# USABILITY OF POLYLACTIDE BIOPOLYMER AS THERMOPLASTIC MATRIX FOR WOVEN FIBER COMPOSITE LAMINATES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GÖKBERK DEMİROK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

APRIL 2022

Approval of the thesis:

**USABILITY OF POLYLACTIDE BIOPOLYMER AS THERMOPASTIC MATRIX FOR WOVEN FIBER COMPOSITE LAMINATES**

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## ABSTRACT

### USABIILITY OF POLYLACTIDE BIOPOLYMER AS THERMOPLASTIC MATRIX FOR WOVEN FIBER COMPOSITE LAMINATES

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April 2022, 80 pages

The first purpose of this study was, as the first time in the literature, to investigate usability of polylactide (PLA) biopolymer as the matrix of high-performance composite laminated structures having woven forms of glass and carbon fibers. For this purpose, 2-14 layers of 2x2 twill Carbon Fiber (CF) and 1x1 plain weave Glass Fiber (GF) forms were stacked by PLA powders followed by consolidation of these layers by compression molding technique. After conducting various tests and analysis it was observed that significant improvements in the mechanical and thermal properties could be obtained by laminating PLA with woven CF and GF layers.

Another purpose of this study was to compare mechanical performance of the PLA matrix laminates with Epoxy matrix laminates having exactly the same type and number of GF and CF layers. It was revealed that mechanical properties of the PLA/CF laminates were approaching to the values of the Epoxy/CF laminates, while due to poor adhesin between the PLA matrix and Glass Fiber surfaces, the properties were lower in the PLA/GF laminates.

Therefore, it could be generally concluded that, in terms of mechanical performance; traditional thermoset Epoxy matrix could be replaced with the renewable biopolymer PLA matrix in the Woven Carbon Fiber laminates. For the Woven Glass Fiber laminates, a proper sizing treatment with a PLA compatible silane coupling agent would be necessary.

Keywords: Polylactide, Biopolymer, Woven Carbon Fibers, Woven Glass Fibers, Composite Laminates

# ÖZ

## POLİLAKTİT BİYOPOLİMERİN TERMOPLASTİK MATRİS OLARAK DOKUMA ELYAFLI KOMPOZİT LAMİNATLARDA KULLANILABİLİRLİĞİ

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Bu çalışmanın ilk amacı, literatürde ilk kez, cam ve karbon elyafların dokuma formlarını içeren yüksek performanslı kompozit lamine yapıların matrisi olarak polilaktit (PLA) biyopolimerinin kullanılabilirliğini araştırmaktır. Bu amaç için 2-14 arası katmana sahip 2x2 twill karbon elyaf (CF) ve 1x1 düz dokuma cam elyaf (GF) formları arasına PLA tozları yerleştirilmiş ve bu tabakalar sıkıştırmalı kalıplama tekniği ile konsolidasyona tabi tutulmuştur. Çeşitli testler ve analizler yapıldıktan sonra, PLA'nın dokuma CF ve GF katmanları ile lamine edilmesiyle mekanik ve termal özelliklerde önemli gelişmeler elde edilebileceği gözlemlendi.

Bu çalışmanın bir diğer amacı, PLA matrisli laminatların mekanik performansını, tamamen aynı tip ve sayıda GF ve CF katmanlarına sahip Epoksi matrisli laminatlar ile karşılaştırmaktır. PLA/CF laminatların mekanik özelliklerinin Epoksi/CF laminatların değerlerine yaklaştığı, PLA matrisi ile Cam Elyaf yüzeyler arasındaki zayıf yapışma nedeniyle PLA/GF laminatlarda ise özelliklerin daha düşük olduğu ortaya çıktı.

Bu nedenle, genel olarak, mekanik performans açısından; geleneksel termoset Epoksi matrisi, Dokuma Karbon Elyaf laminatlarda yenilenebilir biyopolimer PLA matrisi ile değiştirilebilir. Dokuma Cam Elyaf laminatlar için ise, PLA uyumlu bir birleştirme ajanı ile silanlama işlemi gerekli olacaktır.

**Anahtar Kelimeler:** Polilaktit, Biyopolimer, Dokuma Karbon Elyaf, Dokuma Cam Elyaf Kompozit Laminatlar

*In the memory of my father, Hasan Sadi Demirok*

## ACKNOWLEDGMENTS

First of all, I would like to give my thanks to my supervisor Prof. Dr. Cevdet Kaynak for his guidance, support, criticism and also for his patience and understanding throughout this study.

I would like to thank to the examining committee members; Prof. Dr. Rıza Gürbüz, Prof. Dr. Necati Özkan, Prof. Dr. Bora Maviş and Assist. Prof. Dr. Ayşe Çağıl Kandemir for their valuable remarks and suggestions.

I would like to give my gratitude to technical staff and board of the Middle East Technical University, Metallurgical and Materials Engineering department for providing research facilities and laboratories used in this study. I am also grateful to Dr. Süha Tirkeş for providing the mold material and its machining. I also appreciate METU Central Laboratory for conducting thermal analyses used in the study.

I would like to thank my laboratory mate Burcu Sarı for conducting SEM analyses and her aid in using laboratory equipment together with her friendship and support.

I also want to give thanks to my friends: Oğuz Gözcü, Münevver Güllü Eryılmaz, Ender Eryılmaz, Umutcan Önel, Elif Kaldırım and Hüseyin Can Çamiçi for their friendship and support.

I am indebted to my father, Dr. Hasan Sadi Demirok, who passed away during this study and my mother Meryem Nesrin Demirok for their limitless love, support and patience, also my brother Görkem Demirok for his never-ending friendship and guidance.

Last and most, I am exceptionally thankful to Neris Taymaz, who has always shared my stress, given her support and kept me standing during this long period. I will always be grateful for her unlimited support and patience.

## TABLE OF CONTENTS

ABSTRACT ..... v

ÖZ ..... vii

ACKNOWLEDGMENTS ..... x

TABLE OF CONTENTS ..... xi

LIST OF TABLES ..... xiv

TABLES ..... xiv

LIST OF FIGURES ..... xv

FIGURES ..... xv

NOMENCLATURE ..... xviii

**CHAPTERS**

1 INTRODUCTION ..... 1

1.1 Carbon and Glass Fibers ..... 1

1.2 Woven Forms of Carbon and Glass Fibers ..... 3

1.3 Polymer Matrices Used for Composite Laminates ..... 5

1.4 Polylactide ..... 7

1.5 Literature Overview on Fiber Reinforced PLA Composites ..... 11

1.6 Literature Survey on PLA Composite Laminates with Woven Forms of Natural Fibers ..... 12

1.7 The Aim of This Thesis ..... 13

2 EXPERIMENTAL WORK ..... 15

2.1 PLA Matrix Material Used ..... 16
2.2 Grinding of PLA Granules into Powders ..... 16
2.3 Woven Forms of the Carbon and Glass Fibers Used ..... 18
2.4 Cutting of Woven Fiber Forms ..... 19
2.5 The Mold Used During Production of Composite Laminates ..... 20
2.6 Stacking of PLA Powders in Between the Woven Fiber Forms ..... 21
2.7 Consolidation of Layers by Compression Molding ..... 23
2.8 Cutting of Test Specimens from Composite Laminate Plates ..... 25
2.9 Fiber Weight Percent Determination ..... 26
2.10 Interlaminar Shear Strength (ILSS) Tests ..... 26
2.11 Three-Point Bending Tests ..... 29
2.12 Scanning Electron Microscopy (SEM) ..... 30
2.13 Thermogravimetric Analysis (TGA) ..... 30
2.14 Differential Scanning Calorimetry (DSC) ..... 31
3 RESULTS AND DISCUSSIONS ..... 33
3.1 Fiber Content of the PLA Composite Laminates ..... 33
3.2 Interlaminar Adhesion in the PLA Composite Laminates ..... 34
3.2.1 Interlayer Performance by ILSS Tests ..... 35
3.2.2 Interlayer and Interfacial SEM Analysis ..... 37
3.2.3 Comparison of the Interlaminar Adhesion of PLA Laminates with Traditional Epoxy Laminates ..... 43
3.3 Mechanical Performance of the PLA Composite Laminates ..... 43
3.3.1 Flexural Properties via Three-Point Bending Tests ..... 43

3.3.2 Comparison of the Mechanical Performance of PLA Laminates with Epoxy Laminates ..... 48
3.3.3 Flexural Failure Modes by Visual Observation and SEM Analysis . 50
3.3.4 Fracture Surface Morphology by SEM Analysis ..... 56
3.4 Thermal Behavior of the PLA Composite Laminates ..... 61
3.4.1 Thermal Degradation Temperatures of PLA Matrix and Percent Residue of Fibers by TGA ..... 61
3.4.2 Thermal Transition Temperatures and Crystallinity Amount of PLA Matrix by DSC ..... 66
4 CONCLUSIONS ..... 73
REFERENCES ..... 75

## LIST OF TABLES

### TABLES

**Table 2.1.** Certain properties of the PLA matrix given in its TDS..... 16

**Table 3.1.** Fiber content of the specimens determined by matrix chemical decomposition method, and wt% residue values of certain specimens, determined by TGA for certain specimens comparison ..... 34

**Table 3.2.** Interlaminar Shear Strength (ILSS), Flexural Strength and Flexural Modulus of the composite laminates ..... 37

**Table 3.3.** Comparison of the Flexural Strength and Modulus values of the present study (PLA matrix) with our previous studies (Epoxy matrix) having the same type and number of GF and CF layers ..... 49

**Table 3.4.** Thermal Degradation Temperatures ($T_{5\%}$, $T_{10\%}$, $T_{25\%}$, $T_{max}$) and % Residue of the specimens..... 63

**Table 3.5.** Transition Temperatures ($T_g$, $T_c$, $T_m$), Enthalpies ($\Delta H_m$ and $\Delta H_c$) and %Crystallinity ($X_c$) of the specimens..... 69

## LIST OF FIGURES

### FIGURES

**Figure 1.1.** Woven fiber form styles [6]. ..... 5
**Figure 1.2.** Global bioplastic production over the years [9]. ..... 7
**Figure 1.3.** Chemical structure of polylactide mer [10]. ..... 8
**Figure 1.4.** Chemical structure of two lactic acids and their cyclic dimers [13] ..... 9
**Figure 1.5.** Various routes for high molecular weight PLA production [16]. ..... 10
**Figure 2.1.** General flowchart for the production of PLA composite laminates .... 15
**Figure 2.2.** PLA granules ..... 17
**Figure 2.3.** PLA powders after grinding ..... 17
**Figure 2.4.** Polymer grinding equipment ..... 18
**Figure 2.5.** Cutting of woven fiber forms ..... 19
**Figure 2.6.** Cut layers of woven carbon and woven glass fibers ..... 20
**Figure 2.7.** Pieces of the mold machined from a steel plate ..... 20
**Figure 2.8.** Vacuum oven ..... 21
**Figure 2.9.** An example of the stacking sequence for the laminate having 2 woven fiber layers ..... 22
**Figure 2.10.** An example of the empty mold frame, woven carbon fiber layer, and stacking of the layers with PLA powders ..... 22
**Figure 2.11.** Closer view of the laminate consolidation ..... 23
**Figure 2.12.** Hot press (left) and cold press (right) used for the consolidation by compression molding ..... 24
**Figure 2.13.** An example of the PLA/CF composite laminate plate produced ..... 24
**Figure 2.14.** Examples of the specimens after water jet cutting ..... 25
**Figure 2.15.** Instron 5565A testing machine ..... 27
**Figure 2.16.** An example view of the ILSS testing ..... 28
**Figure 2.17.** An example view of the three-point bending test ..... 29
**Figure 3.1.** Effects of increasing number of layers on the interlaminar shear strength of the composite laminates ..... 36

**Figure 3.2.** General (above) and closer (below) through thickness SEM images showing "interlaminar" adhesion between PLA/GF layers ..... 39
**Figure 3.3.** General (above) and closer (below) through thickness SEM images showing "interlaminar" adhesion between PLA/CF layers ..... 40
**Figure 3.4.** Closer view SEM images showing rather "lower" adhesion between PLA matrix and individual glass fiber surfaces ..... 41
**Figure 3.5.** Closer view SEM images showing rather "higher" adhesion between PLA matrix and individual carbon fiber surfaces ..... 42
**Figure 3.6.** Flexural stress-strain curves of the PLA/GF (above) and PLA/CF (below) composite laminates ..... 46
**Figure 3.7.** Effect of increasing number of layers on the flexural strength (above) and flexural modulus (below) of the composite laminates. ..... 47
**Figure 3.8.** Possible flexural failure modes of composite laminate specimens given in ISO 14125 standard [46] ..... 51
**Figure 3.9.** Photographic images showing general flexural failure modes of PLA/GF laminate specimens ..... 52
**Figure 3.10.** Photographic images showing general flexural failure modes of PLA/CF laminate specimens ..... 53
**Figure 3.11.** Through-thickness SEM images showing certain interlaminar shear failure in the PLA/GF laminate specimens ..... 54
**Figure 3.12.** Through-thickness SEM images showing certain interlaminar shear failure in the PLA/CF laminate specimens ..... 55
**Figure 3.13.** Fiber Bridging mechanism of Glass Fibers (above) and Carbon Fibers (below) over PLA matrix cracking ..... 57
**Figure 3.14.** Fiber Fracture mechanism of PLA/GF laminates (images with increasing magnification) ..... 58
Figure 3.15. Fiber Fracture mechanism of PLA/CF laminates (images with increasing magnification) ..... 59
**Figure 3.16.** Debonding and Fiber Pull-out mechanism of Glass Fibers (above) and Carbon Fibers (below) from the PLA matrix ..... 60

**Figure 3.17.** TGA curves of neat PLA and its GF (above) and CF (below) laminate specimens..... 65
**Figure 3.18.** First heating DSC thermograms of neat PLA and its GF and CF laminate specimens ..... 71

## NOMENCLATURE

| | | |
|---|---|---|
| $\Delta H_m$ | : | enthalpy of melting |
| $\Delta H_c$ | : | enthalpy of crystallization |
| $\Delta H^{\circ}_m$ | : | enthalpy of melting for 100% crystalline PLA |
| $T_{5\%}$ | : | thermal degradation temperature at 5% weight loss |
| $T_{10\%}$ | : | thermal degradation temperature at 10% weight loss |
| $T_{25\%}$ | : | thermal degradation temperature at 25% weight loss |
| $T_{max}$ | : | thermal degradation temperature at maximum weight loss |
| $X_C$ | : | percent crystallinity |
| $T_g$ | : | glass transition temperature |
| $T_c$ | : | cold crystallization temperature |
| $T_m$ | : | melting temperature |
| $w_{PLA}$ | : | PLA weight percentage |
| $w_{fiber}$ | : | fiber weight percentage |
| SEM | : | scanning electron microscopy |
| DSC | : | differential scanning calorimetry |
| TGA | : | thermogravimetric analysis |
| DMA | : | dynamic mechanical analysis |
| ILSS | : | interlaminar shear strength |

# CHAPTER 1

# INTRODUCTION

Composites, as structural materials, are in great demand in both aerospace and other structural applications, for their high specific strength and specific modulus. The word ‘specific’ indicates the ratio of property in question to density of the material [1]. Because of their high strength and low density, composites are convenient materials in terms of fuel efficiency in structural aerospace [2] and other transportation applications [3]. In the industry, a variety of structural composites containing high strength fiber reinforcements such as glass, carbon and aramid bound together by many polymer matrices are present. Through this combination of matrix and reinforcement, high performance composites are engineered with various properties. The reinforcing fibers carry the applied stress while the polymer matrix material holds them together and transfers these stresses to the fibers. A good interfacial strength between matrix and reinforcement is favored because as load is applied, it is transferred from matrix to reinforcement through the interfaces [4].

## 1.1 Carbon and Glass Fibers

For the polymer matrix composites, there are various types and forms of reinforcing fibers. Even though natural fibers such as hemp, flax, cotton, jute etc. are emerged as reinforcement materials for biopolymer matrices, their mechanical properties are usually not sufficient for high performance demanding engineering structures; therefore, traditional high-performance carbon, glass or aramid fibers are preferred in such applications. In this study, for the polylactide biopolymer matrix, woven forms of carbon and glass fibers are used.

*Carbon fibers* are mainly produced from three precursors: polyacrylonitrile (PAN), pitch and rayon. Production using these three precursors roughly follows the same route. First the precursor is spun and drawn into polymeric fibers through various spinning methods. Then, the fibers are heat treated under tension (to decrease the fiber diameter) for a more stabilized structure for high temperature heat treatment. After stabilization step, fibers are carbonized under inert atmosphere at elevated temperatures around 1000-2000 °C.

By adjusting the process parameters of these steps, mechanical and other properties of the carbon fibers can be tailored. For example, standard, intermediate and high modulus carbon fibers can be produced. Properties of produced carbon fiber differ according to the precursor used. In the following table, tensile mechanical properties of the three different types of a typical PAN based carbon fiber are given [5,6].

| **Carbon Fiber Classes** | **Tensile Strength (MPa)** | **Tensile Modulus (GPa)** | **Elongation at Break, %** |
|---|---|---|---|
| Standard Modulus | 3450 | 228 | 1.6 |
| Intermediate Modulus | 5380 | 276 | 2.1 |
| High Modulus | 3450 | 441 | 0.5 |

Normally carbon fibers are sized (coated) with a suitable silane coupling agent to protect these very sensitive fibers during handling and processing, and more importantly to provide a sufficient interfacial bond between the fiber surfaces and the polymer matrix.

*Glass fiber* is another widely used reinforcement material for polymer matrix composites. Its high specific strength and relatively low price makes it an attractive one for various structural applications.

Glass fiber, similar to conventional glass, is an amorphous structure of silica and other modification additives such as boron, limestone etc. [6]. Production of glass fibers starts with mixing and melting of these ingredients. The mixture usually melts at about 1200 °C; then, glass melt is flown through bushings (metal plates with several tiny holes) to form them into filaments. These filaments are then quenched by water or air forming glass fibers. Fiber diameter and type can be controlled by adjusting bushing diameter, temperature, melt viscosity and cooling rate [6].

Most widely used glass fiber types in composites are; E-glass, S-glass and C-glass fibers. In the following table, tensile mechanical properties of these glass fiber types are given [6,7]:

| Glass Fiber Type | *Tensile Strength (MPa)* | *Tensile Modulus (GPa)* | *Elongation at Break (%)* |
|---|---|---|---|
| E-glass | 2400 | 72 | 3.3 |
| S-glass | 4600 | 88 | 5.2 |
| C-glass | 2200 | 72 | 3.1 |

## 1.2 Woven Forms of Carbon and Glass Fibers

In the composite industry, just like other fibers, carbon and glass fibers can be used in several forms. Commercially available forms can be listed as; short fibers (or chopped fibers or discontinuous fibers), continuous unidirectional rovings or yarns, and woven rovings or yarns as fabrics. Composite processing methods may differ by the form of the fibers used. Each form may provide certain advantages in terms of manufacturing and/or properties obtained.

In structural engineering applications, in order to decrease anisotropic properties, continuous fiber forms are used as layers in various numbers and angles called composite laminates. Laminated composite structures are stacked plies of fiber forms impregnated with a polymer resin. These plies in question can be woven fabrics,

chopped fiber strand mats, unidirectional fibers or even foams for sandwich structures.

In composite structure design, fibers are oriented along the loading direction in order to obtain maximum strength. However, there are several applications where loading direction varies. When the tensile load is not parallel to fiber direction, some of the load will be applied to matrix/reinforcement interface possibly causing anisotropy and debonding or delamination [6]. At this point, laminates come to the rescue as they provide strength in different directions. Fabrics with different fiber angles can be used for each ply providing strength along various directions.

In this study, composite laminates are produced by using woven forms of carbon and glass fibers with PLA matrix. There are several woven fabric forms available in the industry. Most widely used weaving styles are given in Figure 1.1.

*Plain weave,* the simplest type of weaving, is formed of alternating yarns with under and over pattern. There is one warp and one fill for each fiber. This style is the most stable and firm weaving style providing uniform strength in both planar directions [6].

