DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THERMAL AND MECHANICAL PROPERTIES OF CONTINUOUS FIBER REINFORCED THERMOPLASTICS

by Hamdi BAL

November, 2009 İZMİR

THERMAL AND MECHANICAL PROPERTIES OF CONTINUOUS FIBER REINFORCED THERMOPLASTICS

A Thesis Submitted to the

Graduate School of Natural and Applied Sciences of Dokuz Eylül University In Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering, Energy Program

> by Hamdi BAL

November, 2009 İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled "THERMAL AND MECHANICAL PROPERTIES OF CONTINUOUS FIBER REINFORCED THERMOPLASTICS" completed by HAMDİ BAL supervision of ASSOC.PROF. DİLEK KUMLUTAŞ and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assoc. Prof. DİLEK KUMLUTAŞ

Supervisor

Prof. Dr. İsmail Hakkı TAVMAN

Prof. Dr. Sevgi ULUTAN

(Jury Member)

(Jury Member)

Prof. Dr. Cahit HELVACI Director Graduate School of Natural and Applied Sciences

ACKNOWLEDGEMENTS

I wish to express gratitude to my advisor, Assoc. Prof. Dilek KUMLUTAŞ for her continuous support and guidance through this work. I would like to thank Research Assistant Mr. Haktan KARADENIZ for his benevolence during thermal tests.

Thanks are also extended to my work mates Mr. Serkan BENGÜ, Mr. Kenan ÖZGÜLENLER, and Mr. Gürhan GERELİ for their unconditional support during this study.

Special gratitude must be expressed to my parents, Nermin and Ertuğrul BAL, and my brother Ertuğ BAL for their continuous support, understanding, and encouragement.

Hamdi BAL

THERMAL AND MECHANICAL PROPERTIES OF CONTINUOUS FIBER REINFORCED THERMOPLASTICS

ABSTRACT

In this study the composite materials explained first. Then some general thoughts about thermoplastic and thermoset based composites were given. General information about the developments of production methods for the continuous fiber reinforced thermoplastic composites was given.

The thermal conductivity and mechanical properties such as tensile strength, elongation at break, modulus of elasticity, flexural and impact properties of composites are investigated experimentally. After then the test results are compared with existing theories. First of all continuous fiber reinforced thermoplastic prepreg tape production process is developed to make these thermoplastic composite specimens. Unidirectional carbon and glass fiber reinforced polypropylene prepreg were produced using this process.

Tests were grouped in two sections as mechanical and thermal. Tensile, flexural and impact tests were applied which are common tests for mechanical properties. Transverse thermal conductivity tests were made with the specimens for thermal tests. Test results were compared with theoretical models which are also explained detailed within the tests.

In addition these tests, SEM photographs were taken both prepreg materials with different magnification to understand matrix-fiber interaction.

Keywords: composite materials, unidirectional thermoplastic composite, tensile test, thermal conductivity.

SÜREKLİ ELYAF TAKVİYELİ TERMOPLASTİKLERİN MEKANİK VE TERMAL ÖZELLİKLERİ

ÖZ

Bu çalışmada öncelikle kompozit malzemeler tanıtılmıştır. Termoset ve termoplastik kompozit malzemeler hakkında genel bilgiler verilmiştir. Daha sonra sürekli elyaf takviyeli termoplastik kompozit malzemelerin üretimine ilişkin gelişmeler aktarılmıştır

Termal iletkenlik ve çekme dayanımı, kopma uzaması, elastisite modulu, eğilme ve darbe dayanımı gibi mekanik özellikler, testler ile araştırılarak mevcut teorik modeller ile karşılaştırılmıştır. Bu testler için gerekli test numunelerinin elde edilebilmesi için öncelikle sürekli elyaf takviyeli termoplastik prepreg üretim yöntemi geliştirilmiştir. Bu yöntem kullanılarak sürekli karbon ve cam elyaf takviyeli polipropilen prepreg malzemeler üretilmiştir.

Gerçekleştirilen testler termal ve mekanik testler olmak üzere iki grupta incelenmiştir. Mekanik test olarak malzemenin genel mekanik karakteristiğini veren çekme testi ile eğme ve darbe testleri uygulanmıştır. Termal test olarak ise elyaf düzlemine dik yöndeki termal iletkenlik testleri yapılmıştır. Elde edilen test sonuçları teorik modeller ile karşılaştırılarak değerlendirilmiştir. Bu teorik modeller testlerle birlikte detaylı bir şekilde anlatılmıştır.

Bu testlere ek olarak incelenen prepreg malzemelere ait SEM fotoğrafları alınmıştır. Bu fotoğraflar ile matris ile elyafın birbirleri ile olan etkileşimi araştırılmıştır.

Anahtar sözcükler: kompozit malzemeler, tek yönlü termoplastik kompozit, çekme testi, termal iletkenlik.

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CHAPTER ONE

INTRODUCTION

A composite material consist two or more constituents and they combined at a macroscopic level to get a unique combination of properties. The Modern structural composites, frequently referred to as "Advanced Composites", are a blend of the reinforcing phase and the one in which it is embedded is called the matrix.

The concept of composite material was not invented by human being. The examples of composite material found in the nature. For example wood is a composite material which is a composite of cellulose fibers in a matrix of natural glue called lignin. The shell of oysters is an example of a composite which are stronger and tougher than man-made advanced composites (Kaw, 2006).

On the other hand mixing two or more material for getting new material is used for a long time. There is lots of information in literature including usage of composite materials in historical ages (Table 1.1). However the most significant composite material is the combination of mud and bamboo shoot which is used in house walls by Egyptians (Mazumdar, 2002).

500BC	Building/Civil	Mud and Straw Bricks Great Wall of China (in desert regions)
	Defense Weaponry	Laminated Bows
	Transport	Laminated Chariot Wheels
500-1000AD	Building/Civil	Wattle & Daub Cottages
	Defense Weaponry	English Longbow
	Transport	Laminated Cart Wheels
1900AD+	Building/Civil	Steel Reinforced Concrete
	Defense Weaponry	Military Aircraft Radomes
	Transport	Doped fabrics for Aircraft Ford Hemp Car Modern fiber reinforced polymer structures (e.g. Aircraft and car body structural components)
	Sport/Leisure	Tennis racquets Golf Club shafts Surf Boards and Skis

Table 1.1 Chronological usage of composite materials (Bond, 2005)

Modern composite materials are first introduced in 1930s using glass fiber and polyester in marine, air vehicles. This composite material called as "fiberglass" and this definition is already in use as a common expression for polyester glass fiber composites (Kaw, 2006).

