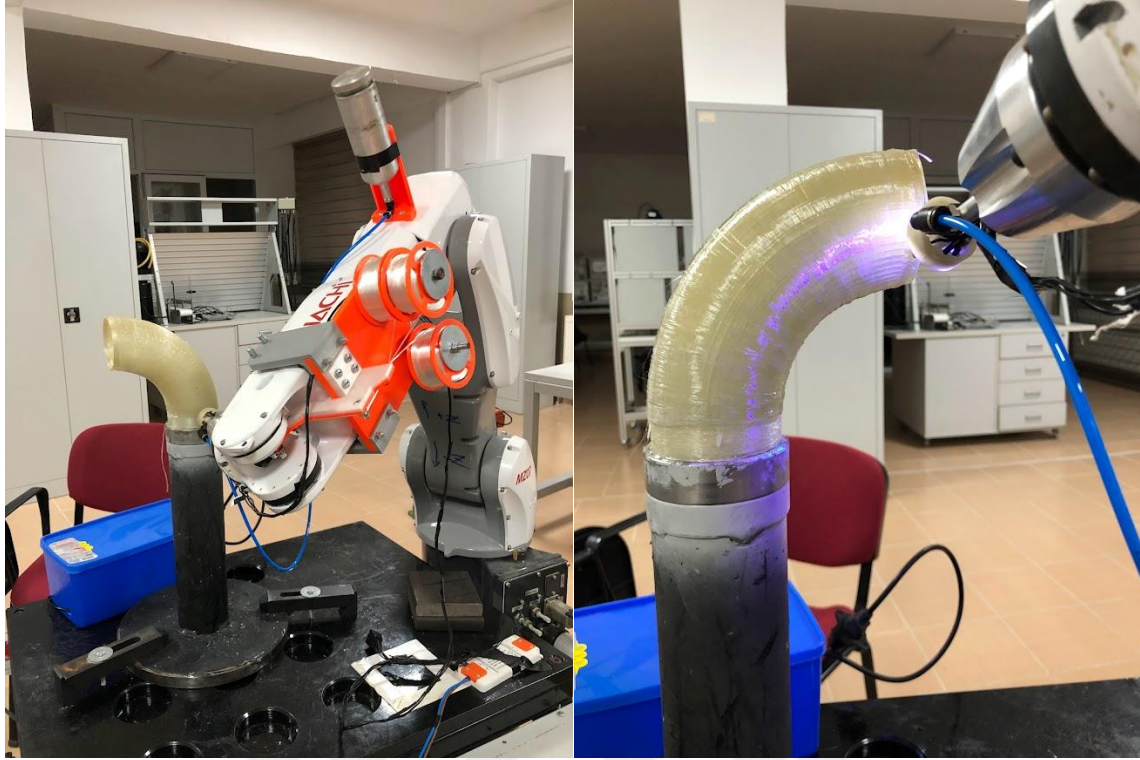


Figure 2.60 Winding from outside perpendicular to straight winding.

2.5.3. Internal pressure testing of 90° composite elbow

After all the productions are finished, it is time to make the necessary preparations for the internal pressure strength test. First of all, it is necessary to cut straight extensions of 10 mm at both ends of the elbow during robotic composite 3D printing. The cut form of these excesses is given in Figure 2.61.



Figure 2.61 Cutting excess 90° composite elbow.

In order to perform the internal pressure test, the openings at both ends of the elbow must be sealed and a pressurized water connection must be installed. For this reason, we will add pressure water connections to our elbow, which will provide both tightness and strong pressure by casting from epoxy resin. First, the shape to be cast in epoxy was produced in a 3D printer. Later, this shape was molded into silicone. Epoxy resin casting is provided by placing water fittings and composite elbows in silicone molds. Figure 2.62 shows the master model part and mold casting produced in the 3D printer.



Figure 2.62 3D printed master model part and silicone mold casting.

Epoxy resin was poured into the silicone molds obtained by the casting method after the pressure water connections and elbows were positioned. Thus, as seen in Figure 2.63, elbows have been prepared for the internal pressure strength test.



Figure 2.63 Composite elbow fitted with sealed and fluid fittings.

Finally, the composite elbow we produced was connected to the pressure test device resistant to 400 bar pressure, shown in Figure 2.64, and closed inside the autoclave oven to be safe against explosion. In this way, three composite elbows produced according to all parameters were exploded under pressure, and the pressures they could withstand until they were damaged were obtained.



Figure 2.64 Application of internal pressure strength test to composite elbows.

3. RESULTS AND DISCUSSION

The most important initial result is to print composite material by combining and curing photo-curable SLA-based resin and fiber. Another important result is to bring this material formation to a level that is balanced, homogeneous and competitive with other equivalent production methods. Since there is no standard or any commercial product or equipment on this subject, all the work is progressing in the form of trial and testing.

3.1. Test results for process parameters

At this stage, RAM process parameters must first be determined in order to obtain a competitively decent product. These determinations were obtained by trial and error. Nozzle diameter, fiber tex, printing speed and number of light levels were determined by performing preliminary tests.

During these preliminary tests, the main problems encountered are the failure of adhesion to the table, non-adhesion between layers, fiber breakage and fiber retraction at the corners until the appropriate parameters are obtained. In Figure 3.1, there are sample pictures of the errors experienced.



Figure 3.1 Fiber break and fiber retraction errors at corners.

In Table 3.1, fiber mass ratio values were calculated by weighing according to the nozzle diameter and fiber TEX values selected by the preliminary tests. As can be seen here, compared to the vertical part of the L-shaped sample produced in the z-axis, approximately 25% fiber mass ratio is obtained when 1.0 mm nozzle diameter and 300 TEX fiber are used, and approximately 75% fiber mass ratio is obtained when 900 TEX fiber with 0.8 mm nozzle diameter is used.

Table 3.1 Measured weights and fiber mass ratio (vertical movement).

Example No	Cured weight (gr)	Fiber weight (gr)	Fiber mass ratio
1	0.046	0.015	0.326
2	0.044	0.015	0.341
3	0.038	0.015	0.395
4	0.04	0.015	0.375
5	0.056	0.03	0.536
6	0.054	0.03	0.556
7	0.053	0.03	0.566
8	0.054	0.03	0.556
9	0.062	0.045	0.726
10	0.062	0.045	0.726
11	0.061	0.045	0.738
12	0.065	0.045	0.692
13	0.04	0.015	0.375
14	0.047	0.015	0.319
15	0.032	0.015	0.469
16	0.05	0.015	0.300
17	0.054	0.03	0.556
18	0.048	0.03	0.625
19	0.059	0.03	0.508
20	0.051	0.03	0.588
21	0.064	0.045	0.703

22	0.067	0.045	0.672
23	0.065	0.045	0.692
24	0.067	0.045	0.672
25	0.054	0.015	0.278
26	0.043	0.015	0.349
27	0.053	0.015	0.283
28	0.046	0.015	0.326
29	0.054	0.03	0.556
30	0.064	0.03	0.469
31	0.066	0.03	0.455
32	0.075	0.03	0.400
33	0.084	0.045	0.536
34	0.082	0.045	0.549
35	0.075	0.045	0.600
36	0.074	0.045	0.608
37	0.044	0.015	0.341
38	0.036	0.015	0.417
39	0.053	0.015	0.283
40	0.057	0.015	0.263
41	0.069	0.03	0.435
42	0.058	0.03	0.517
43	0.078	0.03	0.385
44	0.07	0.03	0.429
45	0.081	0.045	0.556
46	0.076	0.045	0.592
47	0.078	0.045	0.577
48	0.078	0.045	0.577

In Table 3.2, fiber mass ratio values were calculated by weighing according to the nozzle diameter and fiber TEX values selected by the preliminary tests. As can be seen here, compared to the L-shaped sample produced horizontally in the xy axis, approximately 25% fiber mass ratio is obtained when 1.0 mm nozzle diameter and 300 TEX fiber are used, and approximately 75% fiber mass ratio is obtained when 900 TEX fiber with 0.8 mm nozzle diameter is used. Similar fiber mass ratios were obtained in the productions made on both axes. It can be observed from here that the fiber mass ratio between 25% and 75% can be arranged in productions with the composite production method in this way.