*Basket weave* is similar to plain weave with a difference of two fiber yarns are woven in an alternating under and over manner instead of one. This weaving style is less stable than plain weave, on the other hand it provides higher strength along the fabric plane. Higher strength originates from fewer crossing points as the more crossing points may lead to fiber damage [6].

*Twill weave* is another style that fill fibers pass over one and under two or more warp fibers [6]. The number of warp fibers that fill fibers pass under gives the pattern its name such as 2x2 twill or 3x3 twill. Impregnation of this weaving type is excellent with a slight decrease of stability compared to plain weave. Also, the number of crossing points are less in this pattern providing higher strength [6].

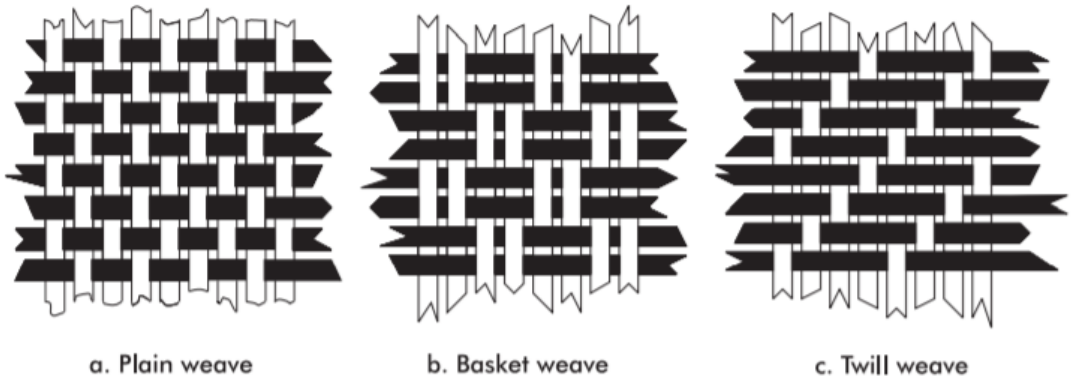


**Figure 1.1.** Woven fiber form styles [6].

## 1.3 Polymer Matrices Used for Composite Laminates

Just like "monoblock" composite structures, three main classes of polymers (thermosets, thermoplastics, elastomers) can be also used as the matrix materials for "laminated" composite structures. In the industry, the most widely used polymer matrices are still traditional thermoset liquid resins, such as epoxy, unsaturated polyester, and phenolic resins. Although these thermoset matrices have certain advantages and consistent properties, they have also significant drawbacks; for instance, these resins require not only complicated curing operations to get rigid solid state, before the curing operation, they also require subzero storage conditions with limited shelf life. Another drawback is; after shaping processes are complete, it would not be possible to re-soften and reshaping, which leads to enormous amounts of waste and scrap leading to significant environmental issues.

In the last few decades, in order to overcome these problems of thermoset matrix polymers, composite industry is trying to shift from thermoset resins into thermoplastic counterparts. Today, there are significant applications of thermoplastic matrix materials such as PA, PPS, PEEK and PAEK, not only for the monoblock composite structures, but also for the laminated composite structures.

On the other hand, both thermoset and thermoplastic matrix polymers are predominantly polymerized by using non-renewable petroleum by-products. Although still being the most practical way, producing polymers from petroleum or related limited resources will not be sustainable in the future. In fact, even if scarcity of the resources were not a problem, environmental issues of petroleum-based products are not ignorable due to their extremely high carbon footprint[7].

Therefore, instead of using petroleum-based thermoset and thermoplastic matrix materials, bio-based polymer materials derived from renewable resources have been emerged to overcome these challenges. The research on bio-based polymer materials have gained momentum considerably in the last decade.

Bio-based polymer is simply defined as the polymer resin obtained from renewable biological resources. Most of the bio-based polymers are also biodegradable in the nature [8]. In the *"Biopolymer Facts and Statistics Report"* which is published by *Institute of Bioplastics and Bio-composites*, it is estimated that global production capacity for bioplastics will increase from 2.6 million tons in 2018 to 4.3 million tons by 2023 [9] as indicated in Figure 1.2.

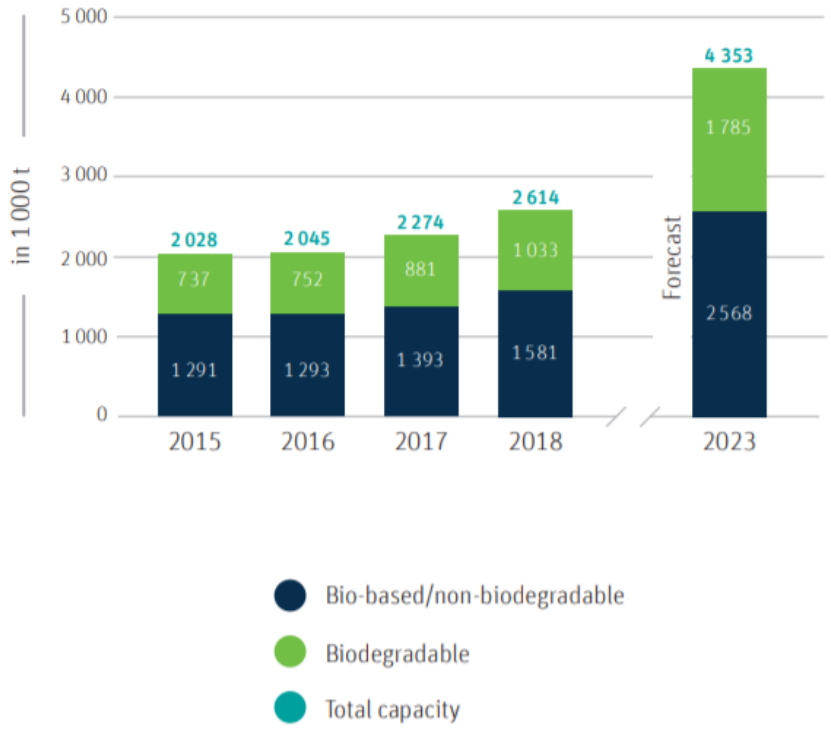


**Figure 1.2.** Global bioplastic production over the years [9].

## 1.4 Polylactide

Although production of various biopolymers are under significant consideration, poly (lactic acid) also named as polylactide (PLA) can be considered as one of the best alternative to petroleum-based polymers as it stands out with its relatively higher mechanical and thermal properties and mass production. Chemical structure of polylactide is given in Figure 1.3.

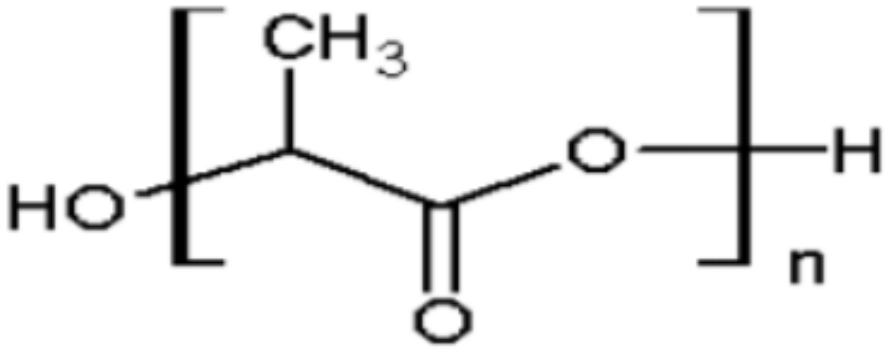


**Figure 1.3.** Chemical structure of polylactide mer [10].

Most of the mechanical and thermal properties of thermoplastic polymers are related to molecular weight of the polymer. The first attempts of PLA synthesis yielded low molecular weight polymers with poor thermal and mechanical properties. However, in 1954, first high molecular weight PLA was produced and patented by DuPont followed by comprehensive research on high molecular weight PLA worldwide. Production of high molecular weight PLA increased its use in certain applications. In 2002, the first large scale PLA production plant with a capacity of 150 thousand tons annual production has started operating [11].

Lactic acid can be either synthesized by bacterial fermentation or chemical synthesis. Due to a chiral atom (C*), there are two isomers of lactic acid as L (+) lactic acid or D (-) lactic acid. These isomers can create 3 different cyclic dimers such as L-L lactide, D, D – lactide and D, L – lactide (meso-lactide). Generally, L, L and D, D lactides are produced by bacterial fermentation, on the other hand, synthesis of D, L lactide (meso – lactide) is carried out through chemical methods [12]. Chemical structure of L and D lactic acid isomers and their three cyclic dimers are given in Figure 1.4. Polymerization of L, D and D-L cyclic dimers results in PLLA, PDLA and blend of PLLA and PDLA respectively.

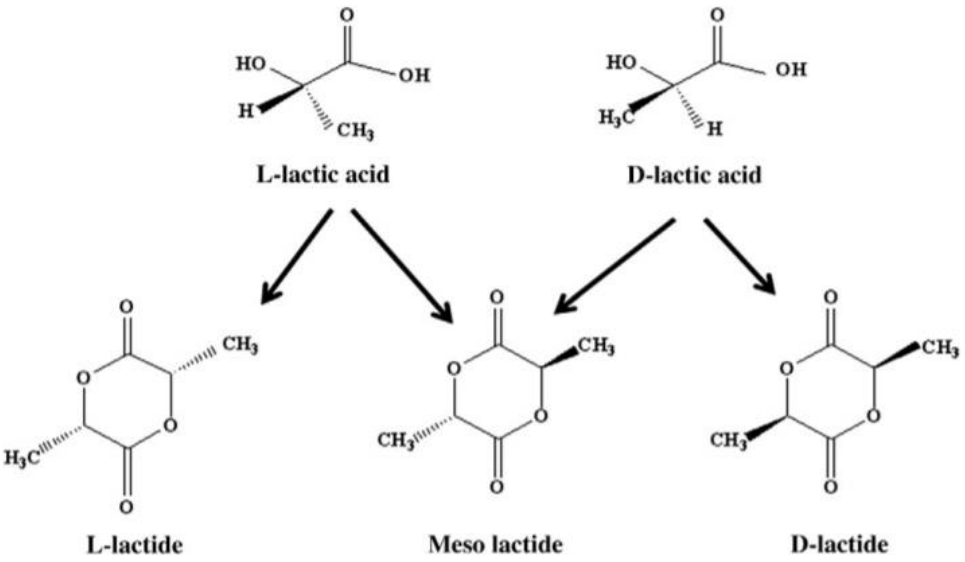


**Figure 1.4.** Chemical structure of two lactic acids and their cyclic dimers [13]

The simplest method for high molecular weight PLA synthesis is ring opening polymerization of lactide given in Figure 1.5. The process starts with condensation polymerization of lactic acid forming low molecular weight PLA which forms cyclic lactide through back – biting depolymerization process and eventually forming high molecular weight PLA by ring opening polymerization [14]. Other methods given in Figure 1.5. contains direct condensation of lactic acid into high molecular weight PLA and increasing the molecular weight of the polymer with the help of chain coupling agents. The purity of intermediate products during the synthesis is crucial as thermal and degradation properties of the product depends on it [15].

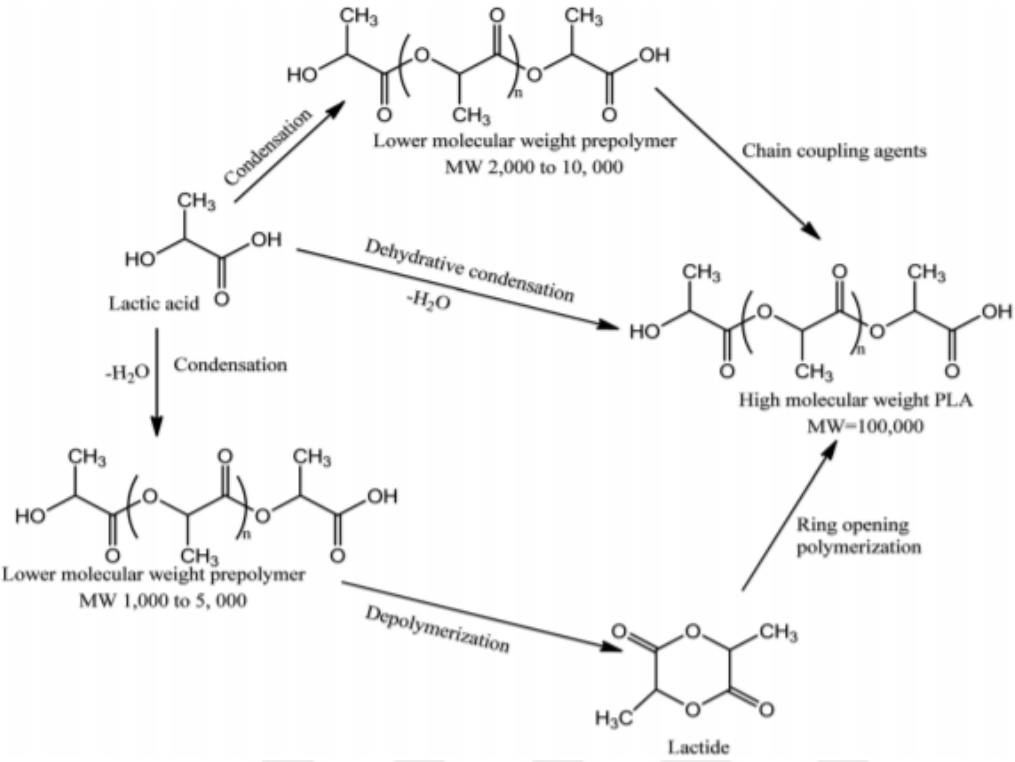


**Figure 1.5.** Various routes for high molecular weight PLA production [16].

As mentioned before, thermal and mechanical properties of PLA are strongly dependent on molecular weight and purity. PLA available in the industry is generally a copolymer of PLLA and poly (D, L – lactide) [17].

PLA outstands among other biobased polymers in terms of thermal and mechanical properties with 3-4 GPa of tensile and flexural modulus, 60-100 MPa of flexural strength, 50-70 MPa of tensile strength, 55-60 ℃ of glass transition temperature and 150-230 ℃ of melting range which is intermediate between PP and PET. Hence, it is a suitable substitute for replacing petroleum-based polymers in several structural applications. It is also currently used in biomedical applications and food packaging due to its biodegradability. As the annual production amount increases and the production cost decreases, application areas of PLA is expected to increase with the help of enhancements on mechanical and thermal properties as an environmentally friendly approach in industry.

Therefore, in this thesis, the matrix polymer chosen is PLA produced from corn-starch and being a “thermoplastic biopolymer”.

## 1.5 Literature Overview on Fiber Reinforced PLA Composites

Polylactide as a biopolymer, holds a significant volume in the literature due to its comparably higher mechanical performance. There are studies ranging from biomedical area to automotive applications. Although PLA among other biopolymers has higher mechanical properties, it still needs to be reinforced in order to use in structural applications. Since this thesis focuses on the mechanical properties of fiber reinforced PLA matrix composites, literature survey mainly focused on this type of studies.

The first group of studies [18-24] are on the PLA matrix composites reinforced with short (discontinuous) fibers such as carbon, glass and natural fibers (jute, hemp, flax etc.) by using melt mixing method (via twin screw extruder). Specimens were shaped especially with 3D printing techniques.

In the second group of studies [25-31], PLA matrix was reinforced with long or continuous (UD) fibers such as carbon and natural (jute, flax, hemp etc.) fibers. Composite specimens are produced with 3D printing and compression molding methods.

These studies generally indicated that when PLA matrix was reinforced with short, long or continuous fibers; mechanical properties of the composites are improved significantly. They also indicated that certain thermal properties are increased slightly.

Since in this study the reinforcements used were woven fiber forms; detailed literature survey was conducted on this subject. However, it was observed that previous studies on the use of woven fiber forms for PLA matrix composite laminates were all focused on “natural” woven fibers; as summarized in the following section.

## 1.6 Literature Survey on PLA Composite Laminates with Woven Forms of Natural Fibers

Tanaka *et al.* [32] used plain woven jute fabrics. In the study, PLA films were inserted between jute fabric layers followed by compression molding. Before that, jute fabrics were immersed in sodium hydroxide solution in order to enhance interfacial adhesion. They conclude that molding temperature can be adjusted to increase the crystallinity of PLA matrix, while jute fabrics improve impact and flexural properties.

Similarly, Chen and Lin [33] used cotton and jute fabrics by pressing these layers in between PLA sheets. They also compared cotton and jute fabric reinforced PLA laminates with epoxy matrix laminates by conducting tensile, compression and bending tests. They concluded that these mechanical properties of the PLA laminates were divergent to that of epoxy laminates.

In the study of Quintero *et al.* [34], a fabric produced from palm trees were inserted between PLA films with different ply angles and numbers. The study indicated that ply angle and stacking sequence affect the tensile properties of the laminates significantly.

In the study of Siengchin and Wongmanee [35], 2x2 twill and 4x4 hopsack weave flax fabrics are combined with PLA sheets using compression molding process. They showed that impact and tensile properties of PLA laminates increased significantly with both 2x2 and 4x4 flax fabric reinforcements.

Porras and Maranon [36] reinforced PLA matrix with plain woven bamboo fabric. PLA granules were first converted into films using single screw extruder. Then, composite laminates were produced by stacking bamboo fabric and PLA film layers under compression molding. Tensile, flexural and impact tests carried out on the composite laminate specimens in 0° (warp) and 90° (weft) directions indicated that all mechanical properties of the specimen were increased, the improvement being higher in the weft directions.

Battegazzore *et al.* [37] compared PLA matrix and polyhydroxy butyrate (PHB) copolymer matrix reinforced with 2x2 twill cotton fabric. Matrix films and 9 layers of cotton fabric were stacked alternately followed by compression molding. They indicated that increases in the flexural strength, impact toughness and heat deflection temperature (HDT) in the PLA laminates were higher compared to PHB matrix laminates.

In the study of Rubio-López *et al.* [38] different weaving styles of jute, cotton and flax fabrics were compared. Similar to other studies, granules of PLA were first converted into films with a specific thickness using compression molding. Then films were inserted between 2 and 4 layers of plain weave jute, basket weave cotton, basket weave flax and plain weave flax fabrics under compression molding. They revealed that laminates with 2 plies of basket and plain-woven flax fabric had the highest tensile strength as flax is the strongest natural fiber used in the study. However, due to the processing problems, tensile strength of 4 ply laminates were not improved.

Durante *et al.* [39] investigated mechanical properties of the PLA/woven hemp fiber composites having three different fiber percentages in volume (20%, 30%, 40%). Composite laminates were produced again by stacking hemp fabrics and PLA films in compression molding. It was observed that the highest flexural properties are obtained in the specimens with 20% and 30% hemp fabrics. It was also stated that when the volume percentage of the hemp fiber fabrics are 40%, certain processing problems occurred leading to lower performance.

## 1.7 The Aim of This Thesis

Literature survey indicated that although there is a certain number of studies on the PLA matrix composites reinforced with glass and carbon fibers; they are all used in the form of either chopped short fibers or continuous UD fibers. On the other hand, many engineering applications require composite laminate structures having woven forms of high-performance glass or carbon fibers.

To the best of our knowledge, studies on the PLA matrix laminates with woven forms of glass or carbon fibers are not present. Researchers used woven forms of only natural fibers, such as flax, hemp, cotton etc. Therefore, the main purpose of this study is, as the first time in the literature, to investigate usability of PLA biopolymer as the matrix of high-performance composite laminated structure having woven forms of glass and carbon fibers.

Studies on the use of woven forms of natural fibers also revealed that PLA matrix during stacking of the laminates were always inserted in the form of sheets. In this study, PLA matrix would be placed in the form of powders, which would be another contribution of this study to the literature.

Another contribution of this study would be comparison of the flexural mechanical performance of biopolymer PLA matrix laminates with those of traditional thermoset Epoxy matrix laminates having the same number and type of woven glass and woven carbon fiber layers.