By the 1960s the carbon and boron fibers are developed. These developments help understanding of composite materials capabilities in various applications.

Especially in military and aerospace, new materials are needed and composite materials developed in parallel these needs. New advanced engineering composites play an important role for the future aerospace design concepts. The main factor using composite material is the high ratios of strength/density and rigidity/density.

Besides composite materials used in transportation, sporting goods or other house equipments. The main obstacle for composites to become a common material is the price of the composite material and its constituents. However new generation composite materials and production methods will increase the composite material usage.

Composite material consists of two or more constituents and these constituents called as matrix and reinforcement. Matrix phase is usually continuous. Matrix phase is tougher than reinforcement; it supports and binds the reinforcement together. Matrix material provides environmental protection for the reinforcement. It transmits load from one piece of reinforcement to the other (usually by shear load), and carries the shear stresses of the composite. Matrix material protects reinforcement from mechanical and chemical damages. Reinforcements are continuous or discontinuous. Reinforcements increase the thermal stability and the load carriage capability of composites. Reinforcements are stiffer than the matrix material (Bond, 2005).

Composite materials may have different forms using different polymer, metal and ceramic combinations.

In polymer composite which is the main subject of this study, thermoset and thermoplastic are used as matrix material. Glass fibers, carbon fiber, aramid, boron and natural fibers are used as reinforcing materials.

Both thermoset and thermoplastic materials have some advantages – disadvantages however in composite production applications usually thermosets are used as matrix material. Thermoset has a ratio of 85% in composite material production market in 1995 (Hamada, Fujihara & Harada, 2000).

For a few last decades thermoplastics are began to use in composite production because of their production capabilities and environmental advantages. Usage of thermoplastic composites in automotive, transportation, naval and aerospace industries increase for these benefits (Bureau & Denault, 2004).

After the first modern plastics synthesized in 1900s, the development of thermoplastics make them useful in as an engineering material by the end of the 1930s. The most important properties of the thermoplastics compared with metals are low density, easy processing, high surface quality and resistance to corrosive affects. Although thermoplastics have all these advantages, the mechanical properties of the thermoplastics are low compared with metals. To make the thermoplastics as a competitive material to metals, reinforcing them with fibers have been studying. First polymeric composites introduced 1950s which are made of thermoset materials. These polymeric composite materials have high mechanical properties, good dimensional and thermal stability. With the new developments in fiber, material studies make polymeric composite materials as a competitive material for metals and become popular in industrial applications.

On the other hand thermoplastics are used instead of thermosets in polymeric composite productions. Especially with the development of the advanced engineering thermoplastics which are polyetheretherketone (PEEK), polyphenysulfide (PPS) or polycarbonate (PC) makes thermoplastics as composite matrix material.

Besides polypropylene (PP) which is synthesized first by Natta in 1955 has good thermal stability, resistance to corrosion, easy processing and low cost makes PP as candidate matrix material for thermoplastic composites (Hamada et al. 2000).

Discontinuous or continuous composite materials can be produced by using thermoplastics. With the development in continuous reinforced polymeric materials, the "Laminated Plate Theory" was generated (Bond, 2005).

The amount of the polymeric composite material used for composite production is increasing day by day. For this reason the composite materials which are ready to make composite parts are needed to increase production speed and capacity. These materials called as "prepreg" which are designed for different manufacturing techniques to make end product. The expression prepreg comes from the pre-impregnation. They already contain an amount of the matrix which can be thermoset or thermoplastic material used to bond them together and to other components during manufacture. Prepregs can be made from unidirectional, mat or fabric fibers which can be glass, carbon or aramid. Prepregs are also used with honeycombs to make sandwich structures (Mazumdar, 2002)

In unidirectional reinforced prepregs, the thermal and mechanical properties are designed by orientation of the plies.

Usually epoxy is used in thermoset prepreg and hand lay-up is used for as production process. These prepreg plies are stowed and made a sheet which is stored in refrigerated room.

For thermoplastic prepreg production, usually melt-impregnation, powderimpregnation and film stacking processes are used (Mota, Nunes & Pouzada, 2000).

The machineries and equipments change according to the forms and using matrix material. There are also some methods which are not for continuous production process and used to produce sample for studies (Kumar, Bhatnagar & Ghosh, 2007).

The most important point for composite production is the adhesion between the fibers and matrix material. To improve the bond structure between the fibers and matrix, some additives are used in matrix material. On the other hand the coating is applied on to the fibers to improve the adhesion.

Mäder, Rothe & Gao (2007) used commingled glass fiber-polypropylene and they studied mechanical properties of this thermoplastic composite material. They investigated transverse tensile strength and compression shear strength of commingled glass fiber polypropylene. They found that coating aminosilane on to glass fiber and maleic anhydride grafted polypropylene (MAH-g-PP) improve the mechanical properties of glass fiber polypropylene composites. They used 3% MAH-g-PP by weight in this study.

Another study made by Denault & Dumouchel (1998) which investigates the effect of the crystalline morphology on to the mechanical properties of thermoplastic composites. They used unidirectional PEEK-carbon fiber prepreg and made tensile tests at transverse axis and $\pm 45^{\circ}$ orientation. They found out crystalline morphology affect on tensile tests using different consolidation times. Couque, Albertini & Lankford (1993) also used unidirectional PEEK-carbon fiber prepreg as material and studied compressive strength under hydrostatic pressure.

Jang & Lee (1998) studied mechanical properties of glass and carbon fiber reinforced polypropylene composites. They used glass and carbon fiber as discontinuous (chopped) and the volumetric fiber content is 20%.

There is another study for a mechanical property of glass fiber reinforced thermoplastic material which is polyamide (PA6) have realized by Han, Liu & Yu (2005). They have mentioned that the glass fiber content in the marketed short fiber reinforced polymers is usually limited to 33% wt with a maximum of about 45% wt. This means that the stiffness and strength of the resultant composites may still be too

low for some potential applications. Although they have investigated long glass fiber reinforced PA6 to increase fiber content, they can only reach 60% wt fiber contents.