Table 3.2 Measured weights and fiber mass ratio (horizontal movement).

Example No	Cured weight (gr)	Fiber weight (gr)	Fiber mass ratio
1	0.027	0.015	0.556
2	0.035	0.015	0.429
3	0.043	0.015	0.349
4	0.045	0.015	0.333
5	0.048	0.03	0.625
6	0.052	0.03	0.577
7	0.047	0.03	0.638
8	0.045	0.03	0.667
9	0.061	0.045	0.738
10	0.064	0.045	0.703
11	0.065	0.045	0.692
12	0.067	0.045	0.672
13	0.04	0.015	0.375
14	0.042	0.015	0.357
15	0.039	0.015	0.385
16	0.046	0.015	0.326
17	0.048	0.03	0.625
18	0.052	0.03	0.577
19	0.054	0.03	0.556
20	0.051	0.03	0.588
21	0.062	0.045	0.726
22	0.064	0.045	0.703
23	0.065	0.045	0.692
24	0.064	0.045	0.703
25	0.067	0.015	0.224
26	0.062	0.015	0.242
27	0.051	0.015	0.294
28	0.043	0.015	0.349
29	0.075	0.03	0.400
30	0.067	0.03	0.448
31	0.065	0.03	0.462
32	0.059	0.03	0.508
33	0.083	0.045	0.542
34	0.08	0.045	0.563
35	0.075	0.045	0.600
36	0.075	0.045	0.600
37	0.038	0.015	0.395
38	0.058	0.015	0.259
39	0.049	0.015	0.306
40	0.059	0.015	0.254
41	0.071	0.03	0.423
42	0.063	0.03	0.476
43	0.063	0.03	0.476
44	0.075	0.03	0.400
45	0.08	0.045	0.563

46	0.08	0.045	0.563
47	0.077	0.045	0.584
48	0.077	0.045	0.584

After the curing and printing parameters are determined, it is an important issue to obtain a well-ordered block. By creating the material here, whether the internal structure is homogeneous or not will be determined by SEM images. At this stage, many attempts have been made to properly stack. Here, examples of faulty products are given in Figure 3.2.

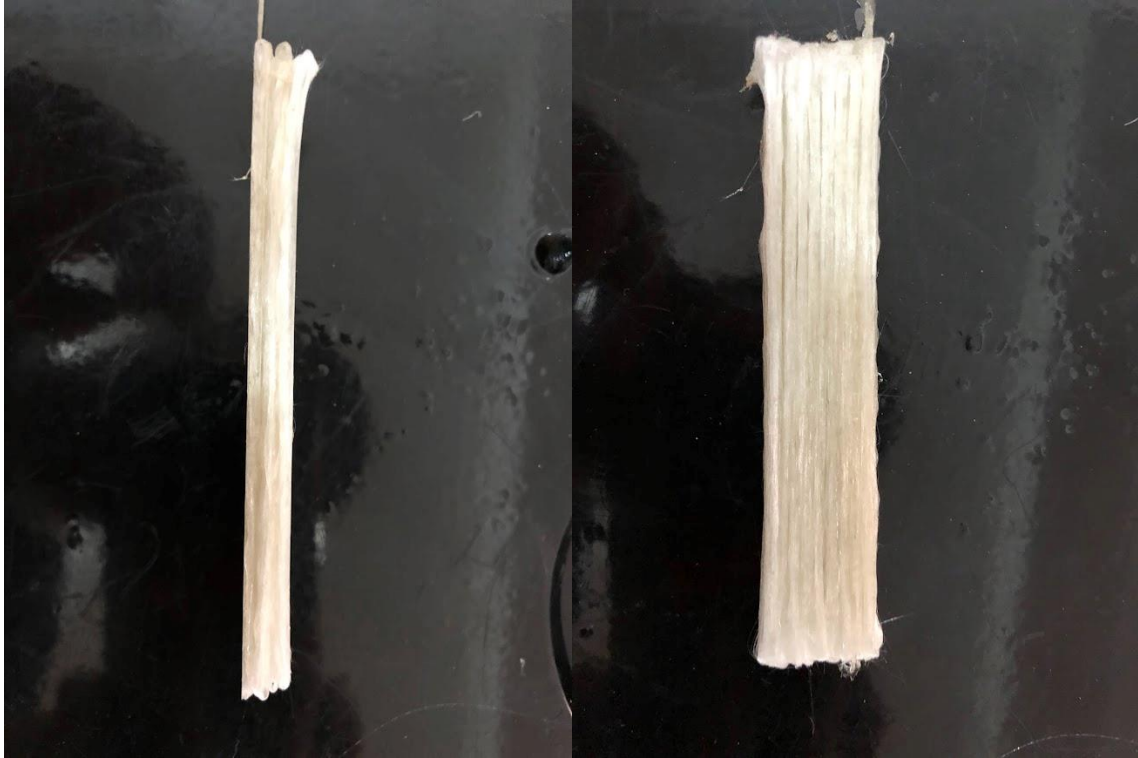


Figure 3.2 Errors during composite stacking with RAM.

In addition, resin flow becomes uncontrolled at fiber density less than 40% and curing and adhesion failures occur when fiber density is higher than 65%. An example production picture with uncontrolled flow as an example of this error is given in Figure 3.3.



Figure 3.3 Production with lower fiber density which creates uncontrolled resin flow in RAM process.

In Figure 3.4, cross-sectional SEM microscope images were taken of the L-shaped samples for which we calculated the fiber mass ratio, with a nozzle diameter of 0.8 and variable TEX values. As can be seen from here, the resin can penetrate properly between the fiber fibers and the selected light can fully cure up to the center.