# CHAPTER 2

## EXPERIMENTAL WORK

In this study, PLA matrix composite laminates were produced with 2, 4, 6, 8, 10, 12, 14 layers of woven forms of glass and carbon fibers. Composite laminates are designated by using the format of **PLA/GF – *x*L** or **PLA/CF – *x*L**; where ***x*** denotes the number of layers, while **GF** and **CF** denote "Woven Glass Fiber" and "Woven Carbon Fiber", respectively. For instance, **PLA/GF-14L** denotes PLA matrix composite laminate having 14 layers of Woven Glass Fiber form.

General flowchart for the production of PLA laminates is shown in Figure 2.1, while details of these processes and specimen characterization are explained in the following sections.

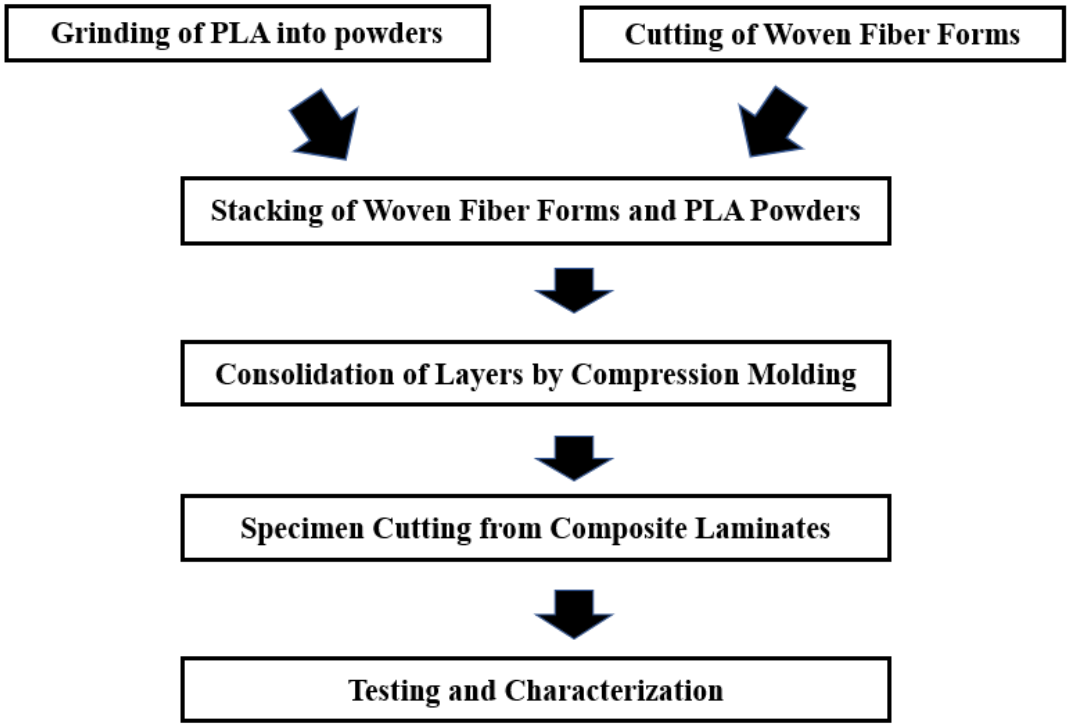


**Figure 2.1.** General flowchart for the production of PLA composite laminates

## 2.1 PLA Matrix Material Used

In this study, L-lactide type PLA produced by NatureWorks LLC with a commercial name "Ingeo™ Biopolymer 3251D" was used as the matrix material for laminates. Certain properties given in the technical data sheet (TDS) of this commercial PLA biopolymer is given in Table 2.1.

**Table 2.1.** Certain properties of the PLA matrix given in its TDS.

| **Property** | **Value** | **ASTM Method** |
|---|---|---|
| Specific Gravity | 1.24 | D792 |
| MFR, g/10 min (190°C, 2.16kg) | 35 | D1238 |
| Melt Temperature (ºC) | 155-170 | D3418 |
| Glass Transition Temperature (ºC) | 55-60 | D3418 |
| Tensile Yield Strength (MPa) | 62 | D638 |
| Tensile Elongation, % | 3.5 | D638 |
| Flexural Strength (MPa) | 108 | D790 |
| Heat Distortion Temperature (ºC) | 55 | E2092 |

## 2.2 Grinding of PLA Granules into Powders

In order to enhance uniform melting, and proper impregnation of woven fiber forms with the matrix, PLA granules (Figure 2.2.) were first ground into fine powders (Figure 2.3.) by using a polymer grinding equipment (IKA MF-10) shown in Figure 2.4.

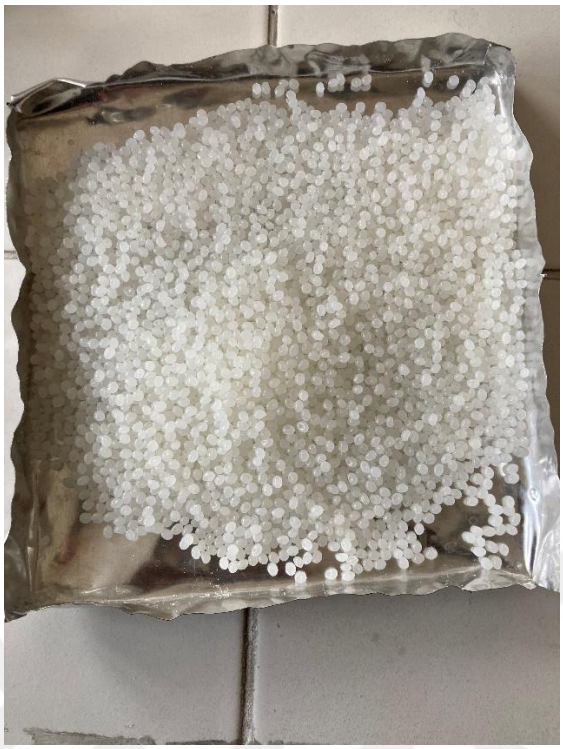

**Figure 2.2.** PLA granules

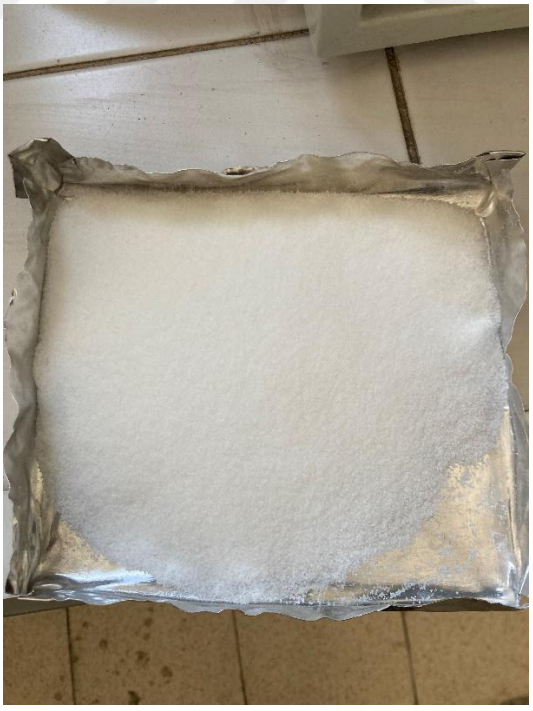

**Figure 2.3.** PLA powders after grinding



**Figure 2.4.** Polymer grinding equipment

## 2.3 Woven Forms of the Carbon and Glass Fibers Used

In the production of PLA composite laminates, two different types of woven fiber forms were used. The first one was the Woven Carbon Fiber form (simply designated as CF) with the tradename of Torayca T-300 Fiberite produced by Toray Inc. The density of the fibers is given as 1.76 g/cm$^3$. Its weave style is 2x2 twill having planar density of 300 gr/m$^2$.

The second one was Woven Glass Fiber form (simply designated as GF) with the tradename of Camelyaf CD-300 produced by Şişecam Inc. The density of the fibers is given as 2.54 g/cm$^3$. Its weave style is 1x1 plain weave with a planar density of 300 gr/m$^2$.

## 2.4 Cutting of Woven Fiber Forms

Woven glass and woven carbon fibers were cut from their reels in order to fit them into laminating mold dimensions (160x120 mm) by using Stanley 11-921 Heavy Duty blade. As shown in in Figure 2.5, mold frame was used as a guiding template to ease the cutting process. Examples of cut layers of Woven Carbon and Glass Fibers are shown in Figure 2.6.



**Figure 2.5.** Cutting of woven fiber forms

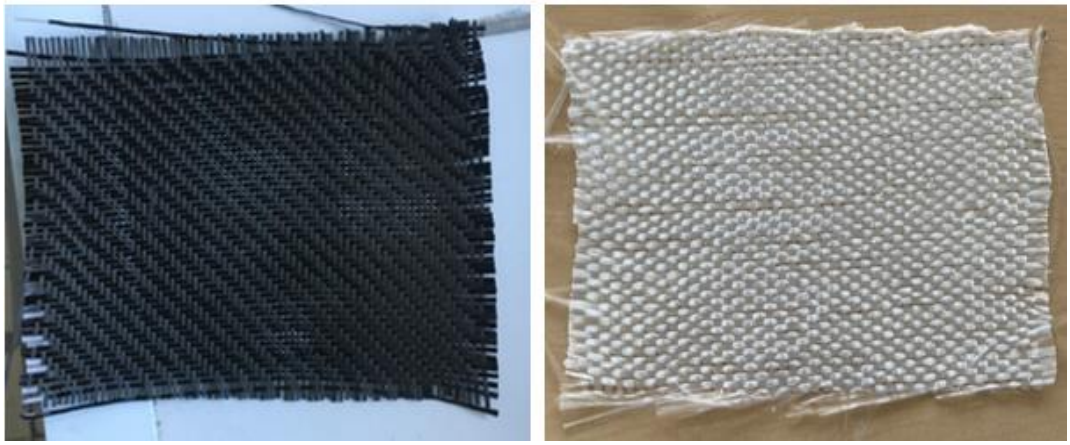

**Figure 2.6.** Cut layers of woven carbon and woven glass fibers

## 2.5 The Mold Used During Production of Composite Laminates

For the lamination, two – piece mold with male core and female cavity frame were machined from 4 mm thick AISI 4140 steel plate by Electrical Discharge Machining (EDM) process. 120x160x4 mm male core plate was removed from the larger 140x180x4 mm plate, leaving the female cavity frame. These pieces of the mold are shown in Figure 2.7.



**Figure 2.7.** Pieces of the mold machined from a steel plate

## 2.6 Stacking of PLA Powders in Between the Woven Fiber Forms

Before stacking of each layer, PLA powders were first dried under -0.5 bar vacuum for 24 hours at 50 ℃ in order to remove moisture and improve homogeneous melting and impregnation. The vacuum oven (NÜVE EV 018) used is shown in Figure 2.8. Before applying silicone-based mold release agent (BEST KA 1000) to the mold frame surfaces, the frame was preheated to 100 ℃ in order to get a uniform release agent film formation on the inner mold frame surfaces.




**Figure 2.8.** Vacuum oven

Then a kind of "Hand Lay-Up" operation, i.e. stacking of PLA powders in between the woven fiber forms was achieved by placing them one by one in the mold cavity. 100 g of PLA powder was used for each different composite laminate plate produced, having 2, 4, 6, 8, 10, 12, 14 layers of woven fiber forms. For $n$ number of woven fiber layer, $n+1$ number of PLA powder layer was placed. For each number of PLA matrix layer, $100/(n+1)$ g of PLA powder was stacked. PTFE release films were also

placed on the upper and lower mold surfaces to obtain smooth laminate surfaces and easy demolding. An example of the stacking sequence during production of the composite laminates are illustrated in Figures 2.9 and 2.10.

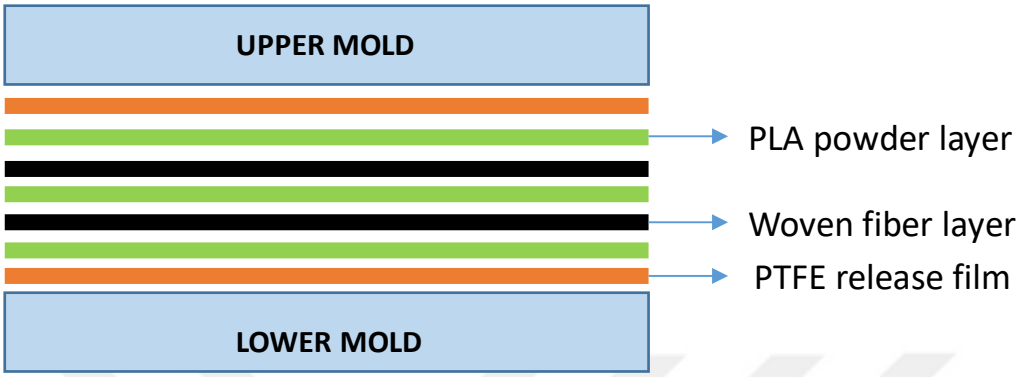


**Figure 2.9.** An example of the stacking sequence for the laminate having 2 woven fiber layers

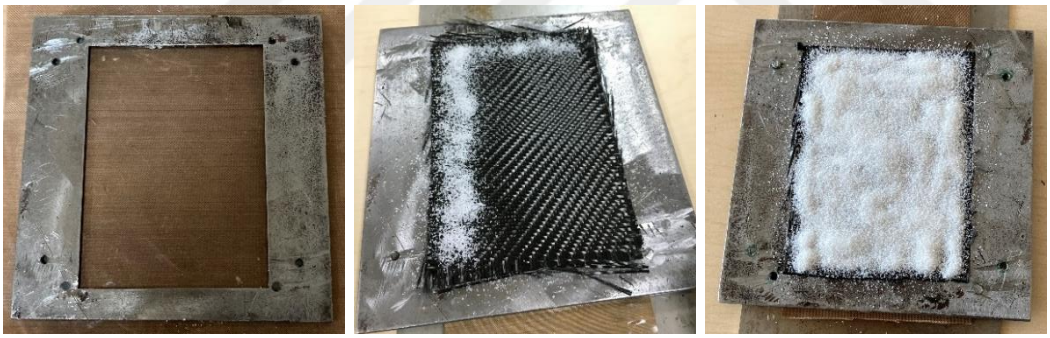

**Figure 2.10.** An example of the empty mold frame, woven carbon fiber layer, and stacking of the layers with PLA powders

## 2.7 Consolidation of Layers by Compression Molding

After stacking specified number of layers, male core mold was placed on top of the last PLA powder layer and placed in between the upper and lower plates of the hot press (LP_M4S50, MSE Teknoloji LTD.) for consolidation by compression molding. Closer and general views of the compression molding equipment are shown in Figures 2.11 and 2.12 respectively.

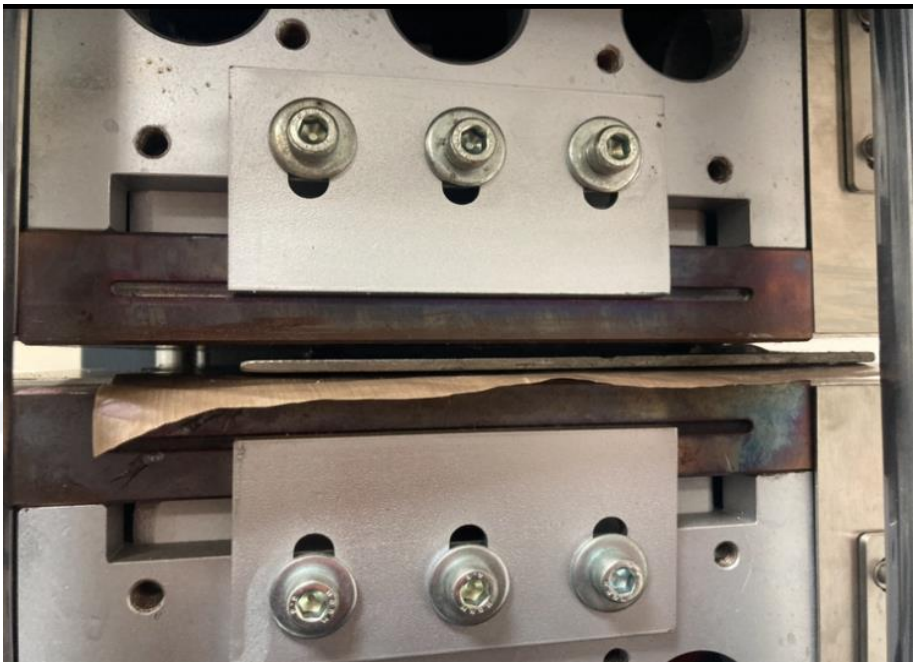

**Figure 2.11.** Closer view of the laminate consolidation

Without pressure application, laminates were first preheated at 175 ℃ for 15 minutes in order to get homogenous melting of PLA powders. After preheating, consolidation of the laminates was achieved by two step compression molding process. First, at 175 ℃ temperature, 0.5 ton pressure was applied for 10 minutes, followed by increasing the pressure to 1 ton for another 10 minutes. After these total 20 minutes of hot pressing, the mold with the laminates was quickly taken from the hot press

and inserted into cold press for the second compression molding step. Mold frame together with the laminates were cooled to room temperature in this cold press under 0.2 ton pressure.




**Figure 2.12.** Hot press (left) and cold press (right) used for the consolidation by compression molding

After room temperature cooling under pressure, composite laminate plates were removed from their mold frames. Figure 2.13 shows an example of the PLA/CF laminate plate produced.



**Figure 2.13.** An example of the PLA/CF composite laminate plate produced

## 2.8 Cutting of Test Specimens from Composite Laminate Plates

Test specimens were extracted from composite laminate plates according to the dimensions specified by testing standards given in the following sections. In order to prevent damages to woven fiber forms and thermal degradation of the PLA matrix, a CNC Water Jet Cutting system (Figure 2.14) was used. After water jet cutting, specimens were dried with compressed air and kept in desiccators in order to prevent moisture absorption. Examples of the specimens extracted after water jet cutting are also given in Figure 2.14.

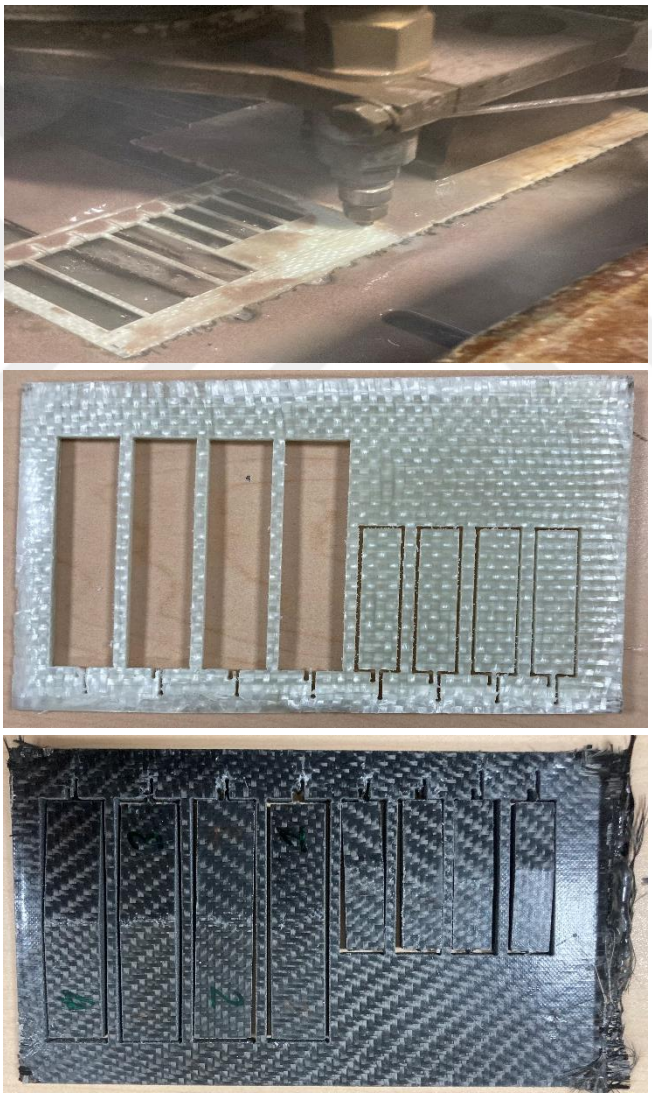

**Figure 2.14.** Examples of the specimens after water jet cutting

## 2.9 Fiber Weight Percent Determination

After the production of composite laminates, their fiber-matrix weight ratio was determined according to the procedure given in *ASTM-D-3171 - Standard Test Methods for Constituent Content of Composite Materials, Method B* [40]. First, 1g of each composite laminate were placed into a beaker with 20 mL of sulfuric acid. Then, the beaker was heated on a hot plate until fume release was started. When the solution in the beaker became darker, 35 mL of 30% purity hydrogen peroxide was added. When fibers started to float on the surface of the solution with more clear color, beaker was removed from the hot plate to cool. After cooling, fibers were filtered from the solution under vacuum and washed with deionized water. Then fibers were dried in a vacuum oven at 100 ℃ for 1 hour, followed by cooling to room temperature inside a desiccator. Finally, these fibers were weighed with a precision balance for calculations.