However in this study glass fiber content is 65% wt and mechanical properties are higher than short or long glass fiber reinforced thermoplastics because of continuous fiber phase.

On the other hand there are different studies for thermal properties of composites. Assael, Antoniadis, Metaxa & Tzetziss (2008) studied thermal conductivity of the plain weave glass fabric and carbon multiwalled nanotubes reinforced epoxy composite. They used the transient hot-wire technique for thermal conductivity tests.

McIvor, Darby, Wostenholm, Yates, Banfield, King & Webb (1990) investigated thermal conductivities of carbon and R-glass fiber reinforced plastics (thermoset) over the temperature range (-150)-(130) °C. They studied both axis parallel and perpendicular fiber directions.

During the solidification of the thermosetting composite exothermic reaction occurs. This process is called curing and the structure of the composite modified by this process. The structure of the composite induces the thermophysical properties, especially the thermal conductivity. Bailleul, Delaunay, Jarny & Jurkowski (2001) measured the thermal conductivity of unidirectional fiber glass reinforced epoxy resin for different curing rate.

Tai (1998) studied the fiber shape effects on to the transverse thermal conductivity of unidirectional composite, using the model which is generated by Springer &Tsai in 1967.

There are different studies for thermal conductivity for unidirectional composite using numerical calculations (Rocha & Cruz, 2001) or finite difference method (James, Wostenholm, Keen & Mclvor, 1987).

Recent studies about thermal conductivity of composite materials are mostly for thermosetting materials and there are few studies which are used thermoplastic as matrix materials in unidirectional reinforced composite.

In this study unidirectional reinforced thermoplastic prepregs are used as a material. Polypropylene is used as matrix; glass fiber and carbon fiber are used as reinforcing material. After the prepreg production step the tests were applied. Thermal and mechanical properties of these continuous unidirectional reinforced thermoplastic composites were investigated in this study.

CHAPTER TWO

COMPOSITE MATERIALS

Composite materials are made of combining two or more material at a macroscopic level to get unique properties. The constituents of the composite materials differ as a matrix and reinforcement. Composite material is a very common expression and there are lots of example for the composite materials made of different matrices and reinforcements. In this chapter the polymeric composite materials are studied. In the next chapters "Chapter Three" and "Chapter Four" unidirectional thermoplastic composite materials are explained.

2.1 Matrix Materials

Reinforcement materials are embedded into the matrix materials. The matrix materials have three main missions for the composites. These are;

- a) The matrix materials bids the reinforcement fibers together,
- b) The matrix materials isolate the reinforcement fibers from environmental effects,
- c) The matrix material transfers the load to the fibers.

The adhesion between the matrix and reinforcement, amount of void in the composite and orientation of the fibers into the matrix affect directly the structural properties of the composite materials.

Matrix material differs depending on the fibers which are used in the composite materials. Matrix material can be ceramic, metal alloys or polymeric material.

In this study the composite materials which have thermoplastic materials as matrix was investigated.

In polymeric composite materials two kinds of matrix are used as thermoset and thermoplastic materials.

2.1.1 Thermoset Materials

Thermoset materials are the most common matrix material used in composite material production. These materials are liquid form into the room conditions. After the matrix and fibers combined to make composite part, the heat has to apply on to the composite part for solidification and to get the end product shapes. In this process chemical reaction occurs while the composite get its rigidity.

By the polymerization new molecules come into which have strong adhesion bonding. This molecule bonding is called "cross-linking". The short monomer molecules change in this reaction and long three dimensional new bonds form. This process called "Curing" as production step and chemically "Polymerization". The amount of cross-linking increases the strength of the final composite part. After this process the composite part is rigid. Even heat applied on to the composite part, it will not soften again. So after the curing, composite part can not formed. For this reason thermoset materials keep into low temperature places to avoid curing. Thermoset materials have high thermal and dimension stability, higher electrical and chemical resistance.

The most common thermoset materials are epoxy, polyester, vinyl ester, polyurethane and phenolic resins which are used for making composite materials.

2.1.1.1 Epoxy

Epoxy is a versatile resin which can be used in different processes. The first epoxy resin introduced by "The Shell Chemical Corporation" in 1941 and its good property profile has been utilized in a wide range of applications (Harper, 2000).

Epoxy's physical properties may be changed by applying some processes. These physical properties can be curing rate, the processing temperature, the cycle time, variation of the drape and tack, the toughness, the temperature resistance, etc. To modify these properties the most common process is using mixture of different epoxies.

Epoxy resin is a product of reaction between bisphenol A (DGEBA) and epichlorhdyrin in basic conditions (Baker, Dutton & Kelly, 2004). (Figure 2.1)



Figure 2.1 The reaction of Bisphenol A and Epichlorhdyrin

Epoxy material needs adding catalyst (curing agent) and applying temperature to get its toughness. The catalyst material changes the epoxy's properties also and there are different catalyst materials for the needs to get epoxy. The typical properties of cast epoxy resin are given at Table 2.1.

Table 2.1 Typical Properties of Cast Epoxy Resin (at 23°C) (Mallick, 2008)

Density (g/cm ³)	1.2-1.3
Tensile strength (MPa)	55-130
Tensile modulus (GPa)	2.75-4.10
Poisson's ratio	0.2-0.33
Coefficient of thermal expansion (10 ⁻⁶ m/m.°C)	50-80
Cure shrinkage (%)	1-5

The most common catalyst materials are aliphatic amines, aromatic amines and organic anhydrides.

Catalyst materials are added into the resin at stoichiometric proportions. After adding catalyst into the epoxy resin, heat is applied on to the epoxy at 70-90 °C for curing process. At the end of this process polymerization occurs and the bonding structure changes to cross-links.

After the polymerization the epoxy structure withstands 90–120 °C. By using special epoxy resins or additives, this temperature value can be increased to 200 °C.

Besides to make processing of epoxy resin easier and to increase viscosity of the resin diluents are used. Diluents decrease the mechanical and electrical properties of the resin but increased the production ability. In applications the reactive monoglycerides ethers and non-reactive diluents are used. The reactive diluents are preferred because they get into the structure in curing process.

Epoxy resins are used in different reinforcement materials with great combination. Its physical properties are much better than other thermoset materials relatively. However the cost of the epoxy resin is higher than other thermoset materials.