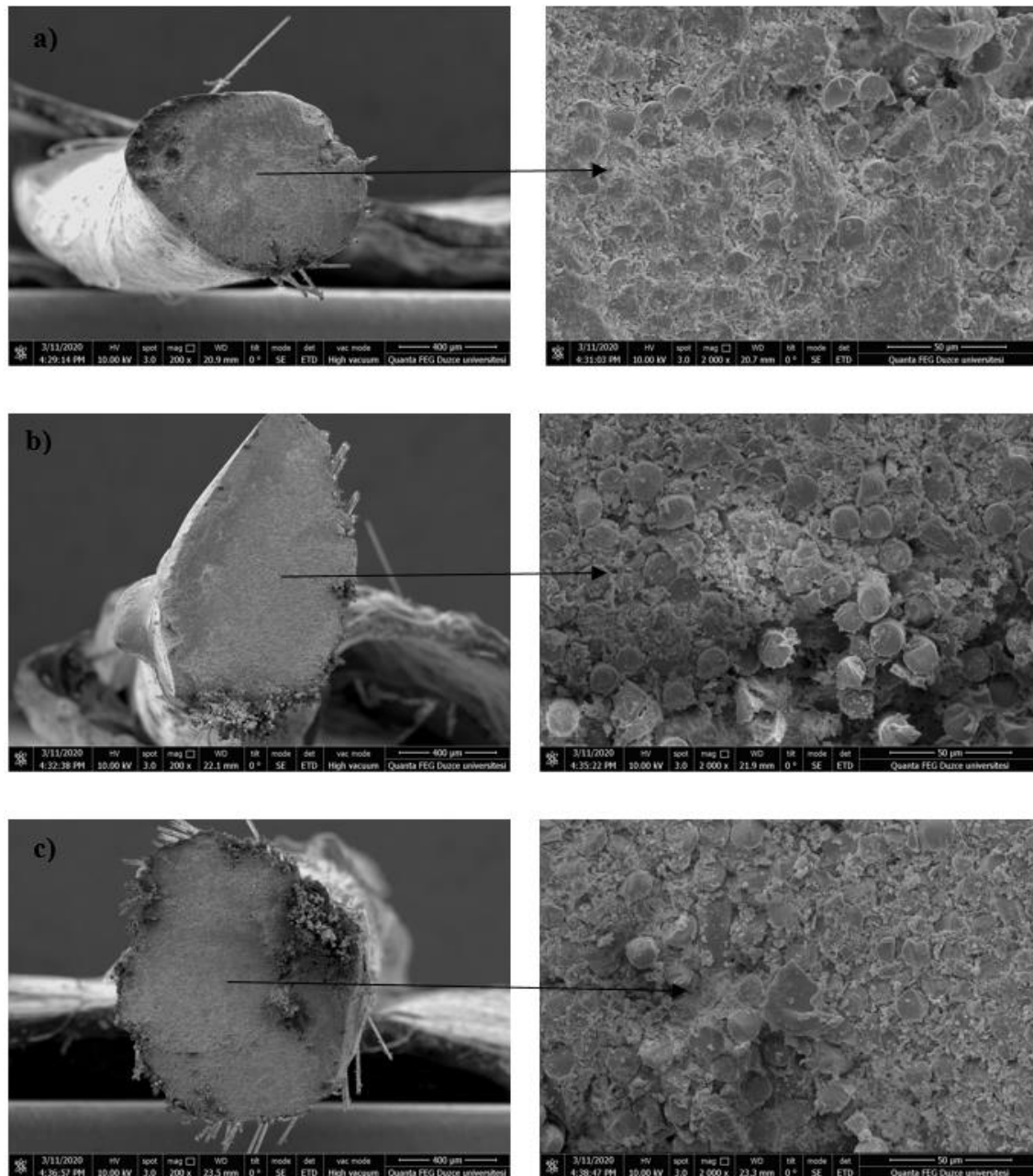


Figure 3.4 SEM images of printed vertical lines. a) 0.8 mm nozzle diameter and 300 tex fiber density, b) 0.8 mm nozzle diameter and 600 tex fiber density, c) 0.8 mm nozzle diameter and 900 tex fiber density.

In Figure 3.5, cross-sectional SEM microscope images were taken of the L-shaped samples for which we calculated the fiber mass ratio, with a nozzle diameter of 1.0 and variable TEX values. As can be seen from here, the resin can penetrate properly between the fiber fibers and the selected light can fully cure up to the center.

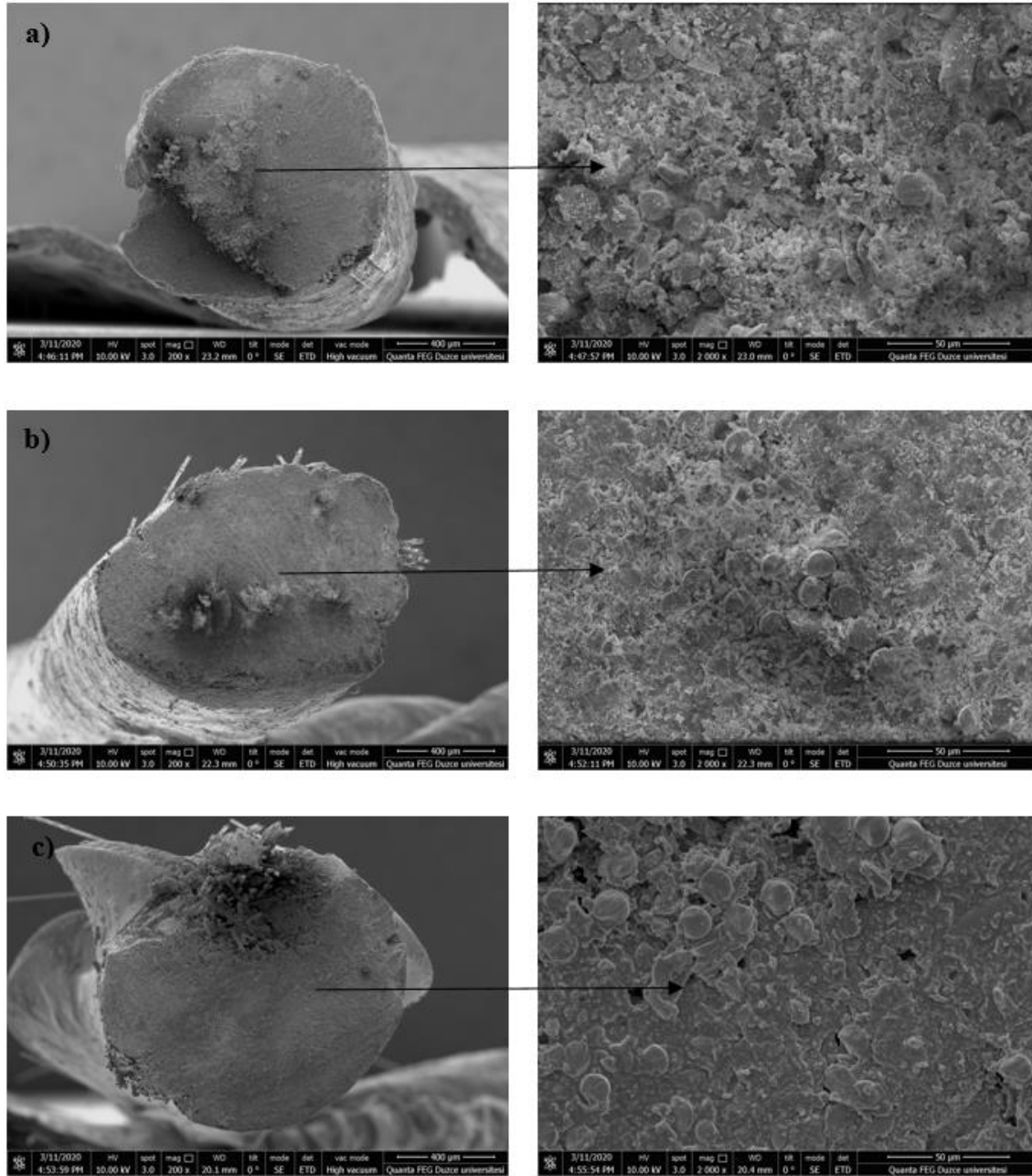


Figure 3.5 SEM images of printed vertical lines. a) 1.0 mm nozzle diameter and 300 tex fiber density, b) 1.0 mm nozzle diameter and 600 tex fiber density, c) 1.0 mm nozzle diameter and 900 tex fiber density.