## 2.10 Interlaminar Shear Strength (ILSS) Tests

In this study, in order to determine mechanical performance of the composite laminates produced, two different mechanical tests were conducted under 5kN Universal Testing System (Instron 5565A) shown in Figure 2.15. For each laminate type, at least four specimens were tested, and the results are tabulated as average values with standard deviations.

Before starting the flexural three-point bending tests, first ILSS tests were conducted in order to determine interlayer performance of the composite laminates. Tests were carried out in accordance with *ISO-14130 – Fibre reinforced plastic composites – Determination of Apparent Interlaminar Shear Strength by Short–Beam Method* standard. Specimens were prepared according to the ratio requirements of *l/h* and *b/h* [42]. Therefore, specimen dimensions used in this study are, 4 mm in thickness (*h*), 40 mm in overall length (*l*) and 20 mm in width (*b*), while the span length is set as 5*h* which is 20 mm.

Tests were carried with 1 mm / min test speed and continued until a or sudden drop in applied load was observed. An example view of this testing is given in Figure 2.16.

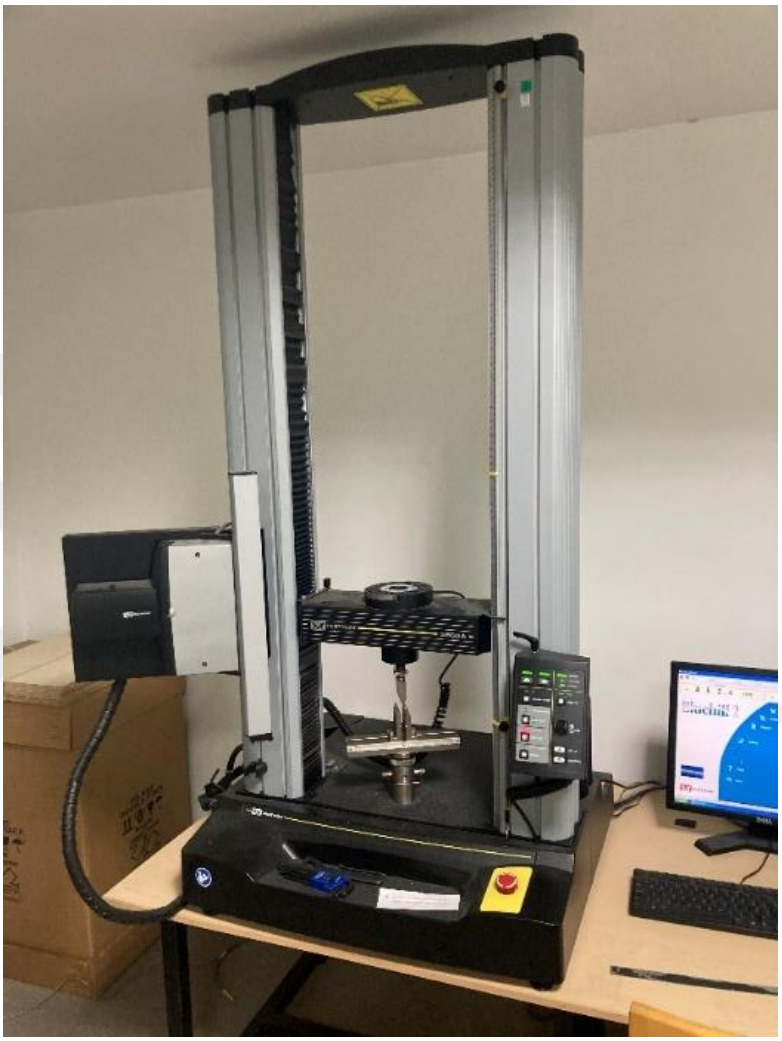

**Figure 2.15.** Instron 5565A testing machine



**Figure 2.16.** An example view of the ILSS testing

Apparent interlaminar shear strength (ILSS) in megapascals is calculated using the equation below [42]:

$$\tau = \frac{3}{4} \times \frac{F}{bh}$$

Where:

F: Maximum load in Newtons,

b: Specimen width in millimeters,

τ: Interlaminar shear stress in megapascals,

h: Specimen thickness in millimeters.

## 2.11 Three-Point Bending Tests

In order to determine Flexural Strength and Flexural Modulus values of the specimens, three-point bending tests were conducted in accordance with *ISO-14125 – Fibre Reinforced Plastic Composites – Determination of Flexural Properties* standard, where specimens were prepared according to *Class – II (Plastics reinforced with fabrics)* size. Specimen length (l) is 80 mm, width (b) is 15 mm and thickness (h) is 4 mm, while span length (L) is given as 64 mm. Radius of the support rollers is 5 mm. Tests are carried with 1 mm/min test speed and continued until a sudden drop in applied load is observed. An example view of this testing is given in Figure 2.17.



**Figure 2.17.** An example view of the three-point bending test

Flexural stress and flexural strain curves are determined by using the equations given below [41]:

$$\sigma_f = \frac{3FL}{2bh^2} \ , \varepsilon = 6\frac{sh}{L^2}$$

Where:

$\sigma_f$: Flexural stress in megapascals,

ε: Flexural strain,

F: Load in Newtons,

L: Span in millimeters,

b: Width of the specimen (mm),

h: Thickness of the specimen (mm),

s: Flexural deflection (mm).

Then "Flexural Strength" and "Flexural Modulus" values of the specimens were determined by using these curves.

## 2.12 Scanning Electron Microscopy (SEM)

Apart from visual inspections, SEM (FEI Nova Nano 430) analysis was carried out in order to observe failure modes and fracture morphology of the composite laminates. For the electrical conductivity, specimens were first sputtered with gold.

## 2.13 Thermogravimetric Analysis (TGA)

In order to observe changes in the thermal degradation temperatures of the PLA matrix, and to support the fiber weight percentage determination, TGA (Perkin Elmer Pyris 1) was conducted for 20 mg of samples with a heating profile from 25 °C to 550 °C with 10 °C/min rate under nitrogen purge.

## 2.14 Differential Scanning Calorimetry (DSC)

For the transition temperatures, enthalpies and crystallinity amount of PLA matrix, DSC (Perkin Elmer Diamond) analyses were conducted for 20 mg of samples with a heating profile from 25 ℃ to 250 ℃, with a heating rate of 10 ℃/min under nitrogen purge.

# CHAPTER 3

# RESULTS AND DISCUSSIONS

## 3.1 Fiber Content of the PLA Composite Laminates

Fiber content either in vol% or wt% in the polymer matrix composites is extremely important especially in terms of mechanical properties. Thus, after the production of PLA matrix composite laminates with woven forms of GF and CF layers; fiber content determination was conducted by chemical decomposition of PLA matrix (with sulfuric acid and hydrogen peroxide), in accordance with ASTM-D-3171 standard. The results obtained are given in Table 3.1. Using fiber weight percent values obtained by chemical decomposition method, fiber volume percent values are calculated by rule mixtures using the densities given in datasheets of the materials used. In calculation, void content is assumed to be zero.

It was observed that, apart from the laminates having only 2 and 4 layers, fiber content in the rest of the laminates were in between 40-45 wt%; which could be considered as a reasonable content for many structural applications.

It is known that "% residue" left at the end of Thermogravimetric Analysis (TGA) of polymer matrix composite materials are also an indication of the fiber content. Thus, that data of TGA performed for certain number of specimens are also tabulated in Table 3.1 (as wt% Residue left at 550 °C). It is seen that the results are very close to the fiber content percentages determined by chemical decomposition method.

**Table 3.1.** Fiber content of the specimens determined by matrix chemical decomposition method, and wt% residue values of certain specimens, determined by TGA for certain specimens comparison

| Specimens | Fiber content (wt%) | Fiber content (vol%) | % Residue at 550 °C (wt%) |
|---|---|---|---|
| **PLA/GF-2L** | 22.67 | 12.52 | 21.67 |
| **PLA/GF-4L** | 32.53 | 19.05 | - |
| **PLA/GF-6L** | 41.86 | 26.01 | 40.86 |
| **PLA/GF-8L** | 42.15 | 26.24 | - |
| **PLA/GF-10L** | 43.23 | 27.10 | 44.23 |
| **PLA/GF-12L** | 44.88 | 28.44 | - |
| **PLA/GF-14L** | 45.64 | 29.07 | 45.14 |
| | | | |
| **PLA/CF-2L** | 18.55 | 13.83 | 19.71 |
| **PLA/CF-4L** | 30.87 | 23.93 | - |
| **PLA/CF-6L** | 38.74 | 30.82 | 39.54 |
| **PLA/CF-8L** | 40.62 | 32.52 | - |
| **PLA/CF-10L** | 41.06 | 32.92 | 40.15 |
| **PLA/CF-12L** | 41.56 | 33.38 | - |
| **PLA/CF-14L** | 42.09 | 33.87 | 41.23 |

## 3.2 Interlaminar Adhesion in the PLA Composite Laminates

It is known that the most critical parameter for the performance of laminated composite structures is to have certain level of interfacial bonding strength between the polymer matrix and the fiber layers. Otherwise, “delamination” failure will dominate throughout the composite structure. Therefore, the first mechanical test conducted for the PLA composite laminates was Interlaminar Shear Strength (ILSS) test.

### 3.2.1 Interlayer Performance by ILSS Tests

In this test, the highest level of shear stress is created in the mid-plane of the specimen where there is a polymer matrix layer and one or more fiber layers above and below the matrix layer. Thus, ILSS values directly depends on the “interfacial bond strength” between the polymer matrix and the fiber layer surfaces. Type of the fiber layers and number of the fiber layers have also certain influences on the ILSS values of the laminates.

The results of this test for all PLA/GF and PLA/CF laminates were compared in Figure 3.1 while the data are tabulated in Table 3.2 with standard deviations. It is seen that ILSS values for the PLA/GF laminates between 15-19 MPa, while for the PLA/CF laminates are in between 20-38 MPa. One reason for the higher levels of PLA/CF laminates could be higher mechanical properties of carbon fibers compared to glass fibers. Another reason could be higher level of adhesion between the PLA matrix and CF layers, which would be discussed in the following SEM section. It was also observed that increasing the number of layers in the laminates increases the ILSS values slightly, which could be due to the additional strengthening contribution of layer numbers above and below the mid-plane PLA matrix layer.

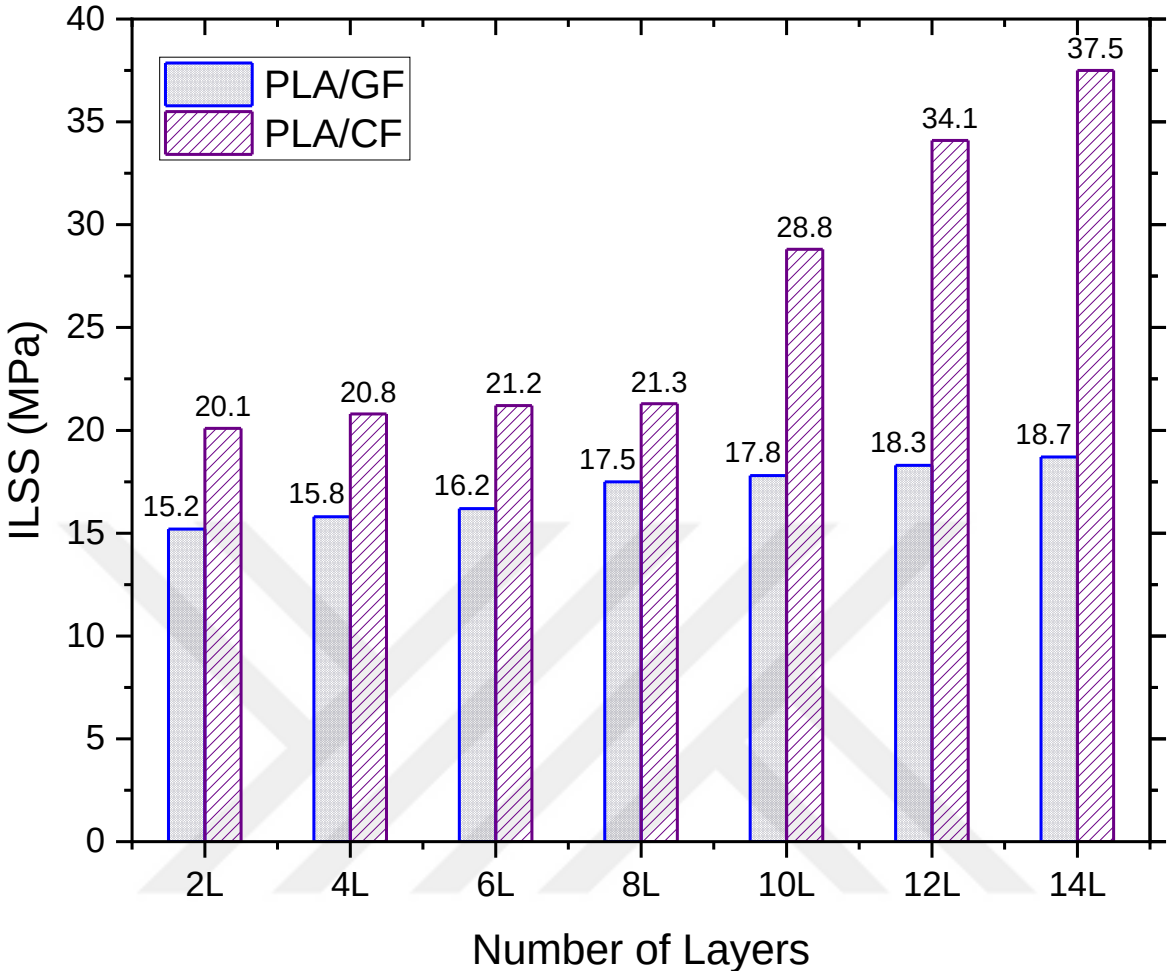


**Figure 3.1.** Effects of increasing number of layers on the interlaminar shear strength of the composite laminates

**Table 3.2.** Interlaminar Shear Strength (ILSS), Flexural Strength and Flexural Modulus of the composite laminates

| Specimens | ILSS (MPa) | Flexural Strength (MPa) | Flexural Modulus (GPa) |
|---|---|---|---|
| **PLA** | - | 88 ± 5 | 2.7 ± 0.2 |
| **PLA/GF-2L** | 15.2 ± 0.6 | 100 ± 5 | 5.9 ± 0.6 |
| **PLA/GF-4L** | 15.8 ± 2.3 | 107 ± 6 | 6.4 ± 0.9 |
| **PLA/GF-6L** | 16.2 ± 0.9 | 122 ± 6 | 7.2 ± 0.4 |
| **PLA/GF-8L** | 17.5 ± 1.7 | 146 ± 4 | 8.6 ± 0.6 |
| **PLA/GF-10L** | 17.8 ± 1.8 | 207 ± 2 | 10.4 ± 1.1 |
| **PLA/GF-12L** | 18.3 ± 0.9 | 274 ± 6 | 11.6 ± 0.8 |
| **PLA/GF-14L** | 18.7 ± 0.6 | 302 ± 5 | 15.1 ± 1.1 |
| **PLA/CF-2L** | 20.1 ± 1.1 | 130 ± 4 | 7.4 ± 1.9 |
| **PLA/CF-4L** | 20.8 ± 2.6 | 210 ± 2 | 11.1 ± 0.6 |
| **PLA/CF-6L** | 21.2 ± 3.5 | 335 ± 4 | 16.7 ± 1.6 |
| **PLA/CF-8L** | 21.3 ± 1.5 | 431 ± 6 | 19.9 ± 1.3 |
| **PLA/CF-10L** | 28.8 ± 2.1 | 531 ± 6 | 25.2 ± 2.1 |
| **PLA/CF-12L** | 34.1 ± 2.4 | 607 ± 7 | 30.8 ± 1.2 |
| **PLA/CF-14L** | 37.5 ± 2.8 | 641 ± 6 | 34.2 ± 3.1 |

### 3.2.2 Interlayer and Interfacial SEM Analysis

SEM studies were conducted first on the through thickness of the laminates to observe the adhesion “between the PLA matrix and woven fiber layers” (Figures 3.2 and 3.3). Then, closer view examinations from the fracture surfaces were also conducted to observe the adhesion level “between the PLA matrix and individual fiber” surfaces (Figures 3.4 and 3.5).

Through thickness images in Figures 3.2 and 3.3 taken away from the fracture point basically show that certain level of adhesion between the PLA/GF and PLA/CF layers was achieved. There was no apparent “delamination” problem in the composite plates. In order to reveal the reason for higher ILSS values of PLA/CF laminates compared to PLA/GF laminates, closer SEM images were also taken from the fracture point. As shown in Figure 3.4, the adhesion between the PLA matrix and individual Glass Fiber surfaces was very poor. On the other hand, Figure 3.5 shows that the degree of adhesion of the interface between the PLA matrix and individual Carbon Fiber surfaces were much better, which might lead to higher ILSS values.

Normally in the composite materials market, woven fiber forms are produced after sizing with certain silane coupling agents suitable with traditional epoxy or polyester thermoset resins. In this study, it was expected that $-COOH^-$ and $-OH^-$ groups present on the macromolecular chain structure of PLA matrix might form certain chemical interactions with the silane coupling agents present on the surfaces of woven GF and CF fiber forms used. Thus, it can be stated that sizing on the woven CF layers was more compatible with the PLA macromolecules compared with the sizing on the woven GF layers used.