Epoxy resin has a brittle structure after the curing process. By special processes epoxy can get tougher by adding thermoplastic materials in to it.

Epoxy resins are used in resin transfer molding (RTM), filament winding, pultrusion and hand lay-up production techniques.

Liquid epoxy resins can be reinforced by different reinforcement fibers such as glass fiber, aramid and carbon fiber. Semi-solid epoxy resins are used in making bonding structure in prepreg. Shelf life of the epoxy resin in room temperature is approximately 24 months.

2.1.1.2 Polyester

Polyesters offer excellent corrosion resistance resin systems. The operating service temperatures and costs for polyesters are lower than for epoxies. Polyester resins are used in different production techniques. The most common processes for the polyester are pultrusion, filament winding, SMC, and RTM. Polyesters can be a thermosetting resin or a thermoplastic form.

Polyester resin is obtained by the condensation polymerization of dicarboxylic acids and the polyhydric alcohols. In addition, the unsaturated polyesters have maleic anhydride or fumaric acid which is constituent of a dicarboxylic acid.

By adding styrene (% 35-50 wt) into the polyester resin the viscosity of the polyester decreased. Styrene is also used for as a catalyst for the polyester. Styrene's another mission is to make cross-links between the monomer molecules and unsaturated polyester. This process is used to get polyester resin rigid. The molecule structures of fumaric acid, ethylene glycol and end product of the reaction between these two molecules are shown in Figure 2.2, Figure 2.3 and Figure 2.4 respectively (Peters, 1998).



Figure 2.2 Fumaric acid

(HO-CH₂-CH₂-OH)

Figure 2.3 Ethylene glycol



Figure 2.4 End product of the reaction between the ethylene glycol and the fumaric acid

For the production of polyester resin;

- a) Glycol,
- b) Unsaturated dibasic acid,
- c) Saturated dibasic acid,
- d) Reactive monomer,

are needed (Cam Elyaf Sanayii AŞ., 2004).

- a) <u>Glycols</u>: The cheaper glycols are used to decrease the production cost of the polyester resin. The most common glycol is ethylene glycol (Figure 2.3) to produce polyester resin. The ethylene glycol molecule tends to crystallization which makes difficulty in bonding to the styrene. For this reason, different glycols mixture are used in production for polyester. In addition, if acetyl or propinol groups would add into the polyester, glycol makes bonding with styrene.
- b) Unsaturated Acids: Unsaturated acids are used to make cross-links into the polyester resin. The amount of the unsaturated acids determines the cross-link number. The direct relationship has between the cross-link and the amount of the unsaturated acid. The rigidity of the composite comes from these cross-links. The rigidity helps thermal resistance under the loadings but makes the composite brittle. Making composite brittle reduces the tensile strength. In practical applications the unsaturated dibasic and the saturated dibasic materials have to be mixed some settled proportions. The most common unsaturated dibasic is maleic acid. The melting temperature of the maleic acid is between 132-140°C. Especially the anhydride form of the maleic acid is preferred which has low melting temperature. Other unsaturated acid is fumaric preferred for production of polyester. Fumaric acid is a trans-isomer of the maleic acid. During the polymerization process some maleic acid molecules changes into the fumaric acid. Use of fumaric acid for polymerization increases the tendency to the crystallization. There are some other unsaturated acids called chloromaleic acid, itachonic acid and

styrachonic acid which are used for production polyester but they are more expensive and not common.

- c) <u>Saturated Acids</u>: The expression of "saturated" used for the dibasic acids and the anhydrides explain there is no bonding structure to make bond between the peroxide catalysts. Using orthophthalic anhydride which is a saturated acid makes polyester transparent. Orthophthalic anhydride also has a good bonding ability with styrene. If the fire or thermal resistance will be needed, the acids which have chlorine or bromine preferred. These acids may be tetrachlorophthalic anhydride or hexachloro-endo-metilen-tetra-hydrophthalic (HET) anhydride. On the other hand, to make polyester resin more flexible the dibasic acid is mixed with aliphatic dibasic acids. The sebacic acid and adipic acid are the example of these aliphatic acids.
- <u>Reactive Monomers</u>: There are two aims using monomers for production polyester resin. These are;
 - \succ To decrease the resin viscosity,
 - ➤ To create cross-link bonds.

The most common monomer used for production process of polyester is styrene. The factors for using styrene in this process are low cost, low viscosity and easy to supply.

If the resistance to ultraviolet rays will be needed, methyl meta chloride or n-butyl meta chloride is used as a monomer. Besides dichloro styrene or dibromostyrene are used against the flame and fire resistance.

It is possible to make different composite parts using polyester resin. For this reason, different production processes can be used for polyester resin. The most useful property of the polyester resin is low cost with a good mechanical, electrical, chemical resistance. Polyester resins emit styrene and this emission has hazardous

effects to the human health. The catalyst which has low proportion styrene is used to decrease the styrene emission. Another disadvantage of the polyester is high shrinkage after the production.

2.1.1.3 Phenolic Resin

Phenolic resins are formed by the reaction of phenol (carbolic acid) and formaldehyde (Figure 2.5) then catalyzed by an acid or base.



Figure 2.5 Reaction of phenol and formaldehyde (Harper, 2000)

The phenolic resin has a different curing process than other thermosetting resins such as epoxies, due to the fact that water is generated during the curing reaction. The water is removed during processing and heat is needed for curing.

Phenolics are generally in dark color and therefore used for applications in which color does not matter. The phenolic products are usually red, blue, brown, or black in color. To obtain light-colored products, urea formaldehyde and melamine formaldehyde are used.

Phenolics are used in especially high temperature resistance products. On the other hand phenolics have good electrical, wear and chemical resistance and dimensional stability.

2.1.1.4 Vinyl Ester

Vinyl Ester resin has good mechanical properties as epoxy and good productivity as polyester. Vinyl Ester resins are the most recent addition to the family of thermosetting polymers. Although several types of these resins were synthesized in small quantities during the late 1950s, it was not until the mid-1960s that commercialization, principally by Shell and Dow Chemical led the push to establish an extremely important segment of today's composite industry. Vinyl Esters are unsaturated resins made from the reaction of unsaturated carboxylic acids (principally methacrylic acid) with an epoxy such as a bisphenol A epoxy resin (Harper, 2000).