In Figure 3.6, cross-section SEM microscope images were taken from the rectangular samples produced with a nozzle diameter of 0.8 and variable TEX values to examine with the stacking pattern. As can be seen here, there are gaps between the fiber fibers at 300 and 600 TEX values. However, in 900 TEX production, the fiber ratio is too high and the resin penetration decreases. Dry fibers are available at 900 TEX.

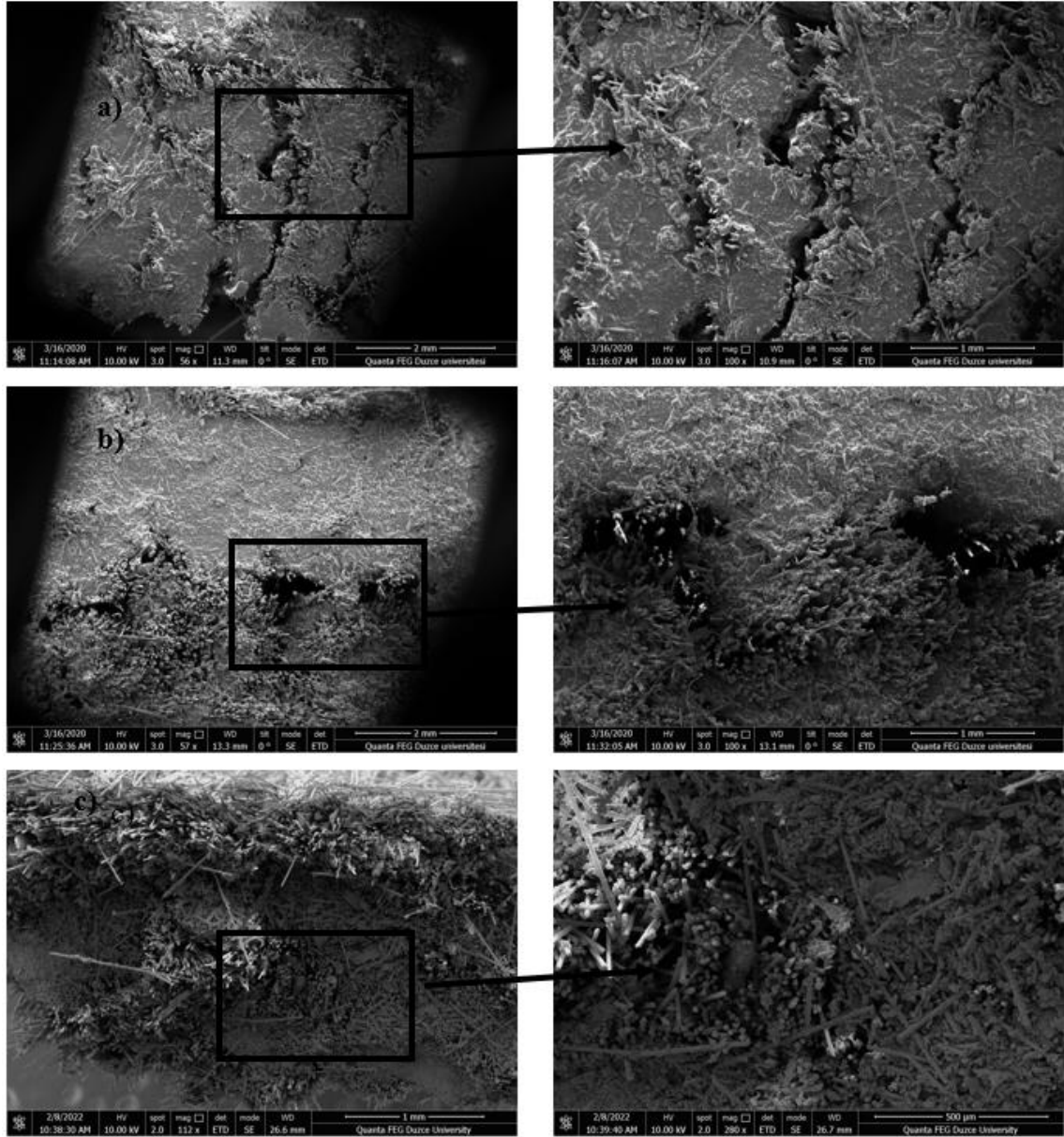


Figure 3.6 Intersection SEM images of rectangular product. a) 0.8 mm nozzle diameter and 300 tex fiber density, b) 0.8 mm nozzle diameter and 600 tex fiber density, c) 0.8 mm nozzle diameter and 900 tex fiber density.

In Figure 3.7, cross-section SEM microscope images were taken from the rectangular samples produced with a nozzle diameter of 1.0 and variable TEX values to examine with the stacking pattern. As can be seen here, gaps of 300 TEX are formed between the fiber fibers. However, in 600 TEX production, the fiber and resin ratio creates a homogeneous internal structure. In 900 TEX fiber density, although there are small gaps between the lines, fiber distribution, resin penetration and curing are ideal.