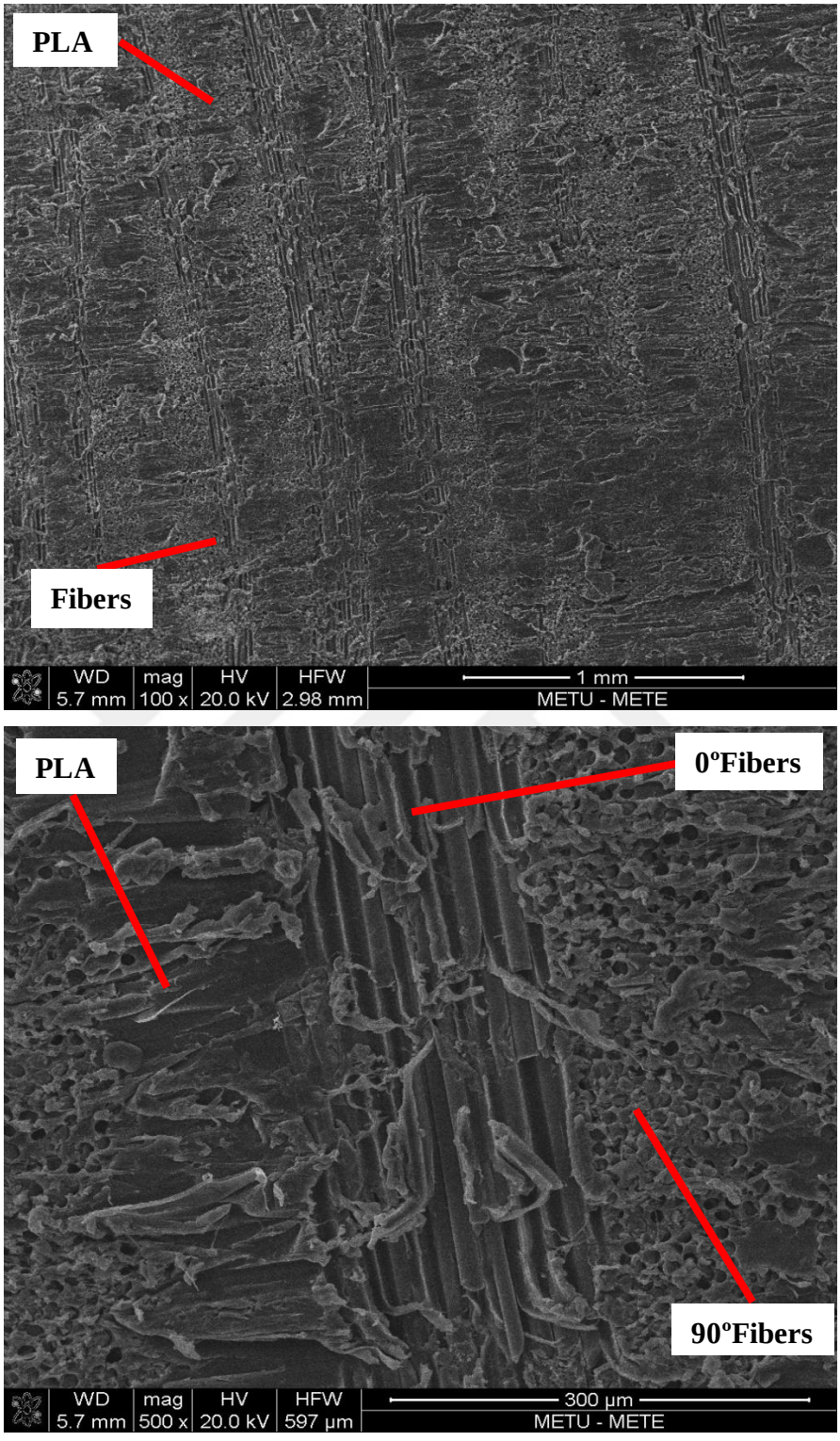


**Figure 3.2.** General (above) and closer (below) through thickness SEM images showing "interlaminar" adhesion between PLA/GF layers

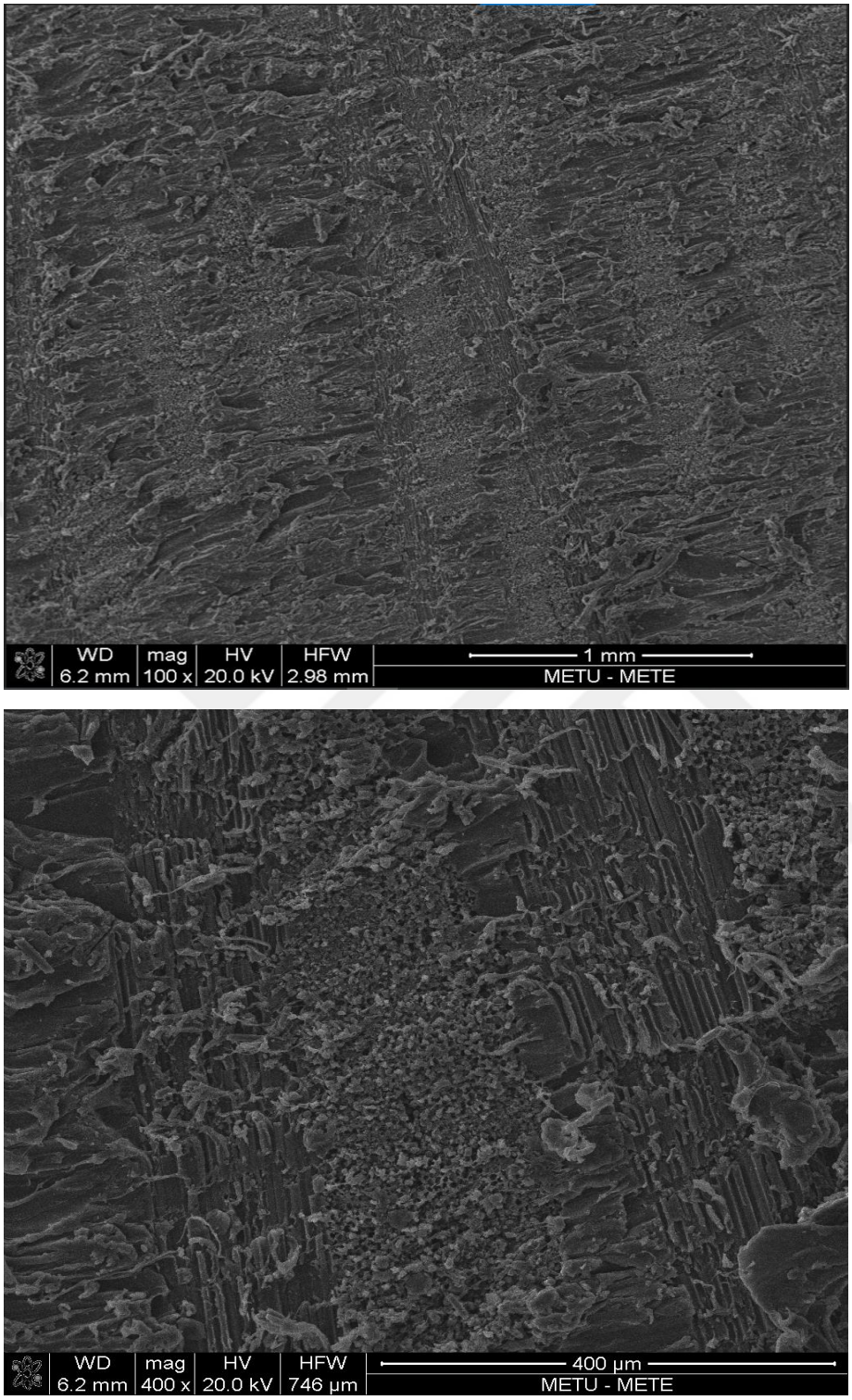


**Figure 3.3.** General (above) and closer (below) through thickness SEM images showing "interlaminar" adhesion between PLA/CF layers

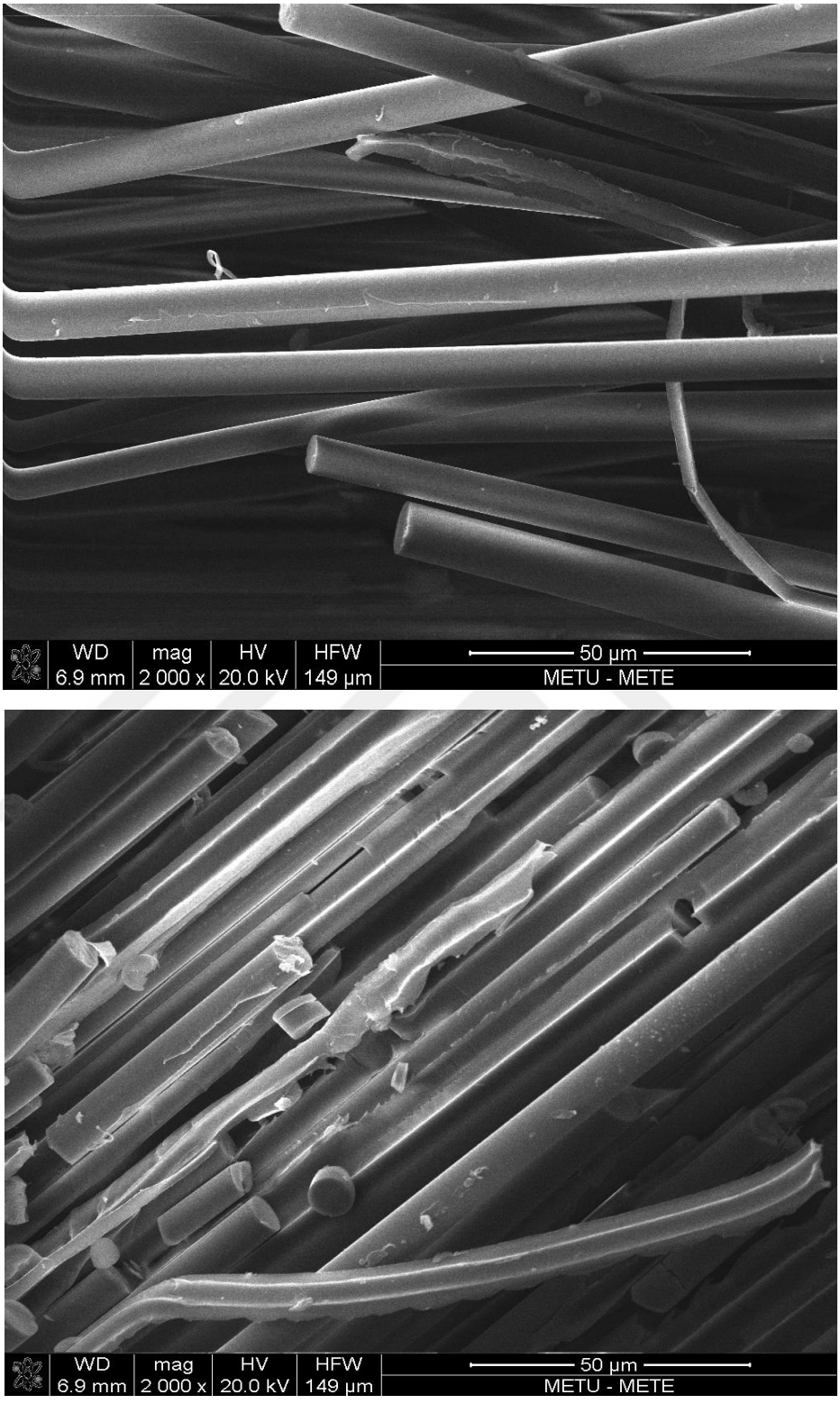


**Figure 3.4.** Closer view SEM images showing rather "lower" adhesion between PLA matrix and individual glass fiber surfaces

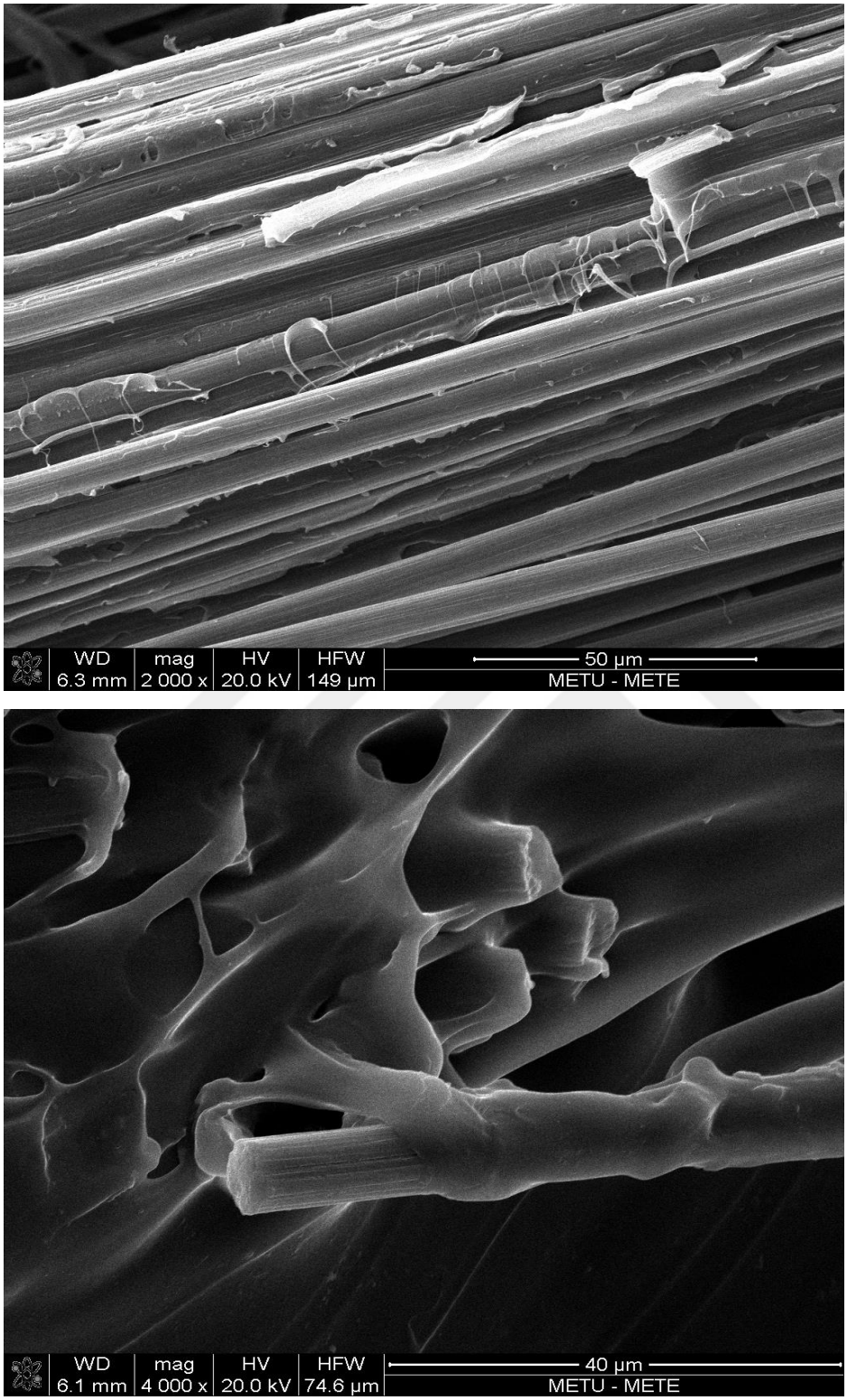


**Figure 3.5.** Closer view SEM images showing rather "higher" adhesion between PLA matrix and individual carbon fiber surfaces

### 3.2.3 Comparison of the Interlaminar Adhesion of PLA Laminates with Traditional Epoxy Laminates

It is known that, for many structural applications of composite laminates, ILSS values should not be lower that 10 MPa. In this respect, PLA laminates produced in this study overcome that limitation, having ILSS values up to 19 MPa in PLA/GF laminates, and up to 38 MPa in PLA/CF laminates.

On the other hand, due to using proper silane coupling agents, it is known that traditional Epoxy/GF laminates have ILSS values greater than 20 MPa [43, 44], while traditional Epoxy/CF laminates have greater than 40 MPa [45, 46].

Therefore, it can be concluded that if GF and CF woven forms were produced by using individual fibers sized with very compatible silane agents with PLA matrix, then much higher ILSS values in the PLA/GF and PLA/CF laminates could be obtained. Then, PLA biopolymer matrix could be an alternative for the traditional Epoxy matrices even in the high-performance composite laminate applications.

## 3.3 Mechanical Performance of the PLA Composite Laminates

It is known that in many engineering structures produced with composite laminates are in general loaded predominantly by flexural stresses. Thus, in this study, mechanical performance of the PLA/GF and PLA/CF laminates are compared under flexural loads via three-point bending tests.

### 3.3.1 Flexural Properties via Three-Point Bending Tests

These tests are conducted for all composite laminates including the neat PLA specimen for comparison. Figure 3.6 shows examples of Flexural Stress-Strain curves obtained for all specimens; while effects of increasing the number of layers in the laminate specimens are compared in terms of Flexural Strength and Flexural

Modulus values in Figure 3.7. These mechanical properties are also tabulated in Table 3.2 together with standard deviation levels.

As expected, these figures indicate that flexural mechanical properties of neat PLA increased enormously when reinforced with increasing number of woven fiber layers. For instance, the increase in the Flexural Strength of neat PLA was more than 3 times when laminated with 14 layers of GF (i.e. from 88 MPa to 302 MPa), while it was more than 6 times when laminated with 14 layers of CF (i.e. from 88 MPa to 641 MPa). Similarly, the increase in Flexural Modulus values was more than 5 times (i.e. from 2.7 GPa to 15 GPa) in PLA/GF-14L laminate, while it was more than 12 times (i.e. from 2.7 GPa to 34 GPa) in PLA/CF-14L laminate. Even use of only two layers of woven fiber forms increased these strength and modulus values more than 2 times.

As shown in Figure 3.7 and Table 3.2, it was also very clear that use of woven CF layers was much more efficient compared to woven GF layers, being more than 2 times both in the Flexural Strength and Flexural Modulus values. As discussed in the ILSS section before; one obvious reason is the well-known higher mechanical properties of individual Carbon Fibers compared to Glass Fibers.

Another important reason would be related to the "degree of impregnation of molten PLA matrix into the woven fiber forms". Since weave style of the CF layers was 2x2 twill, being a rather "loose" form, easier impregnation of molten PLA resin was expected; compared to the rather "tight" form of 1x1 plain weave style of GF layers.

After sufficient degree of molten PLA resin impregnation, it is also important that, in order to have efficient "load transfer mechanism" to operate; "degree of interfacial adhesion between the PLA resin and individual fiber surfaces" are also very critical. As discussed before, closer view SEM images revealed that the type of the "silane coupling agent" used for sizing of individual Carbon Fiber surfaces was more compatible with the PLA matrix compared to sizing of individual Glass Fibers.

Therefore, it can be stated that those three factors discussed above resulted in more than two times higher mechanical properties in the PLA/CF laminates compared to PLA/GF laminates.