Vinyl Ester resins are cheaper than epoxies. For the large scale composite part production Vinyl Ester is used rather than epoxy for this reason. Vinyl Ester is similar to polyester but has a high toughness and good adhesion capability with fibers.

2.1.1.5 Polyurethane

Polyurethane is widely used for structural reaction injection molding and reinforced reaction injection molding processes. Polyurethane is a mixture of organic isocyanate or polyisocyanate and polyol in a ratio 1:1. Then this mixture is injected into mold containing short or long fiber reinforcements.

Polyurethane can be thermoset or thermoplastic. The functionality of the selected polyols determines this property. Thermoplastic-based polyurethane contains linear molecules as other thermoplastics. However thermoset-based polyurethane resin contains cross linked molecules.

Polyurethane offers chemical resistance, good toughness, and high resilience. Polyurethane is used in making car hoods and bumper because of their impact absorption ability.

2.1.1.6 Bismaleimide (BMI) and Polyimide

Bismaleimide (BMI) and polyimide have the highest thermal resistance and stability than other thermosetting resins. Therefore bismaleimide (BMI) and polyimide are used for high-temperature applications especially in aircrafts, missiles, and circuit boards.

BMI is similar to epoxy matrix as processability, although they can have better flow and wet-out properties. Glass transition temperatures (T_g) range is from 180-320°C, and the composites can operate in the range from 175-235 °C for short periods.

Polyimide has glass transition temperatures between 220-400 °C. These values are much higher than for other thermoset materials. The lack of use of BMI and polyimide is their processing difficulty. They emit volatiles and moisture during curing process. Therefore, proper venting is necessary during the curing of these resins. If the ventilation will not be applied, there would be voids and delaminations. The curing process applied at approximately 400 °C.

BMI and polyimide have some disadvantages as low impact resistance, high moisture absorption and relatively high cost.

2.1.1.7 Silicones

The main difference between the silicone resins than other thermosetting material is molecular structure. Silicone resin contains inorganic silicone molecule other than Carbon. Silicone resin obtained by adding silicon molecules to the metyl (-CH3) or phenyl (-C6H5) groups.

Resin structure obtained using cobalt naphthenate, zinc octonate, triethanolamine, morpholine as catalysts. During this reaction heat is also applied.

Silicone resin is used for production of prepregs with glass fiber or asbestos fibers. Silicone resin has low mechanical and high costs. For this reason the production ratios of this resin is low in practical applications.

2.1.2 Thermoplastic Materials

Thermoplastics are another polymer matrix material group which is used for production composite materials. The main difference of the thermoplastic and thermoset is curing process and thermoform ability. The thermoplastic does not need any curing process to get its rigidity and thermoplastics can be reformed applying heat and pressure. This property comes from the chemical structure of the thermoplastics. Thermoset contains cross-links but the thermoplastic materials may be amorphous (Figure 2.6) or semi – crystal (Figure 2.7).



Figure 2.6 Amorphous structure of a thermoplastic



Figure 2.7 Semi crystal structure of a thermoplastic

Thermoplastic materials have crystal regions in bonding. For this reason the thermoplastics can not be 100 % crystalline. Therefore thermoplastics materials are defined as semi-crystal materials in literature. Semi-crystal thermoplastic material has contains amorphous and semi-crystal structure at the same time. The ratio of the crystal structure depends on the cooling rate of the thermoplastic. The high cooling rates increase the amorphous phase and decrease the crystal structure.

The amount of the crystalline structure affects the glass transition temperature (T_g) directly. The crystalline structure increases the glass transition temperature. These high crystalline thermoplastics can be operated at high temperature but their manufacturing process is more difficult than lower crystalline thermoplastic materials. A thermoplastic may be characterized by three temperatures:

<u>Glass Transition Temperature (T_g) </u>: Below this temperature the polymer is rigid (glassy), elastic and dimensionally stable. Above T_g it becomes rubbery and may flow to a limited degree. As the temperature is further raised it becomes more liquid-like. In amorphous thermoplastics there is no sharp melting point - just a progressive softening with increase in temperature.

<u>Crystallization Temperature (T_c) </u>: Some thermoplastics may be partially crystalline. They melt over a narrow temperature range (T_c) usually to a relatively low-viscosity liquid.

<u>Melting Temperature (T_m) </u>: This is an arbitrary temperature at which the melt viscosity is sufficiently low for the material to be processed as a liquid. This is typically in the order of 100°C above T_g , or 50°C above T_c (but this varies for different polymer systems). Thermoplastics are assuming greater importance as matrices for composites although the majority of composites in use today are thermosets due to their greater ease of processing.

Thermoplastics have lower chemical resistance than thermoset but thermoplastic materials can repair more easily than thermosets if the damage will occur.

Thermoplastic resins can be welded together also at repair processes. Repairing process of thermoset composites is more complicated than for thermoplastics.

Thermoplastic composites typically require higher forming temperatures and pressures than comparable thermoset resins. Thermoplastics have higher impact resistance. This property of the thermoplastics makes them useful materials where impact energy absorption needed. Especially thermoplastic composites are used in car body parts where impact resistance needed.

There are different composite production techniques for thermoplastics in practical applications. Thermoplastics can be reinforced by short, long or continuous fiber reinforcements. However the homogeneous fiber distribution is a prerequisite for all the processes. It is necessary to enhance composite reinforcing efficiencies that control tensile, impact and creep behavior. It is important to maximize uniformity of fiber dispersion and decrease the fiber reinforcement ratio.

Previous two decades, fiber reinforced composite materials were fabricated using thermosetting matrices (Hancox, 1989). Commercial prepreg tape such as CF/PEEK (carbon fiber/polyetheretherketone) and later CF/PPS (carbon fiber/polyphenylenesulfide) was introduced in the early 1980s which can be replaced for the thermoset materials. However, reported on improved static strength and fatigue resistance when epoxy was replaced by polyamide 6 as a composite matrix in 1966 (Peters, 1998).

Composites later introduced based on semi-crystalline thermoplastics. Such as PEEK and PPS, which have been introduced more recently, have excellent chemical resistance and are superior to epoxy-based composites in this respect. Thermoplastic composites is generated for, basically three different reasons.