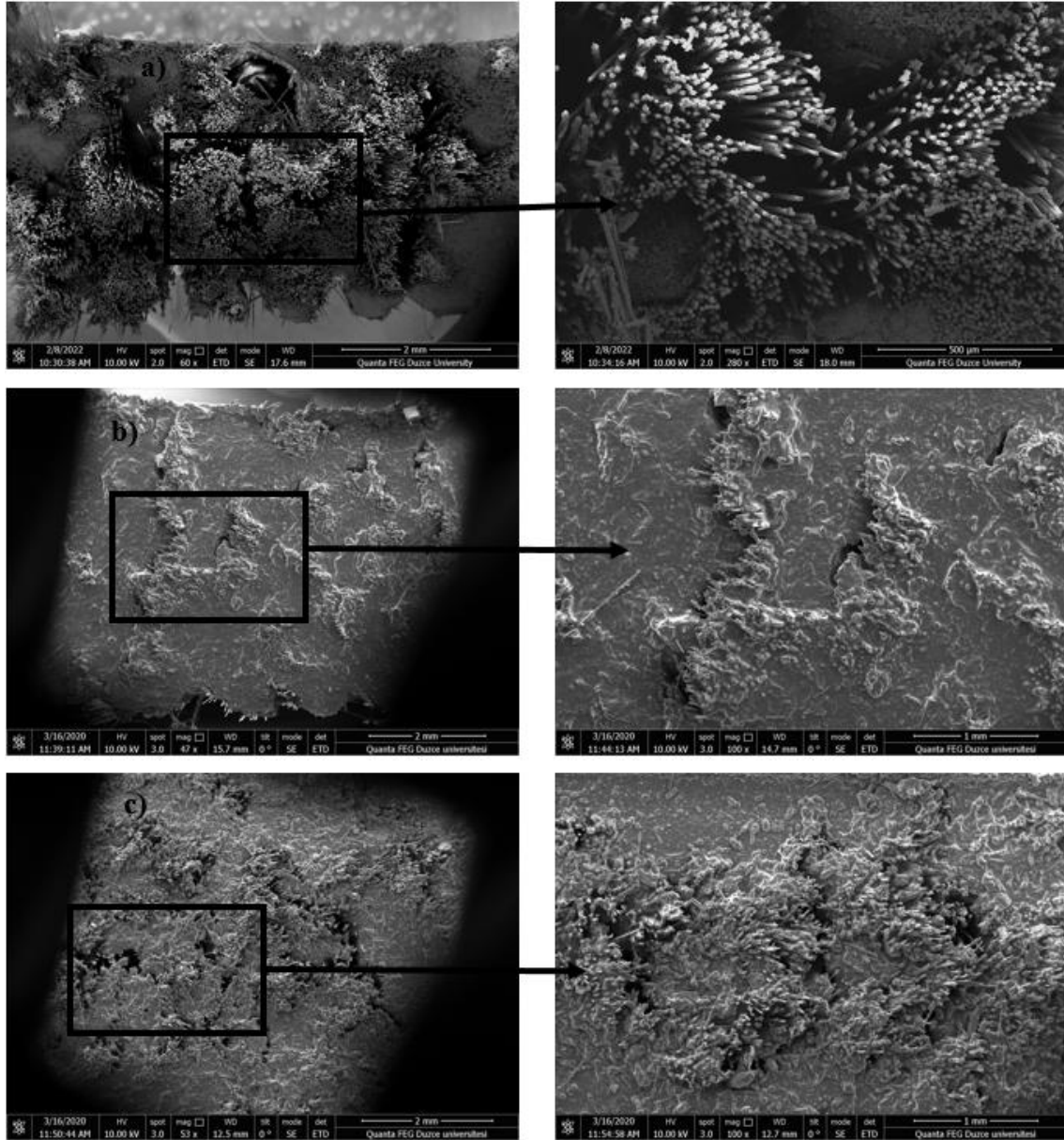


Figure 3.7 Intersection SEM images of rectangular product. a) 1.0 mm nozzle diameter and 300 tex fiber density, b) 1.0 mm nozzle diameter and 600 tex fiber density, c) 1.0 mm nozzle diameter and 900 tex fiber density.

We can state the most suitable parameters for composite production with RAM, based on all the tests and trials we have done, as follows; Layer thickness between 0.4 and 0.8 mm provided that the fiber density is between 45% (1.0 mm nozzle diameter and 600 TEX fiber), 55% (0.8 mm nozzle diameter and 600 TEX fiber) and 65% (1.0 mm nozzle diameter and 900 TEX fiber) and 30 mm/s printing speed, line thickness between 1.0 mm and 2.0 mm can be preferred. When production is made with these parameters, the dimensional accuracy are 0.1 mm sensitive and there is no change in shape or size depending on time after

production. In Figure 3.8, there is a plate produced with the suggested parameters.



Figure 3.8 Sample products with effective parameters by the RAM method.

3.2. Test results of mechanical properties

The most basic mechanical properties are shown as tensile strength, flexural strength and impact strength obtained according to the test results given in Table 3.3, Table 3.4. As can be seen from these tables, fiber orientation is the most influential parameter on mechanical properties. However, fiber density has a directly proportional effect on mechanical properties. It has been observed that there is a slight decrease in mechanical properties as the 3D printing speed increases. It is thought that the reason for this decrease is that although the nozzle diameter is same at every printing speed and resin flow is by gravity feed, so when the printing speed is increased, the flowing resin decreases and the adhesion ability between the layers decreases.

Table 3.3 Tensile test results.

Experiment No	Fiber density (%)	Printing speed (mm/s)	Fiber orientation (°)	Average Tensile Strength (MPa)	Average Percentage Elongation at Break (%)
1	45	10	0	249.19	6.57
2	45	20	0	177.05	5.23
3	45	30	0	189.29	4.38
4	45	10	0/90	113.15	4.37
5	45	20	0/90	117.99	4.37
6	45	30	0/90	130.58	5.61
7	45	10	±45	109.58	5.36
8	45	20	±45	113.97	5.36
9	45	30	±45	110.43	5.36
10	55	10	0	265.65	6.15
11	55	20	0	188.75	4.89
12	55	30	0	201.79	5.36
13	55	10	0/90	120.62	4.27
14	55	20	0/90	125.79	4.68
15	55	30	0/90	139.20	3.88
16	55	10	±45	116.86	5.36
17	55	20	±45	121.51	5.36
18	55	30	±45	117.72	5.36
19	65	10	0	305.54	5.68
20	65	20	0	317.09	4.55
21	65	30	0	323.58	4.50
22	65	10	0/90	127.85	4.55
23	65	20	0/90	133.33	3.60
24	65	30	0/90	147.55	4.37
25	65	10	±45	123.87	4.55
26	65	20	±45	128.79	4.51
27	65	30	±45	124.76	3.94

As a result, 0° fiber orientation and 65% fiber density give the best mechanical properties (approximately 300 MPa tensile strength and 450 MPa bending strength) for the robotic continuous fiber reinforced composite 3D printing method. The mechanical properties of the products obtained by using this method provide the properties that will replace them structurally where iron-based materials are used. 10 mm/s 3D printing speed has a more positive effect on curing efficiency and dimensional accuracy. There is no significant difference in mechanical properties between 0°/90° and ±45° fiber orientations. However, in the tests, the mechanical properties were obtained only in one and vertical axis. Studies examining the effects of fiber orientation on composite fabrication in the literature have reported that the effect on mechanical properties is maximum when fiber direction and stress

directions are in the same direction [261, 262]. In Figure 3.9, the effects of average tensile test data on fiber density versus other parameters are given graphically.