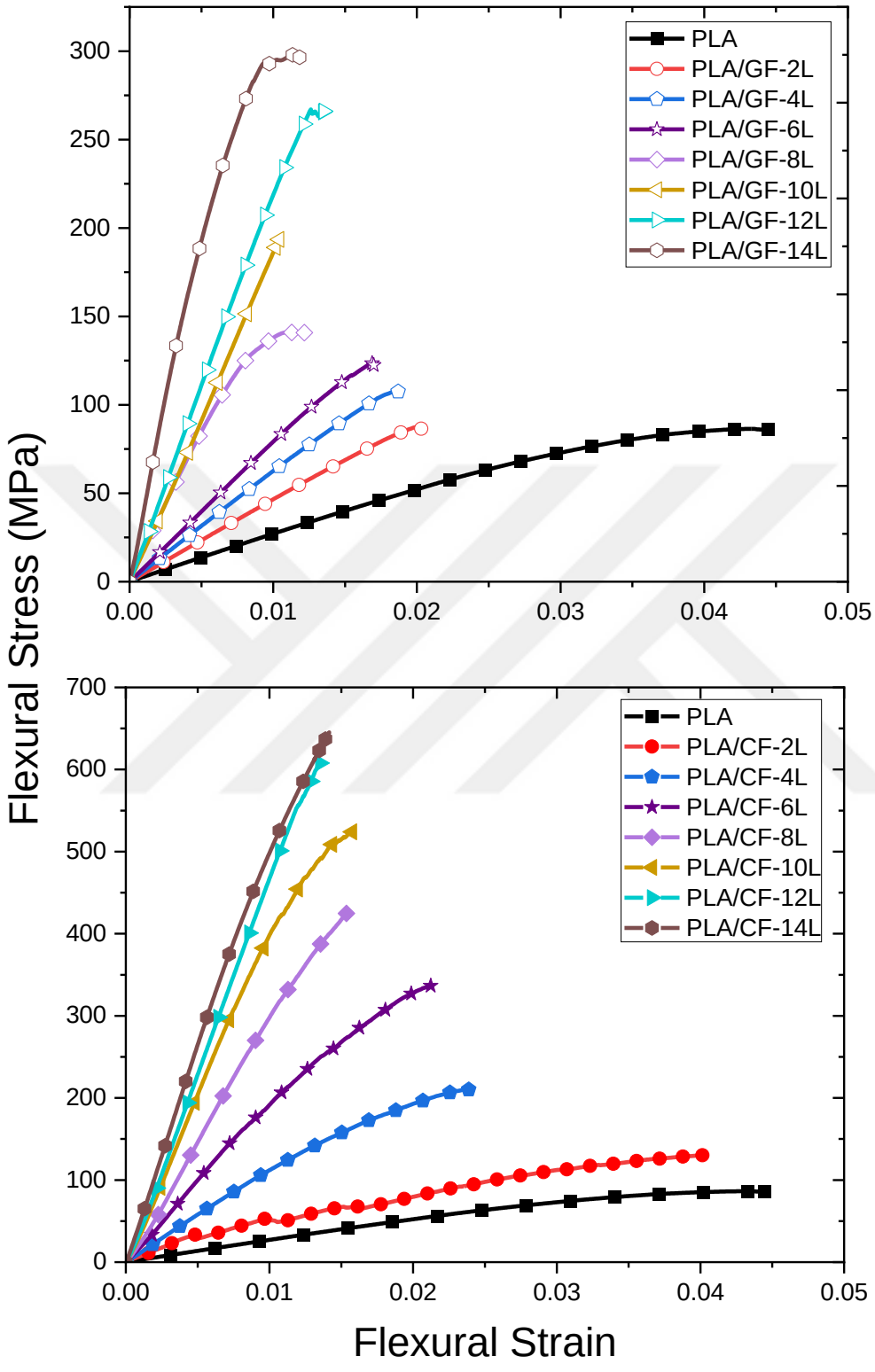


**Figure 3.6.** Flexural stress-strain curves of the PLA/GF (above) and PLA/CF (below) composite laminates

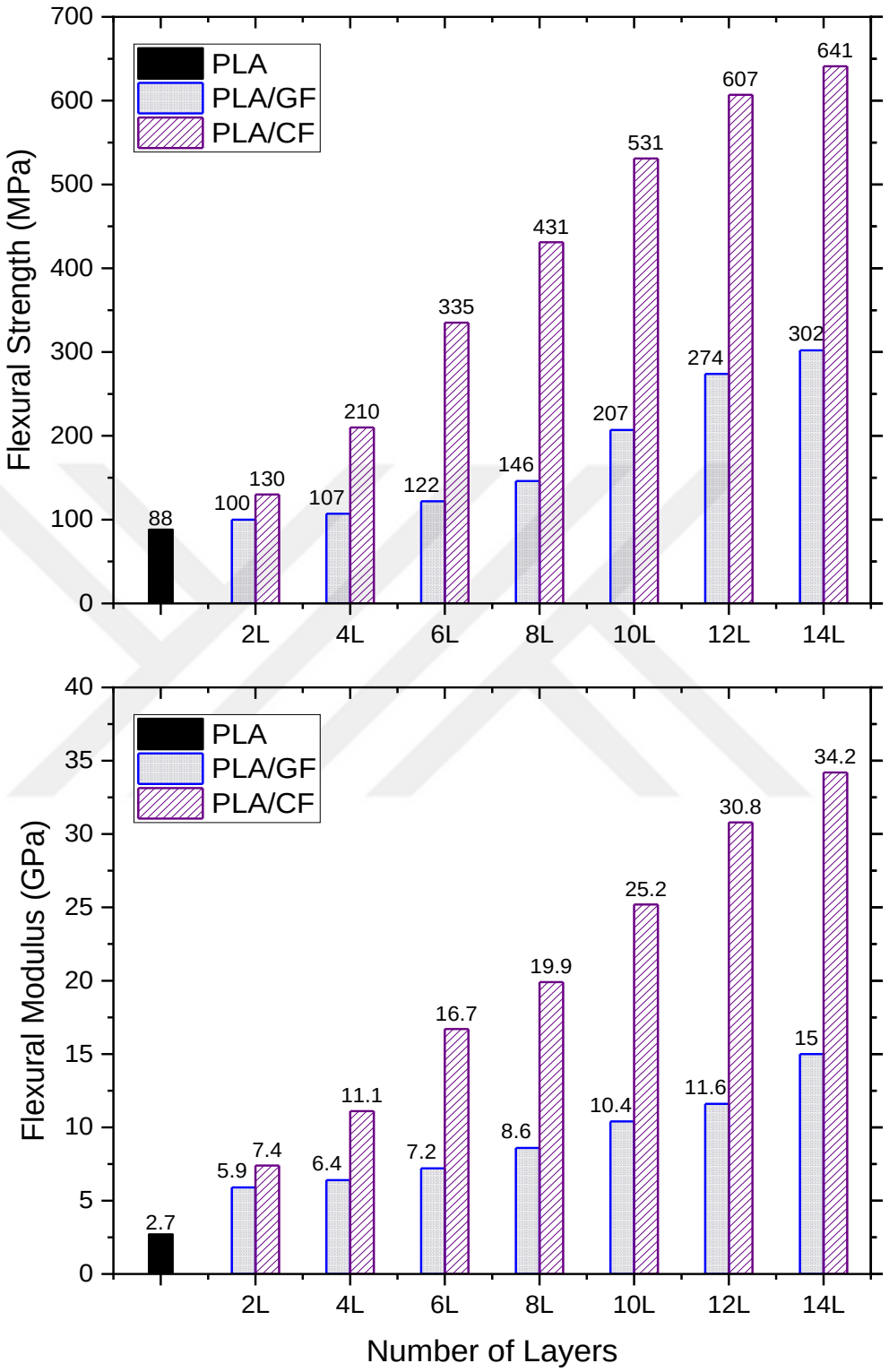


**Figure 3.7.** Effect of increasing number of layers on the flexural strength (above) and flexural modulus (below) of the composite laminates.

### 3.3.2 Comparison of the Mechanical Performance of PLA Laminates with Epoxy Laminates

In the past, since traditional thermoset Epoxy Resin systems were the most widely used matrix material for the laminated composite structures, our research group had certain studies on the Epoxy matrix laminates having exactly the same type of woven GF and CF layers in the beginning of this millennium. Those early studies investigate especially effects of many parameters of Resin Transfer Molding (RTM) method on the performance of Epoxy matrix laminates. In one of the studies [47], 14 layers of the same 1x1 plain weave GF fabrics were used. In the other one [48], 12 layers of the same 2x2 twill weave CF fabrics were used.

In the Table 3.3, flexural mechanical properties of the present study (PLA matrix) are compared with the highest values obtained in our previous studies (Epoxy matrix). When PLA matrix was used, it is seen that the decrease with respect to Flexural Strength of Epoxy/CF laminates was not significant, being only 9%, i.e. from 673 MPa to 607 MPa. On the other hand, the decrease with respect to Epoxy/GF laminate was important, being 45% decrease, i.e. from 553 MPa to 302 MPa. As discussed before, the main reason for this lower strength performance of PLA/GF laminate could be incompatible silane coupling agent of the Glass Fiber surfaces with PLA matrix.

Table 3.3 also indicates that decreases in the Flexural Modulus values compared to Epoxy laminates were around 20%, e.g. from 19 GPa to 15 GPa in GF laminates, while from 39 GPa to 31 GPa in CF laminates.

**Table 3.3.** Comparison of the Flexural Strength and Modulus values of the present study (PLA matrix) with our previous studies (Epoxy matrix) having the same type and number of GF and CF layers

| **Specimens** | **Flexural Strength (MPa)** | **Flexural Modulus (GPa)** |
|---|---|---|
| **Epoxy/GF-14L** | 553 | 19 |
| **PLA/GF-14L** | 302 | 15 |
| **Epoxy/CF-12L** | 673 | 39 |
| **PLA/CF-12L** | 607 | 31 |

However, in terms of structural engineering applications, it can be stated that there would be no significant problem in the stiffness performance of structures. Because, Flexural Modulus values of the PLA matrix laminates are in the same range with Epoxy matrix laminates, i.e. 15-19 GPa range for GF laminates, and 31-39 GPa range for CF laminates.

Therefore, it could be concluded that, in terms of mechanical performance; traditional thermoset Epoxy matrix could be replaced with the renewable biopolymer PLA matrix in the woven Carbon Fiber laminates. For the woven Glass Fiber laminates, a proper sizing treatment with a PLA compatible silane coupling agent would be necessary.

### 3.3.3 Flexural Failure Modes by Visual Observation and SEM Analysis

Flexural "Failure Modes" of the PLA laminate specimens are examined by comparing the possible failure modes given in ISO 14125 standard as illustrated in Figure 3.8 [46].

For this purpose, specimens after their three-point bending tests are first examined visually by taking photographic images as shown in Figure 3.9 for PLA/GF laminates and in Figure 3.10 for PLA/CF laminates. It was generally observed that PLA laminates had both "tensile failure" in the outermost bottom layers and "compressive failure" in the uppermost top layers. On the other hand, it was not easy to observe whether these laminates had "interlaminar shear failure" by these low magnification photographic images.