Firstly, processing can be faster than for thermoset composites since no curing reaction is required. Thermoplastic composites only require heating, shaping and cooling.

Secondly, the properties are attractive, in particular, high delaminations resistance and damage tolerance, low moisture absorption and the excellent chemical resistance of semi-crystalline polymers.

Thirdly, the environmental concerns, thermoplastic composites offer advantages than thermosets. They have very low toxicity since they do not contain reactive chemicals. Therefore the storage life of the thermoplastics is almost infinite and they are recyclable. Because it is possible to remelt and dissolve such thermoplastic resins. After then they and their composites are also easily recycled using them in the market for molding compounds.

These advantages led to the development of the thermoplastic matrix composite system. Compared with thermosets, composites fabricated from thermoplastic materials typically have a longer shelf life, higher strain to failure, are faster to consolidate and retain the ability to be repaired, reshaped and reused as need arises.

However, as in many polymers composite systems, these materials frequently suffer from a lack of proper fiber-matrix adhesion. Thermoplastic have higher viscosity opposite to the thermosets. Thermoplastic matrices must be able to withstand high temperatures in order to effect a sufficient reduction in viscosity.

In this study especially the continuous fiber reinforced thermoplastic composites have been investigated. The continuous thermoplastic composite market growth rate increases for the last years. The growth rate of the continuous thermoplastic composite material in 2002 is 93%. Continuous fiber reinforced thermoplastic composites include a variety of products including unidirectional prepreg, fabric based prepreg, commingled fiber in roving (towpreg). Such thermoplastic composites have a history of about 20-25 years and it differs from discontinuous fiber reinforced thermoplastic composites in terms of fiber length (Babu, Baksi, Srikant & Biswas, 2002).

Historically, continuous fiber reinforced thermoplastic composites were used in niche applications in aerospace and defense market (Bureau & Denault, 2004). However in recent years, the market has expanded to include automotive, sporting, transportation, industrial and other applications. Common reinforcements used with thermoplastic composites are E-glass, carbon and aramid. Resins typically selected are Polyphenylenesulphide (PPS), Polyetheretherketone (PEEK), Polypropylene (PP), Polyamide (PA), Polycarbonate (PC) and Polyetherimide (PEI).

Continuous fiber reinforced thermoplastic composites are even finding their way into furniture, fastener, medical, marine, and other higher performance applications.

Airbus has projected to increase the use of thermoplastic composites by 20% every year (Babu et al., 2002).

There are different thermoplastic matrices which are used in production of thermoplastic composites. They can be grouped as;

<u>Commodity Molding Compounds</u>: These thermoplastics used in composites are typically reinforced with short, long or continuous fiber. They are low cost, have moderate properties and good processability.

- Polypropylene (PP)
- Polyamide (nylon) (PA)
- Polyethylene (PE)

Engineering Thermoplastics: Advanced performance thermoplastic matrices.

- Polyimides (PI)
- Polyethersulphone (PES)
- Polyphenylenesulphide (PPS)

<u>High Performance Thermoplastics</u>: Highly aromatic polymers with very high T_g , and generally aligned continuous reinforcement but some molding compounds are also available.

-Polyethersulphone (PES)

-Polyetheretherketone (PEEK)

-Polyetherketoneketone (PEKK)

-Polyetherimide (PEI)

2.1.2.1 Polypropylene (PP)

Polypropylene (PP) has the lowest density in all thermoplastics and a low-cost versatile plastic. It is similar to polyethylene (PE) in structure, except for the substitution of one hydrogen group with a methyl group on every other carbon. This difference of the polymers changes the symmetry of the polymer chain. This allows for the preparation of different stereoisomers, namely, syndiotactic, isotactic, and atactic chains. PP shows different characteristic properties depending on the stereoisomer which is used. Figure 2.8 is an illustration of polymerization for polypropylene.



Figure 2.8 Polymerization of propylene to polypropylene (Harper, 2000)

Polypropylene offers good strength, stiffness, chemical resistance, and fatigue resistance. PP can be used in different machine parts and car components.

Polypropylene could not be used as commercially until the Ziegler-Natta catalysts came available in 1950s (Harper, 2000).

The isotactic polymer based PP is the most commercially used. PP is processed between the 220-280 °C (Chanda & Roy, 2006). Above these temperatures PP degrades. Polypropylene (PP) has lower degradation temperatures than polyethylene (PE). However PP is more rigid than PE; especially isotactic PP has higher softening temperatures when it is compared with PE. Therefore PP is processed and operates higher temperatures than PE.

PP has a non-polar structure. This structure gives some advantages and disadvantages;

Advantages;

• Has low water absorption,

• Shows good chemical resistance (Except chlorinated solvents, gasoline and xylene),

• Has low dielectric constant and is a good insulator.

But the non-polar structure of the polypropylene presents problem with the glass fiber-PP composite bonding. To overcome this problem, it is necessary to use a reactive coupling agent or coupling system to bond the matrix to the glass surface (Hausmann & Flaris, 1997).

Nygård, Redford & Gustafson (2002) investigated three different principles for glass fiber-PP composites based on using coupling agents or direct reaction of the glass fibers for matrix material.

The most common method is using chemically modified polypropylene (polymeric coupling agents) into the bulk polypropylene. These coupling agents can be polypropylene grafted with either acrylic acid (AA) (Daemen & den Besten, 1991) or maleic anhydride (MAH) (Hausmann & Flaris, 1997). Kumar et al. (2007) studied long glass fiber reinforced polypropylene and used maleic-anhydride grafted polypropylene (MAH-g-PP) for a compatibilizer. They found that 5% MAH-g-PP is the optimum value by weight for mechanical properties. These coupling agents have

the capability interactions and covalent bonds with a sizing based on an aminosilane on to the glass fiber.

On the other hand another approach is coating the glass fiber to make compatible with PP. This approach was studied by Felix & Gatenholm (1993). They used a range of very low molecular substances and found that the best effect from the polymeric coupling agent which has the highest molecular weight.

The third possibility to get over this problem is to cover the glass fiber surface with a directly reactive system such as an azidosilane. The azido-group has the ability to make covalent attachment to any available carbon-hydrogen bond in the bulk polypropylene.

The bonding mechanism of aminosilane and the MAH-g-PP is explained in Figure 2.9.