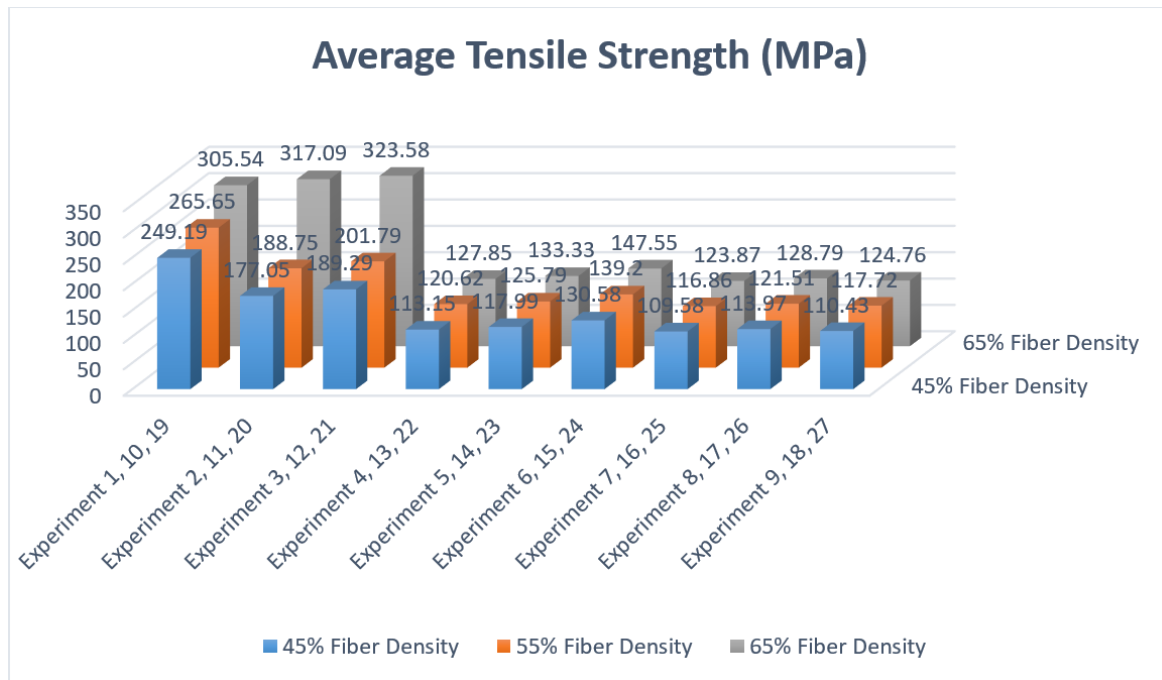


Figure 3.9 Comparison of average tensile strength according to fiber densities.

When Figure 3.9, Figure 3.10 and Figure 3.11 are examined, the effect of fiber orientation and fiber density on mechanical properties according to test numbers is shown graphically. Tensile, bending and impact strength values show similar properties proportionally. Experiments 1 to 9 represent 45% fiber density, experiments 10 to 18 represent 55% fiber density, and experiments 19 to 27 represent 65% fiber density, each starting from test number 1 displays the fiber orientation as 0° , $0^\circ/90^\circ$, and $\pm 45^\circ$ respectively, the fiber orientation repeats continuously. 3D printing speeds of 10, 20 and 30 mm/s were expressed for the three fiber orientations, respectively, at the same speed in the three experiments. As can be seen from these graphs, between $0^\circ/90^\circ$ fiber orientation and $\pm 45^\circ$ fiber orientation, the $0^\circ/90^\circ$ fiber orientation shows slightly more durability, with a difference of about 10% in terms of mechanical properties. However, as the fiber orientation increases from $\pm 45^\circ$ to 0° , it is seen that the strength values increase rapidly and the highest strength values are obtained at 0° fiber orientation.

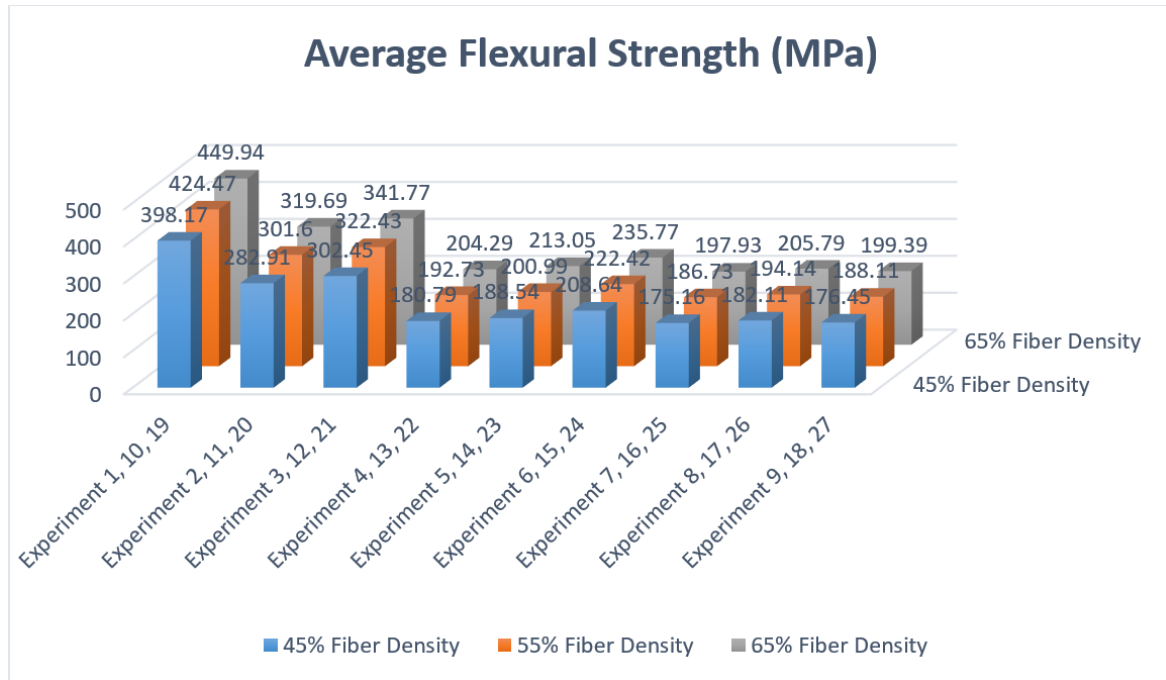


Figure 3.10 Comparison of average flexural strength according to fiber densities,

Table 3.4 Flexural and Izod impact tests results.

Experiment No	Fiber denstiy (%)	Printing speed (mm/s)	Fiber orientation (°)	Average Flexural Strength (MPa)	Average Izod Impact Values (kJ/m ²)
1	45	10	0	398.17	142.28
2	45	20	0	282.91	129.51
3	45	30	0	302.45	138.46
4	45	10	0/90	180.79	82.76
5	45	20	0/90	188.54	86.31
6	45	30	0/90	208.64	95.51
7	45	10	±45	175.16	80.19
8	45	20	±45	182.11	83.37
9	45	30	±45	176.45	80.78
10	55	10	0	424.47	143.21
11	55	20	0	301.60	137.28
12	55	30	0	322.43	146.77
13	55	10	0/90	192.73	87.73
14	55	20	0/90	200.99	91.49
15	55	30	0/90	222.42	101.24
16	55	10	±45	186.73	84.96
17	55	20	±45	194.14	88.37
18	55	30	±45	188.11	85.62
19	65	10	0	449.94	144.65
20	65	20	0	319.69	131.20
21	65	30	0	341.77	140.26
22	65	10	0/90	204.29	83.84

23	65	20	0/90	213.05	87.43
24	65	30	0/90	235.77	96.76
25	65	10	±45	197.93	81.23
26	65	20	±45	205.79	84.45
27	65	30	±45	199.39	81.83

With the continuous fiber support to the pure resin material, the tensile strength and izod impact strength values increased more than 5 times. In addition, the greatest improvement in mechanical properties has been in flexural strength values, with the addition of continuous fiber added to the pure resin material. If thermoplastic matrix is preferred in glass fiber reinforced composite production, the tensile strength cannot exceed 80 MPa. In addition, the flexural strength is limited to values at 150 MPa. All other mechanical properties are of similar characteristic. This is because the bond structure of thermoplastic materials and the compatibility of fiber and matrix material are much weaker than thermoset resin matrices [262 - 265]. In Figure 3.11, the comparison of average izod impact strength values according to fiber densities is given graphically. Similar to other mechanical properties, they vary according to 3D printing parameters.