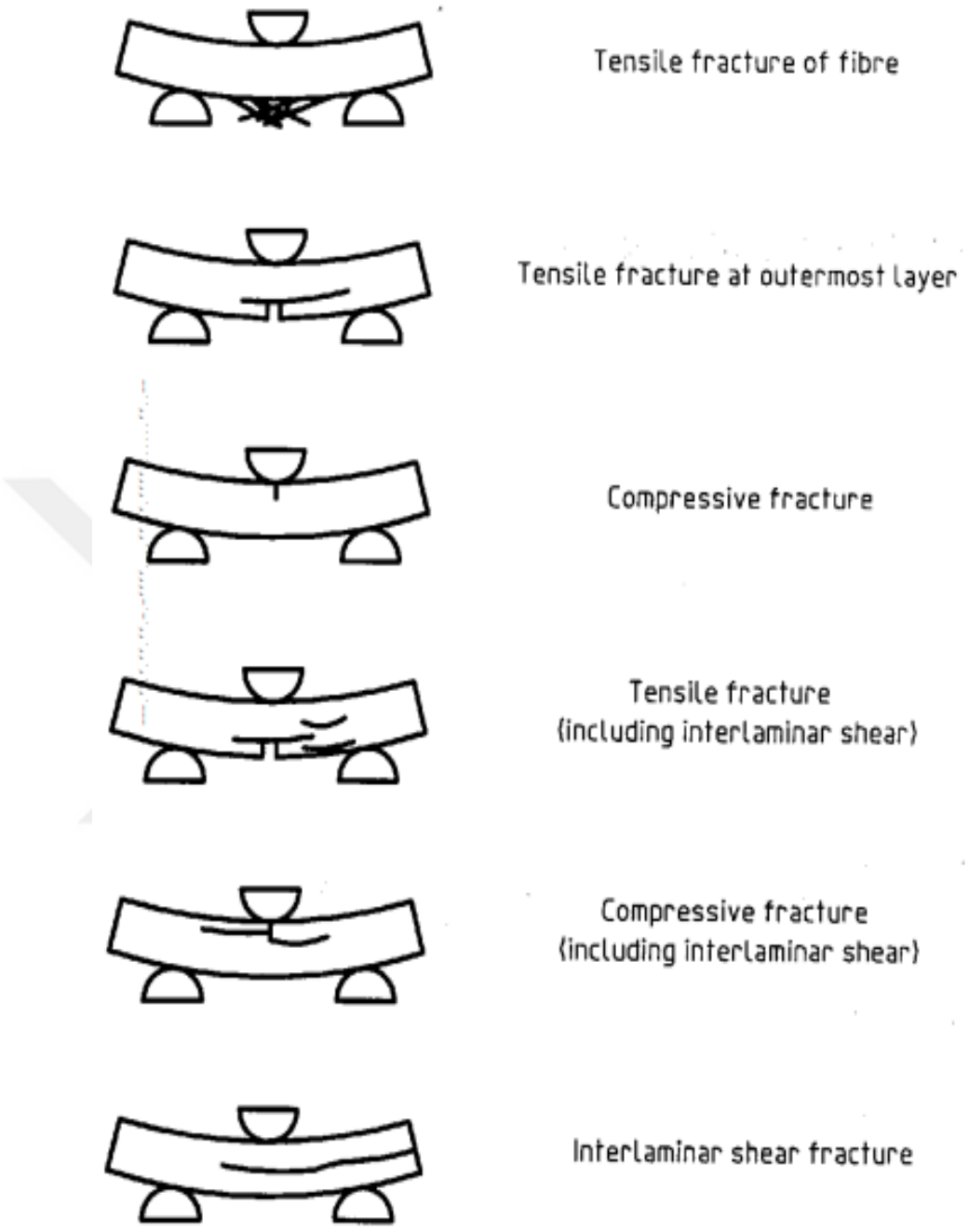


**Figure 3.8.** Possible flexural failure modes of composite laminate specimens given in ISO 14125 standard [46]

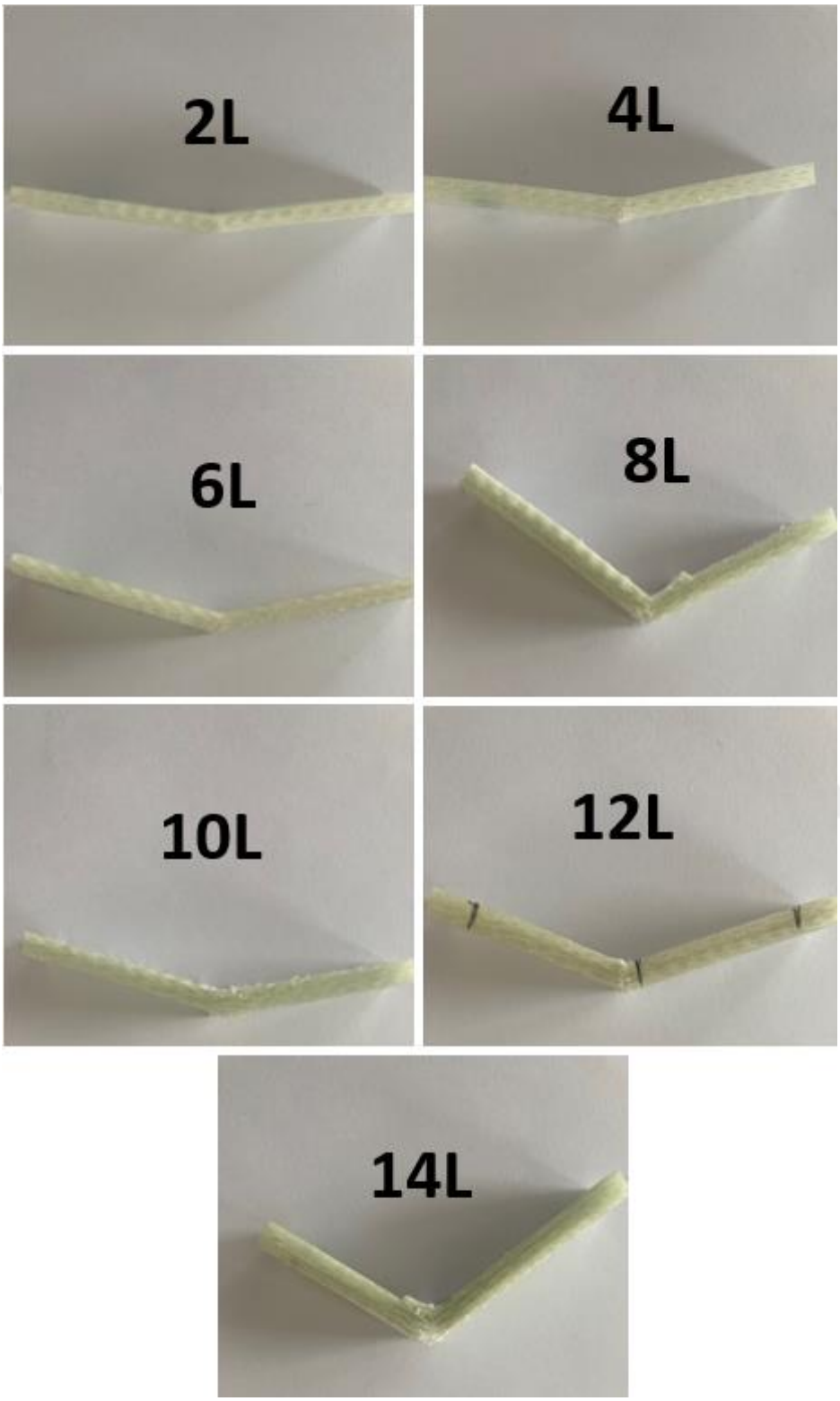


**Figure 3.9.** Photographic images showing general flexural failure modes of PLA/GF laminate specimens

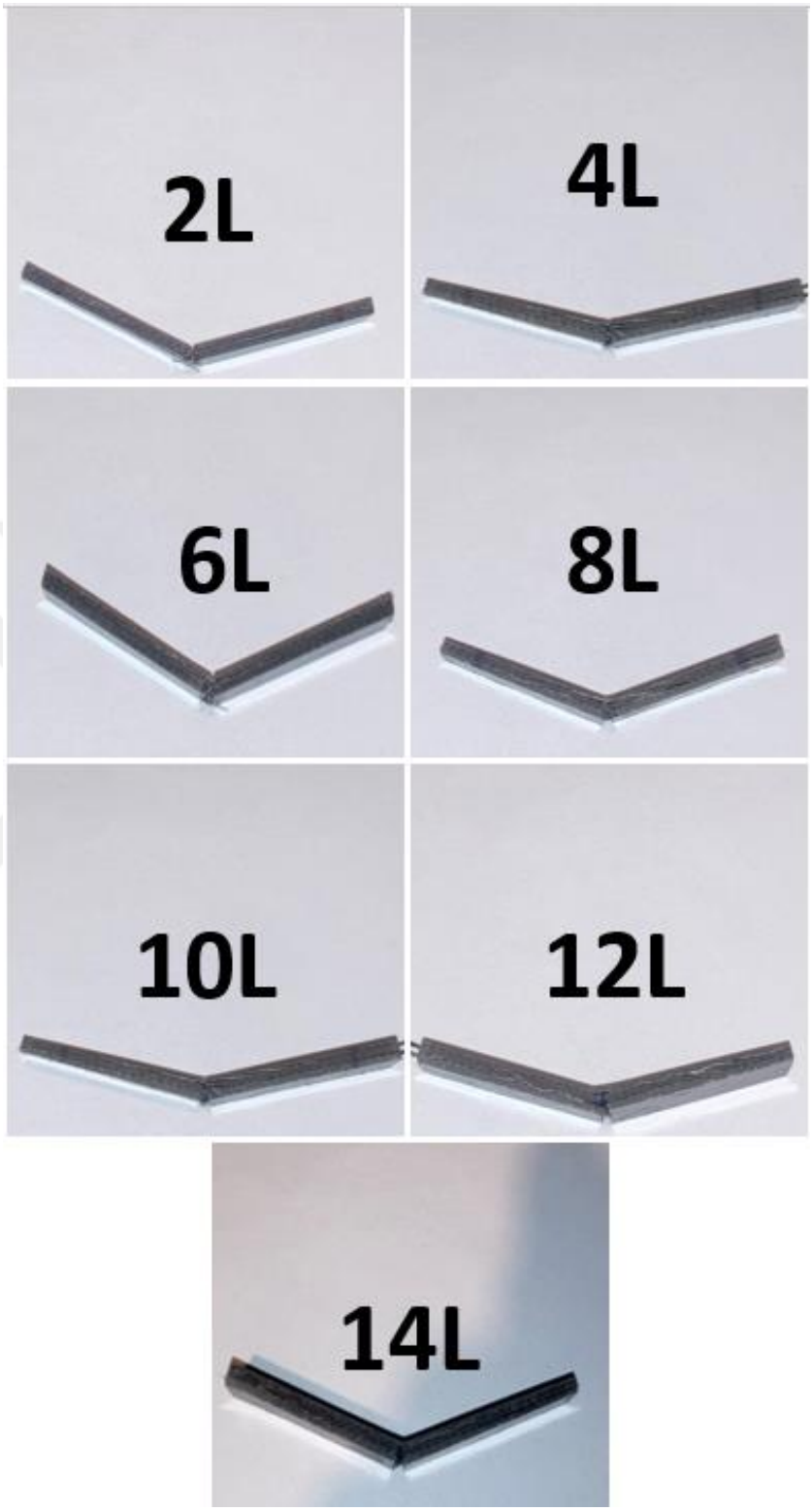


**Figure 3.10.** Photographic images showing general flexural failure modes of PLA/CF laminate specimens

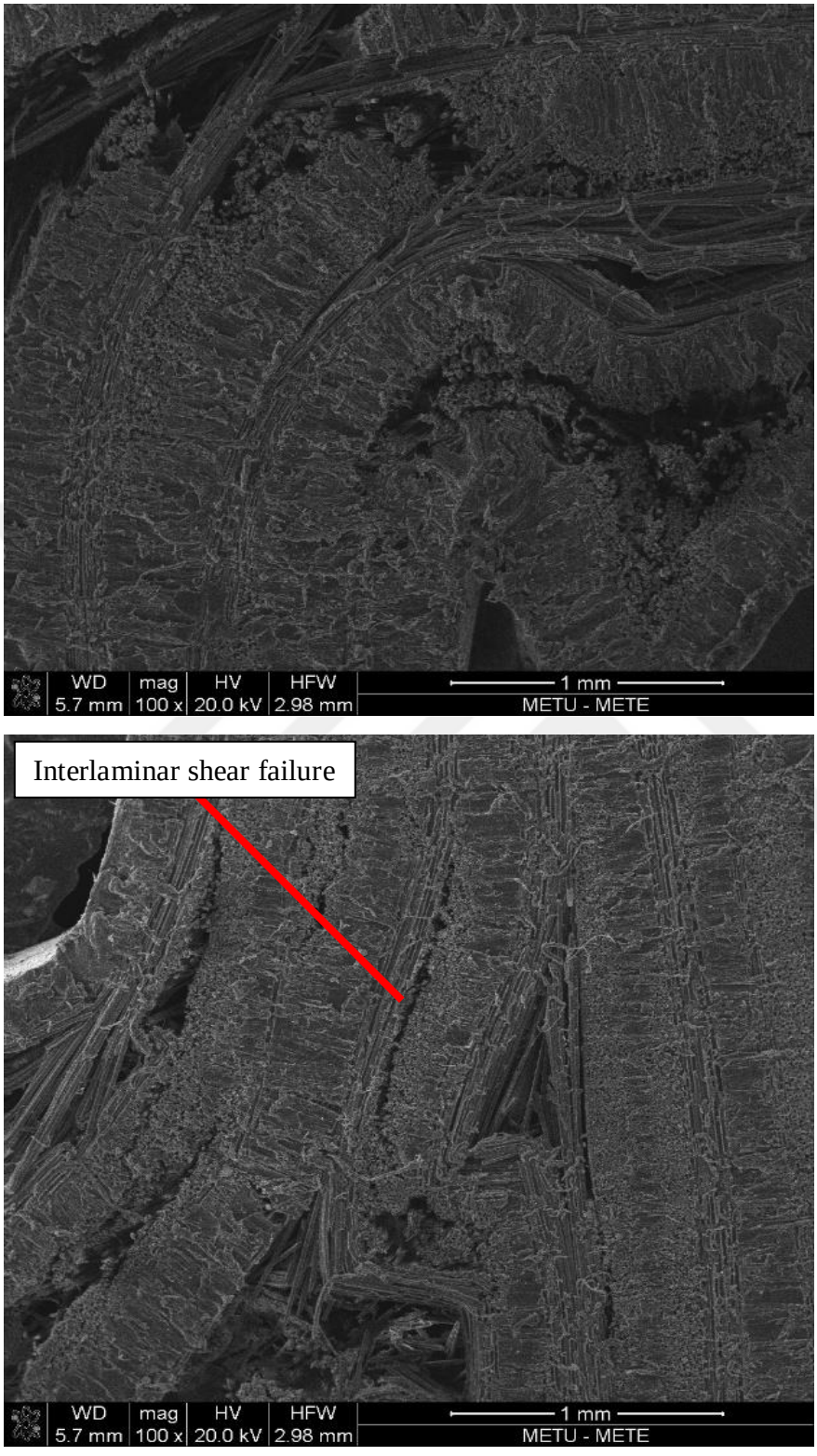


**Figure 3.11.** Through-thickness SEM images showing certain interlaminar shear failure in the PLA/GF laminate specimens




**Figure 3.12.** Through-thickness SEM images showing certain interlaminar shear failure in the PLA/CF laminate specimens

Therefore, higher magnification SEM analyses were also conducted to reveal certain interlaminar failure modes by examining the through thickness failure zones of the PLA laminates specimens. SEM images in Figures 3.11 and 3.12 showed that there is generally a certain level of interlaminar shear failure mode both in the PLA/GF and PLA/CF laminate specimens. Therefore, it can be concluded that flexural failure modes in the PLA laminates were a mixture of tensile failure in the lower layers, compressive failure in the upper layers, followed by interlaminar shear failure.

### 3.3.4 Fracture Surface Morphology by SEM Analysis

In order to observe Fracture Surface Morphology of the PLA laminates, tensile failure areas of the outermost lower layers were examined again by SEM analysis. It can be stated that in all PLA laminate specimens, typical fracture surface morphology features were observed; such as “Fiber Bridging”, “Fiber Fracture”, “Debonding and Fiber Pullout”.

For instance, Figure 3.13 shows “Fiber Bridging” mechanism in both Glass and Carbon Fiber laminates over cracking PLA matrix. After reaching a higher level of flexural stress, fibers started to break into shorter pieces. This “Fiber Fracture” mechanism is shown in Figures 3.14 and 3.15 for PLA/GF and PLA/CF laminates, respectively. As discussed before, due to the better compatibility of the silane coupling agents on the individual carbon fibers with PLA matrix; higher level PLA adhesion to the surfaces of carbon fibers can be seen in the higher magnification image of Figure 3.15.

Finally, Figure 3.16 shows “Debonding and Fiber Pull-out” mechanism of the Glass and Carbon Fibers from the PLA matrix. It is known that, after fracture of fibers, some pieces would remain in the matrix while those pieces having “Debonding” due to poor adhesion would be “pulled-out” from their matrices. Again due to better adhesion between the PLA matrix and Carbon Fibers discussed above; Figure 3.16 indicates that “the number of the pull-out holes” in the matrix was much lower.

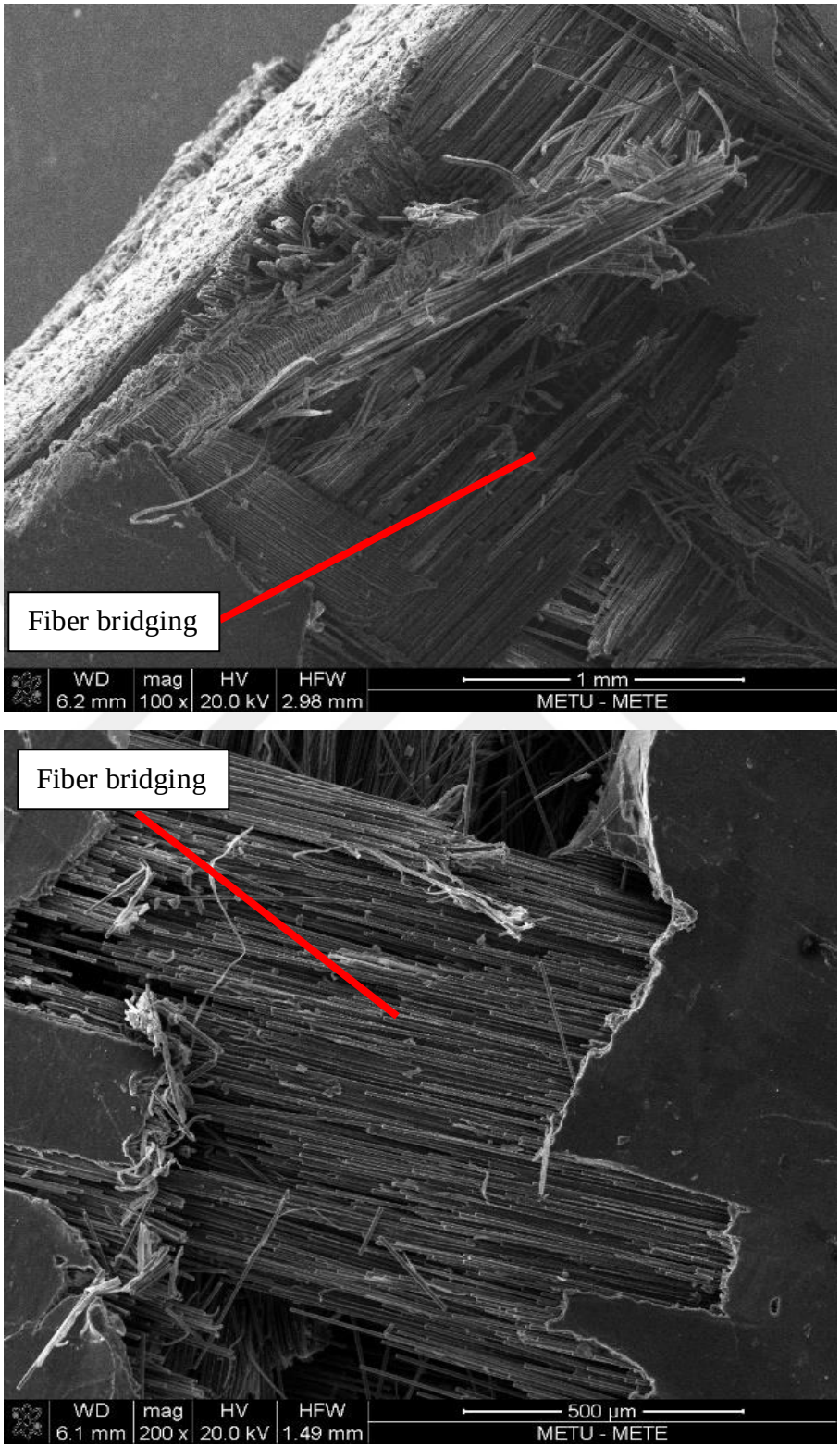


**Figure 3.13.** Fiber Bridging mechanism of Glass Fibers (above) and Carbon Fibers (below) over PLA matrix cracking

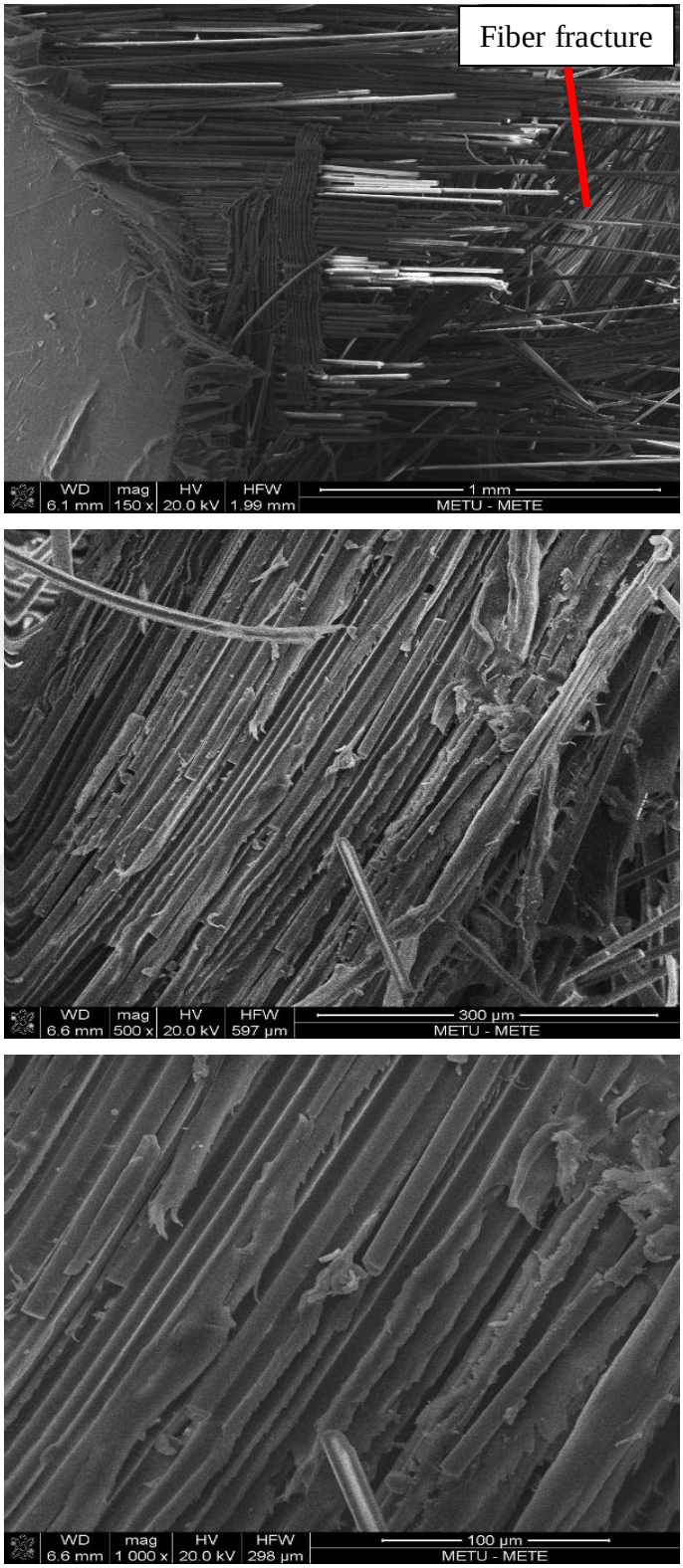


**Figure 3.14.** Fiber Fracture mechanism of PLA/GF laminates (images with increasing magnification)

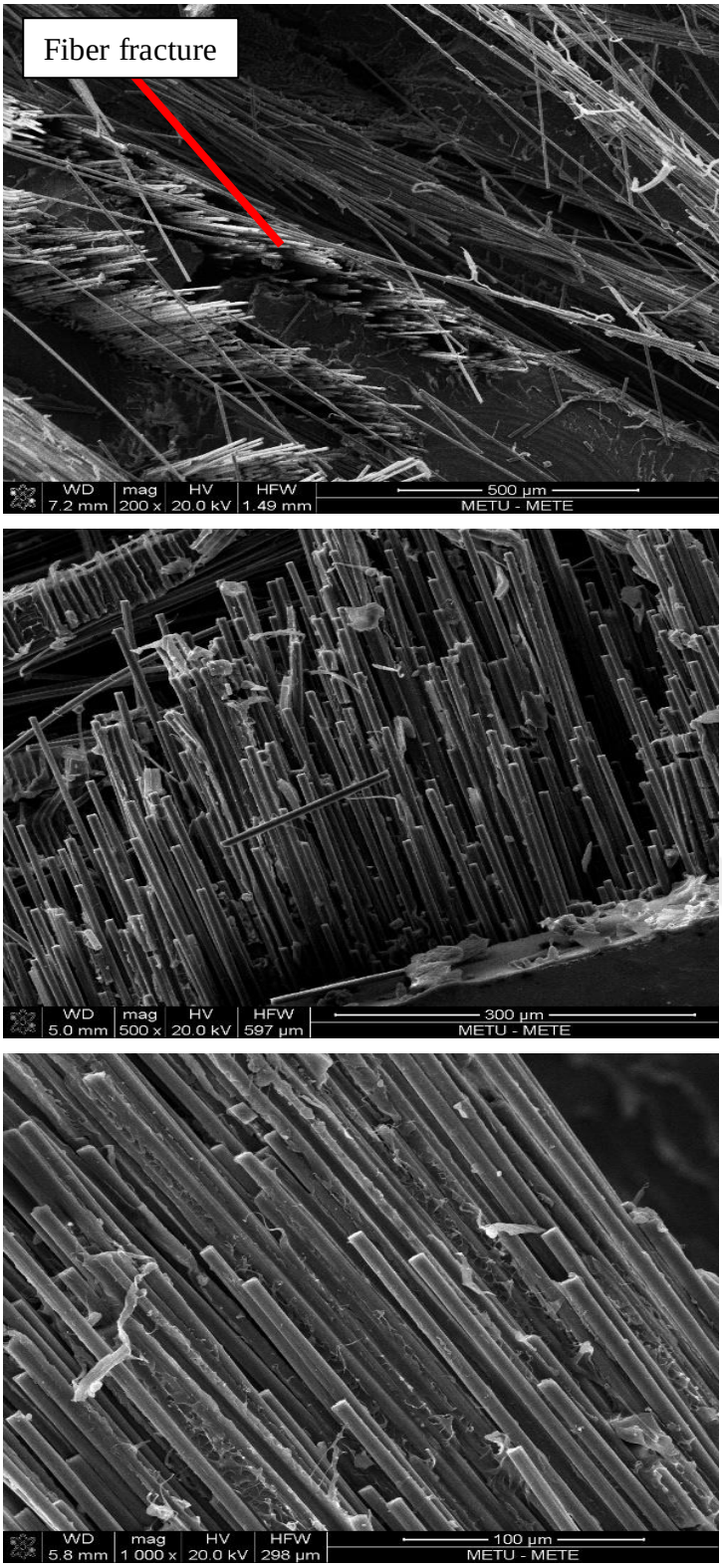


Figure 3.15. Fiber Fracture mechanism of PLA/CF laminates (images with increasing magnification)

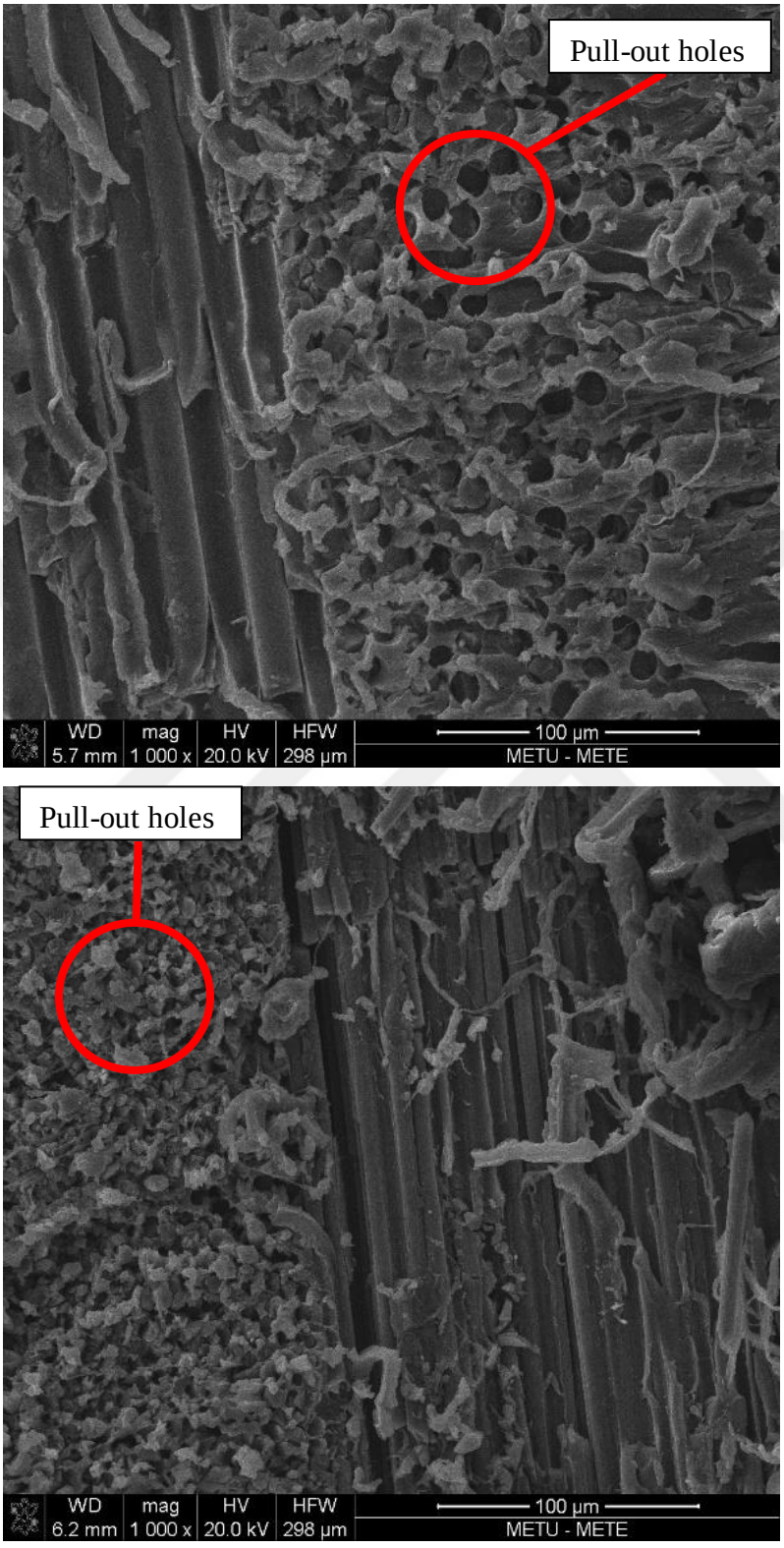


**Figure 3.16.** Debonding and Fiber Pull-out mechanism of Glass Fibers (above) and Carbon Fibers (below) from the PLA matrix

## 3.4 Thermal Behavior of the PLA Composite Laminates

In order to investigate the thermal behavior of the PLA/GF and PLA/CF laminates, two different analyses are carried out for the specimens of neat PLA and its laminates with 2, 6, 10 and 14 layers of GF and CF. The first one was Thermogravimetric Analysis (TGA) while the second one was Differential Scanning Calorimetry (DSC) analysis.