Figure 2.9 Chemical reaction between the amino group and the maleic anhydride molecule grafted on (Nygård et al. 2002)

2.1.2.2 Polyethylene (PE)

Polyethylene (PE) has a high performance/cost value which makes PE highest-volume polymer in the world. PE has high toughness, ductility, excellent chemical resistance, low water vapor permeability, and very low water absorption. PE is limited by its relatively low modulus, yield stress, and melting point. PE is used for making bottles, films, and pipes. It is reinforced with glass fiber as similar to PP.

PE has a chemical stability. PE has a resistance to organic solvents, acids and alkalis. PE has a high dielectric constant, as well. Therefore it is used in insulation materials.

Polyethylene expressed by " $C_{2n}H_{4n+2}$ " chemically. The "n" shows the polymerization degree of the polyethylene. Polymer chain of polyethylene is shown in Figure 2.10.



Figure 2.10 Polymer chain of polyethylene (Béland, 1990)

There are four established production methods for polyethylene. A gas phase method known as the Unipol process practiced by "Union Carbide". A solution method used by "Dow" and "DuPont". A slurry emulsion method is practiced by "Phillips" and last production method is high-pressure method (Harper, 2000).

Polyethylene named by the monomer chain bondings. These chains affect the molecular weight and density of the polyethylene.

Polyethylene named in commercial classes by the difference of the density. Commercially available grades are very low density PE (VLDPE), low density PE (LDPE), linear low density PE (LLDPE), high-density PE (HDPE) and ultra high molecular weight PE (UHMWPE) (Figure 2.11).



Figure 2.11 Polyethylene bonding structures (Harper, 2000)

LDPE has high impact strength, toughness and ductility. These properties make LDPE the material of choice for packaging films. LDPE acts as a seal layer or a water vapor barrier.

HDPE is one of the highest-volume commodity chemicals produced in the world. Two commercial polymerization methods are most commonly practiced; one involves Phillips catalysts and the other involves the Ziegler-Natta catalyst systems (Harper, 2000). HDPE has high crystal and linear chemical structure and rigidity. HDPE is used in pipe and bottle production.

LLDPE has the same density and viscosity of LDPE but higher mechanical properties.

UHMWPE is similar to HDPE but has a higher molecular weight than HDPE. HDPE has a 50000 g/mol molecular weight. The molecular weight of the UHMWPE is between $3x10^6 - 6x10^6$ (Harper, 2000). Therefore UHMWPE has a very high toughness and tenacity at breaking. But these properties make the UHMWPE unconventional for production processes. UHWPE compete with the aramid fibers in ballistic applications.
2.1.2.3 Polyetheretherketone (PEEK)

PEEK (Figure 2.12) is developed for high service temperatures and it is a newgeneration thermoplastic. It is used especially in advanced engineering applications. PEEK is combined with carbon fibers and used for in fuselage, satellite parts and other aerospace structures. This combination named by APC-2 and this is the first PEEK composite application (Cogswell, 1992). They can be used continuously at 250°C however PP is liquid in this temperature. The glass transition temperature (T_g) of PEEK is 143°C and melting temperature is 350-380°C.

PEEK/carbon thermoplastic composites have generated significant interest among researchers and in the aircraft industry because of their greater damage tolerance, better solvent resistance, and high-temperature resistance usage. As well, PEEK has the advantage of almost 10 times lower water absorption than epoxies. The water absorption of PEEK is 0.5% at room temperature, whereas aerospace-grade epoxies have 4 to 5% water absorption.

The cost of the PEEK and carbon fiber are high. As a result of this, the composite parts which are made from this combination have high prices.



Figure 2.12 Chemical structure of Polyetheretherkethone (Béland, 1990)

2.1.2.4 Polyphenylenesulfide (PPS)

PPS (2.13) is generated for high service temperature as similar to PEEK. However PPS has a high crystallinity of 65% at maximum. It provides high operating temperatures and can be used continuously at 225°C but it makes PPS brittle. It has also high chemical resistance compared with PEEK (Mazumdar, 2002). The T_g of PPS is 85°C and crystalline melt temperature is 285°C. It is processed in the temperature range of 300 to 345°C. Prepreg tape of PPS with several reinforcements is available. The trade names of PPS-based prepreg systems are Ryton and Techtron.



Figure 2.13 Chemical structure of PPS (Béland, 1990)

2.1.2.5 Polyetherimide (PEI)

PEI is another thermoplastic which is developed for high service temperature as PEEK and PPS. However the main difference from the PPS and PEEK is amorphous structure. It has high-temperature resistance, impact strength, creep resistance and rigidity. PEI is transparent with an amber color.

PEI is sold under the trade name of Ultem (General Electric) and has the structure shown in Figure 2.14. It is prepared from the condensation polymerization of diamines and dianhydrides. Mostly PEI is reinforced by glass fiber and carbon fiber. It is used for the automotive, electrical and aerospace parts where the dimensional stability and thermal resistance needed.



Figure 2.14 Chemical structure of PEI (Béland, 1990)

There are many thermoplastic matrix and reinforcement combinations in applications. Table 2.2 shows the chemical structure of thermoplastic materials and in Table 2.3 the physical properties of the thermoplastics listed.

Polymer Type	Chemical Name	Structure	$T_{g}(^{\circ}C)$	Processing
				Temp. (°C)
Polyolefin	Polypropylene (PP)	Crystalline	-10	200-240
Polyamides	Polyamide 6,6 (PA 6,6)	Crystalline	55	270-320
	Polyamide 12 (PA 12)		35	220-260
Polyesters	Polyethylene	Crystalline	70	280-310
	Terephthalate (PET)			
	Polybutylene		20	260-290
	Terephthalate (PBT)			
Polyarylene	Polyphenylene	Crystalline	90	300-340
ether or sulfide	Sulfide (PPS)	-		
	Polyketone		205	420-430
	Polyetheretherketone (PEEK)		143	380-400
	Polyarylene	Amorphous	215	330
Dalainidaa	sulfide	A	217	225 420
Polymindes	Polyetherminde (PEI)	Amorphous	217	555-420
	Polyetherimide (TPI)		250	340-360
	Polyimide (TPI)	Crystalline	260	400-420

Table 2.2 Structural properties of thermoplastics (Béland, 1990)