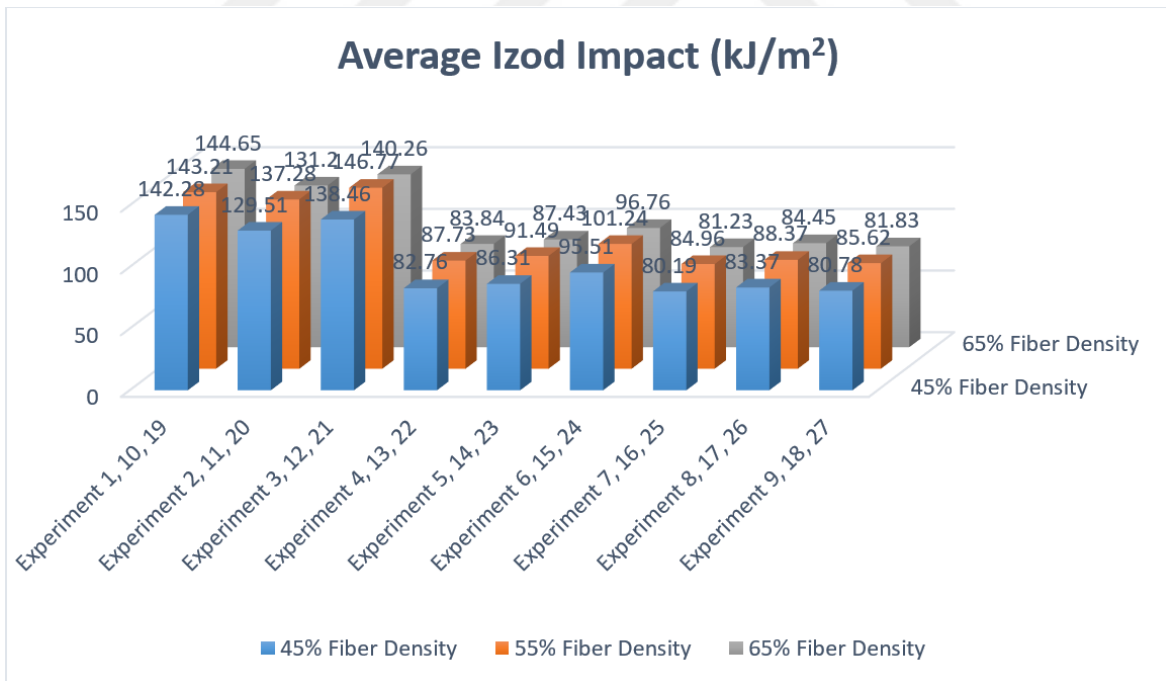


Figure 3.11 Comparison of average izod impact values according to fiber densities.

Shore D hardness test results are given in Table 3.5. Although hardness is a mechanical property, it varied independently of other strength properties. In fact, it has not changed only as a property of the plastic material. In all production parameters and fiber densities, values

close to the hardness values of the matrix material were observed. According to the result, the hardness values in composite materials can be mostly associated with the hardness of the matrix material.

Table 3.5 Shore D hardness test results.

Experiment No	Fiber density (%)	Printing speed (mm/s)	Fiber orientation (°)	Average Shore D hardness
1	45	10	0	84
2	45	20	0	81
3	45	30	0	87
4	45	10	0/90	79
5	45	20	0/90	82
6	45	30	0/90	86
7	45	10	±45	84
8	45	20	±45	81
9	45	30	±45	85
10	55	10	0	82
11	55	20	0	87
12	55	30	0	86
13	55	10	0/90	82
14	55	20	0/90	83
15	55	30	0/90	78
16	55	10	±45	80
17	55	20	±45	83
18	55	30	±45	80
19	65	10	0	82
20	65	20	0	84
21	65	30	0	85
22	65	10	0/90	88
23	65	20	0/90	84
24	65	30	0/90	82
25	65	10	±45	87
26	65	20	±45	83
27	65	30	±45	84

3.3. Internal pressure test results of 90° composite elbow.

As the last and most important experimental part of the study, the strength limits of composite elbows produced by RAM method under internal pressure with variable parameters such as different fiber winding angles, different filling rates and different fiber densities were investigated. Here, the most important factor in choosing the internal pressure strength test is that the geometry of the elbows is the most suitable test for axial testing, the internal compressive strength. In addition, elbows are exposed to internal pressure in many

areas where they are used in industry. Here, all the parameters selected for the manufacture of elbows are the ones that have the most influence on the mechanical properties. In Table 3.6, the pressure values that cause damage for each test as a result of the internal pressure test and the axial and circumferential stress values are calculated according to these pressures as specified in Equations 2.40 and 2.41.

Table 3.6 Internal pressure test results of 90° composite elbow.

Experiment No	Winding angle (revolution)	Fiber density (%)	Filling rate (%)	Average internal pressure (bar)	Average Circumferential stresses (MPa)	Average Axial Stresses (MPa)
1	0	45	50	66	116.42	58.21
2	0	45	75	76	134.06	67.03
3	0	45	100	89	156.99	78.49
4	0	55	50	76	134.06	67.03
5	0	55	75	88	155.22	77.61
6	0	55	100	97	171.10	85.55
7	0	65	50	84	148.17	74.08
8	0	65	75	98	172.86	86.43
9	0	65	100	107	188.74	94.37
10	0.125	45	50	52	91.72	45.86
11	0.125	45	75	63	111.13	55.56
12	0.125	45	100	76	134.06	67.03
13	0.125	55	50	64	112.89	56.44
14	0.125	55	75	75	132.29	66.15
15	0.125	55	100	81	142.88	71.44
16	0.125	65	50	72	127.00	63.50
17	0.125	65	75	84	148.17	74.08
18	0.125	65	100	93	164.04	82.02

When Table 3.6 and Figure 3.12 are examined, as the fiber density increases, the internal pressure strength increases proportionally. Likewise, as the filling rate increases, the internal pressure resistance values increase. If the relationship between fiber winding and internal pressure resistance is examined, the resistance is highest in zero turn winding, that is, in the outer winding perpendicular to the inner layer, compared to the internal pressure. In the literature, similar results are obtained in the manufacture of composite elbows made with other methods. As the winding turn or angle approaches zero, the strength values increase. When the winding turn is zero, it is maximum. The main point here is that it is not possible to get exactly zero in this angle mold winding method, since the mold must be connected to an axis. Therefore, it is stated in the literature that the strength increases as the winding angle approaches zero [266 - 273].