### 3.4.1 Thermal Degradation Temperatures of PLA Matrix and Percent Residue of Fibers by TGA

Thermogravimetric curves obtained for the laminate specimens were first compared with neat PLA as shown in Figure 3.17. Then, thermal degradation temperatures ($T_{5\%}$, $T_{10\%}$, $T_{25\%}$, $T_{max}$) at 5,10, 25% and Maximum mass losses of PLA matrix, and % Residue of Glass and Carbon Fibers left at 550 ℃ were determined from these curves; and the results are tabulated in Table 3.4.

It was observed that significant improvements in the thermal degradation temperatures of PLA matrix could be obtained by laminating with woven GF and CF layers. The improvements in the "Onset Thermal Degradation Temperatures" ($T_{5\%}$, $T_{10\%}$, $T_{25\%}$) was around 15%, while the improvement in the "Maximum Thermal Degradation" ($T_{max}$) was as much as 25%. For instance, $T_{5\%}$ Onset Thermal Degradation of neat PLA increased from 332 ℃ up to 379 ℃ in PLA/CF-14L laminate; and $T_{max}$ Thermal Degradation of PLA increased from 362 ℃ up to 455 ℃ in PLA/GF-14L laminate.

These increases could be related to the heat barrier effects of woven GF and CF layers. Since glass and carbon fibers have higher heat capacity than PLA, they absorb most of the heat and hinder degradation reactions of PLA molecules. Thus,

increasing the number of GF and CF layers resulted in successive increases in these thermal degradation temperatures.

Table 3.4 also revealed that % Residue of Glass and Carbon fibers at 550 ℃ basically resembles % Fiber Content of the PLA composite laminates. It is seen that %Fiber Content increases from around 20 wt% (in the 2L laminates) up to around 45 wt% (in the 14L laminates). As discussed in Section 3.1, these fiber content values are very close to the fiber content values determined by chemical decomposition method.

In previous studies carried out by our research group, temperature which thermal decomposition of epoxy matrix had started is reported between 300-360 ℃ and decomposition end temperature is reported between 650-723 ℃ [48]. It is evident that PLA cannot match high degradation temperatures of thermoset epoxy. Therefore, reinforcement of PLA matrix is necessary to replace Epoxy matrix with PLA for high temperature applications. However, TGA results show that thermal stability of PLA can be improved even when it is reinforced with macro-reinforcements.

**Table 3.4.** Thermal Degradation Temperatures ($T_{5\%}$, $T_{10\%}$, $T_{25\%}$, $T_{max}$) and % Residue of the specimens

| **Specimens** | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{25\%}$ (°C) | $T_{max}$ (°C) | **%Residue at 550 °C** |
|---|---|---|---|---|---|
| **PLA** | 332 | 342 | 353 | 362 | 0.16 |
| **PLA/GF-2L** | 353 | 362 | 377 | 416 | 21.67 |
| **PLA/GF-6L** | 363 | 377 | 395 | 442 | 40.86 |
| **PLA/GF-10L** | 365 | 380 | 399 | 450 | 44.23 |
| **PLA/GF-14L** | 369 | 381 | 401 | 455 | 45.14 |
| **PLA/CF-2L** | 360 | 372 | 387 | 443 | 19.71 |
| **PLA/CF-6L** | 363 | 375 | 392 | 445 | 39.54 |
| **PLA/CF-10L** | 375 | 385 | 400 | 446 | 40.15 |
| **PLA/CF-14L** | 379 | 392 | 408 | 447 | 41.23 |

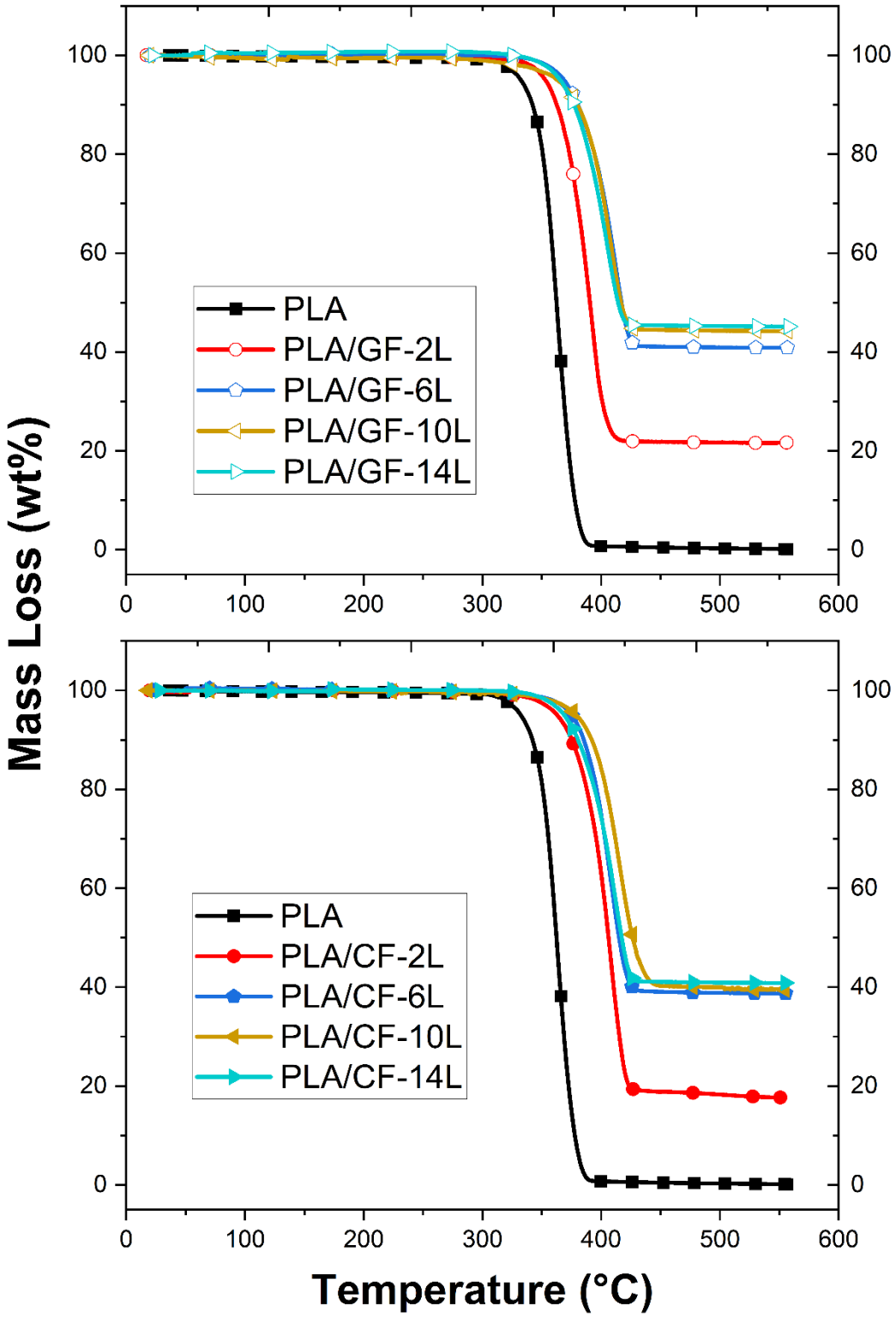


**Figure 3.17.** TGA curves of neat PLA and its GF (above) and CF (below) laminate specimens

### 3.4.2 Thermal Transition Temperatures and Crystallinity Amount of PLA Matrix by DSC

First heating DSC thermograms for the laminate specimens were first compared with neat PLA as shown in Figure 3.18. Then, important transition temperatures, such as Glass transition ($T_g$), cold crystallization ($T_c$) and melting ($T_m$) temperatures as well as enthalpy of melting ($\Delta H_m$) and enthalpy of crystallization ($\Delta H_c$) values together with percent crystallinity ($X_C$) of PLA matrix in the composite laminates determined from these curves are tabulated in Table 3.5. Note that, crystallization amounts were determined by using the equation given below:

$$X_c = \frac{\Delta H_m - \Delta H_c}{W_{PLA} \times \Delta H_m^{\circ}} \times 100$$

Where $W_{PLA}$ is weight fraction of PLA in composites which are reported in the previous sections, and $\Delta H^{\circ}_m$ is the melting enthalpy of 100% crystalline PLA, which is given as 93 J/g in literature [49].

Figure 3.18 shows that PLA matrix experiences three thermal events upon heating, an endothermic glass transition at 61 ℃ followed by exothermic cold crystallization at 109 ℃ and finally endothermic fusion at 169 ℃.

It is noticeable from Table 3.5 that laminating PLA matrix with GF and CF layers had almost no influence on the melting temperature ($T_m$) of PLA. On the other hand, woven fiber layers have important effects on the glass transition ($T_g$) and cold crystallization ($T_c$) temperatures of the PLA matrix.

When PLA matrix was laminated with GF and CF layers, its $T_g$ value increases by 6-7 ℃ reaching to 67-68 ℃; due to basically interlocking actions of the woven fiber layers which restricts the macromolecular chain mobility of PLA polymer.

In terms of cold crystallization ($T_c$) temperature, it is seen in Table 3.5 that $T_c$ of PLA matrix decreases by 6-11 ℃ when laminated with GF and CF layers. This decrease could originate from cooling condition of composite plates after consolidation

process. Also, Table 3.5 shows that % crystallinity of PLA increases when laminated with GF and CF layers. This can be related to the fact that fiber surfaces act as heterogenous nucleation sites for PLA macromolecular chains for crystallite nucleation and growth. Therefore, increasing the number of GF and CF layers increases the % crystallinity ($X_c$) of PLA matrix from around 5% up to around 15%, i.e. an increase of three-fold.

In the literature, average $T_g$ of Epoxy/CF laminates with similar fiber content are given as 163 ℃ [50] and that of Epoxy/GF laminates with similar fiber content are given as 118 ℃ [51]. Even though glass transition temperature of epoxy thermoset is excessively depended on curing conditions and crosslinking, glass transition temperature of Epoxy/CF and Epoxy/GF laminates are incomparably high. Therefore, in order to replace Epoxy matrix with PLA, additional reinforcements (e.g. nanofillers, nanoparticles etc.) must be applied to PLA matrix in terms of thermal properties. However, similar to thermal degradation, a slight improvement in thermal properties of PLA is achieved even with macro-reinforcements.

**Table 3.5.** Transition Temperatures ($T_g$, $T_c$, $T_m$), Enthalpies ($\Delta H_m$ and $\Delta H_c$) and %Crystallinity ($X_c$) of the specimens

| **Specimens** | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $\Delta H_c$ (J/g) | $X_C$ (%) |
|---|---|---|---|---|---|---|
| **PLA** | 61 | 109 | 169 | 48.9 | 44.1 | 5.27 |
| **PLA/GF-2L** | 67 | 100 | 169 | 35.6 | 27.3 | 11.39 |
| **PLA/GF-6L** | 67 | 104 | 169 | 33.2 | 26.1 | 13.09 |
| **PLA/GF-10L** | 65 | 103 | 171 | 24.1 | 17.1 | 13.52 |
| **PLA/GF-14L** | 66 | 102 | 170 | 28.1 | 20.9 | 13.69 |
| **PLA/CF-2L** | 67 | 101 | 171 | 37.3 | 28.1 | 12.15 |
| **PLA/CF-6L** | 68 | 98 | 170 | 34.7 | 26.6 | 14.55 |
| **PLA/CF-10L** | 68 | 98 | 169 | 33.6 | 25.3 | 14.76 |
| **PLA/CF-14L** | 67 | 98 | 168 | 25.1 | 16.9 | 14.82 |

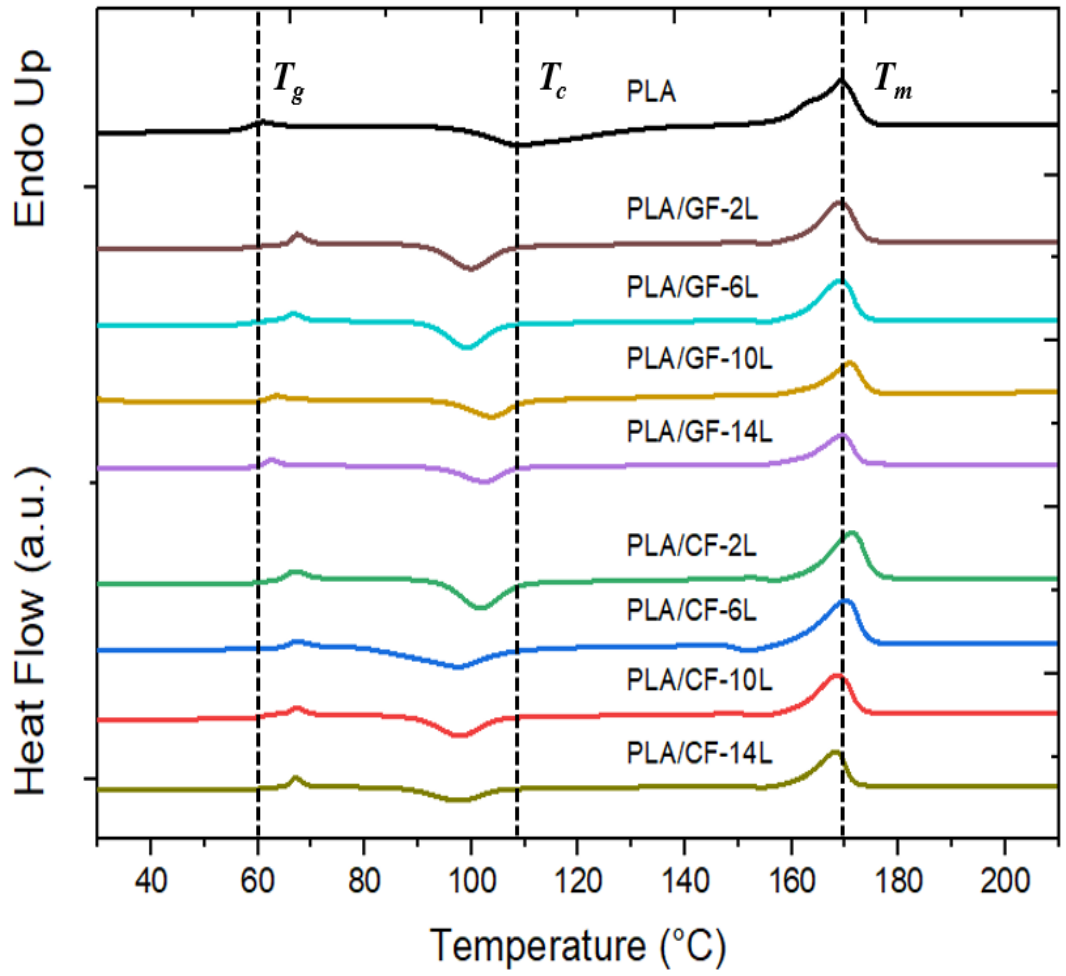


**Figure 3.18.** First heating DSC thermograms of neat PLA and its GF and CF laminate specimens

# CHAPTER 4

# CONCLUSIONS

The main conclusions drawn from this study can be summarized as follows:

- Both Chemical Decomposition method and Thermogravimetric Analysis indicated that, apart from the laminates having only 2 and 4 layers, fiber content in the rest of the laminates were in between 40-45 wt%; which could be considered as a reasonable content for many structural applications.
- Through thickness SEM images showed that certain level of adhesion between the PLA/GF and PLA/CF layers were achieved. There was no apparent "delamination" problem in the composite plates. Closer view SEM images revealed that sizing on the individual Carbon Fibers was more compatible with the PLA macromolecules compared with the sizing on the individual Glass Fibers.
- Interlaminar Shear Strength (ILSS) values for the PLA/GF laminates were between 15-19 MPa, while for the PLA/CF laminates they were in between 20-38 MPa.
- The increase in the Flexural Strength of neat PLA was more than 3 times when laminated with 14 layers of GF (i.e. from 88 MPa to 302 MPa), while it was more than 6 times when laminated with 14 layers of CF (i.e. up to 641 MPa).
- Increases in Flexural Modulus values was more than 5 times (i.e. from 2.7 GPa to 15 GPa) in PLA/GF-14L laminate, while it was more than 12 times (i.e. up to 34 GPa) in PLA/CF-14L laminate.
- Use of woven CF layers was much more efficient compared to woven GF layers, being more than 2 times both in the Flexural Strength and Flexural Modulus values. The main reason would be higher mechanical properties of individual Carbon Fibers compared to Glass Fibers.

- Comparison of the PLA matrix with Epoxy matrix having exactly the same type and number of GF and CF layers indicated that the decrease with respect to Flexural Strength of Epoxy/CF laminates was not significant, being only 9%, i.e. from 673 MPa to 607 MPa. On the other hand, the decrease with respect to Epoxy/GF laminate was 45%, i.e. from 553 MPa to 302 MPa. The main reason for this lower strength performance of PLA/GF laminate could be incompatible silane coupling agent of the Glass Fiber surfaces with PLA matrix.
- Decreases in the Flexural Modulus values of the Epoxy matrix laminates were from 19 GPa to 15 GPa in GF laminates, and from 39 GPa to 31 GPa in CF laminates. In terms of structural engineering applications, these same ranges of modulus values would not be a significant problem in the stiffness performance of structures.
- TG Analysis indicated that significant improvements in the thermal degradation temperatures of PLA matrix could be obtained by laminating with woven GF and CF layers. The improvements in the "Onset Thermal Degradation Temperatures" ($T_{5\%}$, $T_{10\%}$, $T_{25\%}$) was around 15%, while the improvement in the "Maximum Thermal Degradation" ($T_{max}$) was as much as 25%.
- DSC Analysis revealed that GF and CF layers increased glass transition ($T_g$) of the PLA matrix by 6-7°C, while decreased its cold crystallization ($T_c$) temperature by 6-11°C.
- Laminating PLA with GF and CF layers leads to increases in the % crystallinity ($X_c$) of PLA matrix from around 5% up to around 15%, i.e. an increase of three-fold.

Therefore, it could be generally concluded that, in terms of mechanical performance; traditional thermoset Epoxy matrix could be replaced with the renewable biopolymer PLA matrix in the Woven Carbon Fiber laminates. For the Woven Glass Fiber laminates, a proper sizing treatment with a PLA compatible silane coupling agent would be necessary.

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