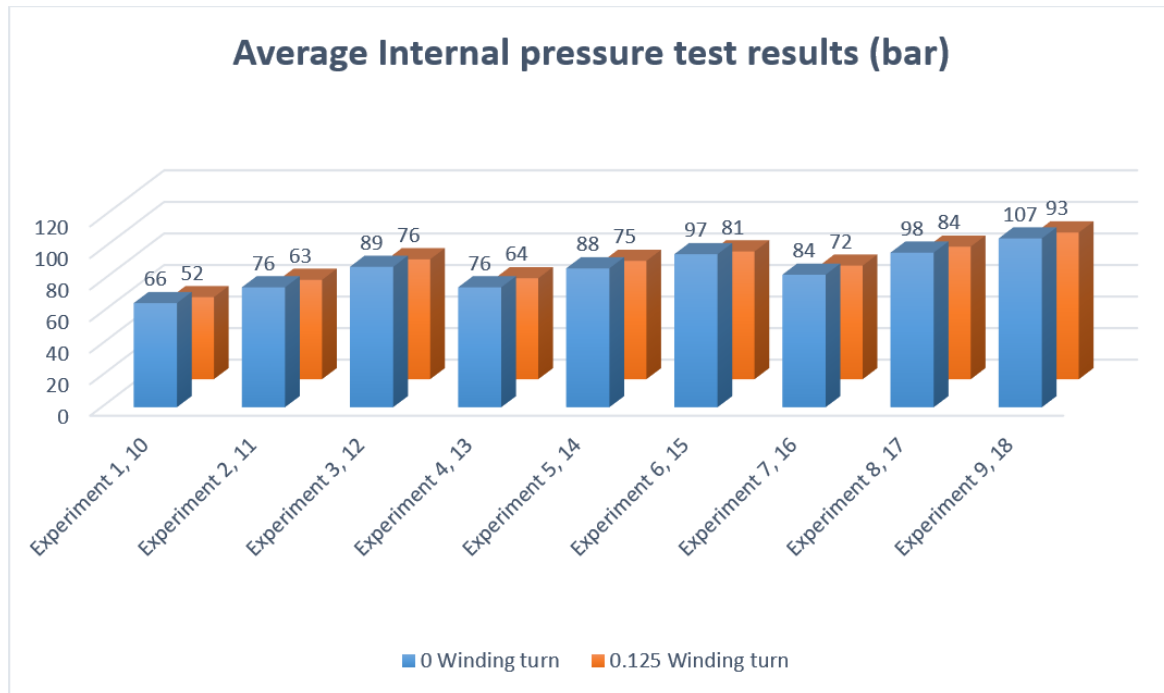


Figure 3.12 Comparison of average internal pressure test results according to fiber winding turn.

It can be understood from the damage area that the stress form of the damage is axial or circumferential. Therefore, the image of the elbow after internal pressure test is given in Figure 3.13. Elbows manufactured to all parameters were similarly damaged. It is evident that the stress that creates this damage is caused by axial stress relative to the rupture section. Although the circumferential stress in the fiber direction created a higher stress, it caused damage to the elbow since the bond of the matrix material between the layers was weaker in the axial tension without causing damage. Glass reinforced plastic pipes are classified in 5 (five) nominal pressure (PN) groups as standard: PN 4 bar; PN 6 bars; PN 10 bar; PN 16 bar; PN 25 bars. However, in accordance with the standards, it is produced to withstand internal pressure up to 35 bar as the pressure class to be forced at the maximum [260]. As a result of the experiments, the minimum pressure value of 35 bar, which is required to be provided in accordance with pressure classes and production standards, was obtained in Experiment 10, which has the lowest internal pressure resistance of 52 bar.

However, considering the pressure value at which the damage occurred, 100 bar pressure is more than sufficient strength in many areas of the industry and it does not exceed these strength values in composite elbows produced with other production methods. For this reason, composite elbows produced by RAM method can be preferred in the industry for products that will operate under functional pressure such as composite elbows and similar

products.



Figure 3.13 Image of the elbow after internal pressure test.

4. CONCLUSIONS

As a result, the printing parameters of the continuous fiber reinforced photopolymer matrix RAM method and the effective printing process were introduced and the mechanical properties of the production with this method were examined. With the RAM method, six axes toolpath can be used. Thus, an approach to the slicing constraint on one axis in traditional AM has been attempted. As an additional application to the materials used in the AM method, a different approach has been examined as a hybrid approach of SLA and FDM methods. In addition, solutions can be provided to mold production and human control requirements of composite production methods. As a result, the process parameters and mechanical behaviors of the RAM method of continuous glass fiber reinforced thermoset matrix composite materials were examined and effective process parameters were introduced.

In addition, angular slicing was made for the 90 degree elbow test sample, which is one of the most difficult composite products to manufacture, and six axes toolpath generation processes were applied. Production was carried out by making fiber winding in different ways and production was carried out without a mould rather than traditional methods.

The main results of the study can be listed as follows;

- Fiberglass and photopolymer material can form a composite structure in harmony.
- 3W UV LED can easily provide enough energy for the curing process.
- Considering the curing time of the photopolymer matrix material resin, a production

speed of up to 30 mm/s can be achieved. When the production speed exceeds 30 mm/s, errors occur in production.

- It can be said that the number of UV LEDs has little effect on fiber density, but lighting from four different directions makes curing effective for production to ensure that the material can be cured in any toolpath movement during printing.
- Fiber mass ratio can be up to 75%, but when it exceeds 50%, internal voids may occur. 65% fiber mass ratio can be preferred for effective production and high mechanical properties. On the other hand, when less than 40% fiber mass ratio is preferred, the resin flow begins to become uncontrolled.
- It can be said that the most effective parameter on mechanical behavior is fiber orientation and the parameter that has the least effect is the printing speed parameter if sufficient curing is provided.
- Fiber density is effective on mechanical properties and provides a high change on mechanical properties up to 45% fiber density, but varies proportionally between 45% and 65% fiber density. If it is above 65% fiber density, it is likely that the fibers will remain dry at the level of manufacturing defects.
- Mechanical properties increase to maximum values in the direction of fiber orientation. It can be said that the best mechanical properties are provided when the fiber direction and the stress direction are the same in the composite material. 6-axis toolpath derivation processes can provide advantages in many areas in order to bring these forcing directions and fiber directions in the same direction in the production of the designed parts.
- Approximately 300 MPa tensile strength and 450 MPa flexural strength can be obtained in composites produced by RAM method. These mechanical properties indicate that this production can be preferred instead of ferrous materials in many areas structurally. Unlike other fiber winding methods, 90 degree composite elbows were produced without the use of molds.
- In other fiber winding methods, external fiber winding was carried out at 0 degrees perpendicular, which cannot be applied due to the mold connection.
- A helical filling structure, which is not commercially available in any software and slicing program, has been applied to wrap the elbow in the desired winding round.

An internal cavity structure in the form of filling rate has been applied to this applied helical winding shape.

- The minimum pressure value of 35 bar, which is required to be provided in accordance with pressure classes and production standards, was obtained all of experiments. 100 bar internal pressure strength value can be obtained and can be preferred industrially in many areas. It is suitable to be preferred especially in areas that will work under corrosion and in aviation and space sectors where lightness is desired. It can provide a mobilized solution in the repair works of composite pipes and transport systems in the field.
- Different fiber supports can be adapted. It is possible to reach higher strength values by diversifying and improving the materials used.
- Different filling structures can also be developed and applied rather than helical winding filling structure.

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Publications

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International Book Chapter on The Thesis

EKİCİ, B, İPEKÇİ, A., “Polimer Kompozit Üretimi: Geleneksel ve Modern Yöntemlerin Karşılaştırılması”, *Mühendislik Bilimlerinde Akademik Çalışmalar-2019/2*. Dr. Öğr. Üyesi Ali KILIÇER, Dr. Öğr. Üyesi Tuncay YILMAZ (Editörler), (s. 189-206). Cetinje: Ivpe, 2019.