	Polypropylene	Polyetheretherketone	Polyetherimide	Polyamide 6	Polyamide 66	Polyphenylene Sulphide	Polyethersulphone
	PP	PEEK	PEI	PA6	PA66	PPS	PES
Density (g/cm ³)	0.937	1.33	1.35	1.12	1.12	1.43	1.4
Linear Mould Shrinkage (cm/cm)	0.033	0.008	0.005	0.12	0.015	0.01	0.007
Melt Flow (g/ 10 min)	19.1	21.9	8.6	23.1	26	-	85
Tensile Strength (MPa)	36.8	110	100	72.6	73.1	86.7	87.4
Tensile Yield Strength (MPa)	30.7	98.8	100	62.4	63.6	69	99.4
Tensile Modulus (GPa)	1.9	4.5	3.7	1.9	2.1	3.6	3.7
Elongation (%)	120	37	42	94	83	4	30
Flexural Strength (MPa)	36.2	170	130	85.8	88.4	140	130
Flexural Modulus (GPa)	1.4	4.8	4.5	2	2.4	4.9	4.3
Compressive Yield Strength (MPa)	48.5	120	120	28.9	32.5	95	100
Shear Strength (MPa)	-	57.7	-	-	61.7	-	50
CTE @ 20°C (µm/m °C)	120	44.1	40	91.1	100	39.2	49.1
Heat Capacity, Cp (J/g°C)	2	2	-	1.6	2.2	-	1
Thermal Conductivity, λ (W/m K)	0.20	0.25	0.52	0.27	0.26	0.3	0.22
Melt Temp (°C)	160	340	220	220	250	280	-
Maximum Air Service Temp (°C)	85	260	200	100	100	160	200
Vicat Softening Point (°C)	83	-	230	170	190	-	220
Glass Transition Temp (°C)	-	140	220	60	-	88	230
Process Temp (°C)	220	370	360	260	290	330	340
Mould Temp (°C)	43	180	140	73	80	-	120

Table 2.3 The physical properties of the thermoplastics

2.2 Reinforcements

To improve strength and toughness in composites, the reinforcements has a high importance. The reinforcements can be in different chemical structures or physical forms. In physically the reinforcements have three different forms. These forms classified as particulates, short (discontinuous) and continuous. The form of the reinforcement acts directly on production method and the composite material properties.

The examples of the particulates are resin powders, micro glass balloons, etc. The discontinuous reinforcements are the chopped, staple form of the continuous reinforcements. The particulates or discontinuous reinforcements mixed with the matrix material before the production process at determined proportions. Continuous reinforcements are used in continuous composite production processes. In continuous reinforced composite production processes glass fiber, carbon fiber, aramid, boron fiber, UHMWPE and natural fibers are used.

The orientation of the particulates and discontinuous reinforcements can not be controlled during the composite material production processes. Because of this factor, the determinations of the properties are difficult in these composites. However continuous fiber reinforced composite show anisotropic properties. For this reason, determinations of the properties of these continuous composite materials are easier than particulates and discontinuous fibers.

In continuous fiber reinforced composite the mechanical properties are higher at the direction of the fibers. However it has low mechanical properties at the other directions. Fibers are used as fabrics or different lamination orientations to overcome this disadvantage.

The fiber diameters of the glass fiber change between the 5-25 μ m which is used many composite applications. The diameters of the carbon fibers are 5-8 μ m and for aramid fibers 12.5 μ m.

2.2.1 Glass Fiber

The most common reinforcement material used for composite application is glass fiber. The history of glass is ancient but commercial fiberglass did not become a reality until in 1939 the joint research efforts of Owen-Illinois and Corning Glass. Glass fibers (Figure 2.15) can be obtained as a continuous fiber on staple or discontinuous fiber. Both forms are made by the same manufacturing process until the fiber drawing operation.

Glass fibers were predominantly used at the end of the World War II for the radar domes. It combined with polyester resin for these products. There are for different types of the glass fibers and the first commercialized glass fiber is A-glass fiber. The other glass fibers are C glass fiber (Chemical), E glass fiber (Electrical) and S glass fiber (Strength).

However there are different glass fiber types, the Silicon Oxide is the main raw material for glass fibers. The ratio of the Silicon Oxides is over the 50 % for all types of glass fiber. The glass fiber chemical ingredients and types are shown in Table 2.4. As mentioned above there are four types of glass fibers these are;

- a) <u>A glass fiber (High alkali)</u>: It contains alkali material at high degrees. It has good chemical resistance, low electrical insulation properties.
- b) <u>C glass fiber (Chemical)</u>: It has high chemical resistance. It is used for chemical solvent storage tanks for this property.
- c) <u>E glass fiber (Electrical)</u>: E glass fiber is generated for getting high electrical resistance. On the other hand it is most common glass fiber and reinforcement type used in composite market. It gives high mechanical properties with low costs. The E glass fiber was used also in this study which is provided from "Cam Elyaf A.Ş."
- d) <u>S glass fiber (Strength)</u>: S glass fiber has the highest mechanical properties for all glass fiber types. The tensile strength of the S glass fiber is 30% higher

than E glass fiber. It can operate at high temperatures. However it has high cost. It is used in aerospace and ballistic applications.

	Grade Of Glass Fiber					
Components	A (High Alkali)	C (Chemical)	E (Electrical)	S (High Strength)		
Silicon oxide (SiO ₂)	72.0	64.6	54.3	64.2		
Aluminum oxide (Al ₂ O ₃)	0.6	4.1	15.2	24.8		
Ferrous oxide (Fe ₂ O ₃)	-	-	_	0.21		
Calcium oxide (CaO)	10.0	13.2	17.2	0.01		
Magnesium oxide (MgO)	2.5	3.3	4.7	10.27		
Sodium oxide (Na ₂ 0)	14.2	7.7	0.6	0.27		
Potassium oxide (K ₂ O)	-	1.7	-	-		
Boron oxide (B_2O_3)	-	4.7	8.0	0.01		
Barium oxide (BaO)		0.9	-	0.2		
Miscellaneous	0.7	-	-	-		

Table 2.4 The ingredients of glass fibers (Peters, 1998)

The glass fiber production is similar to glass production. But there are some other equipments and machines to obtain fibers. Figure 2.16 illustrates production step of the glass fiber production processes.

First of all, the glass fiber ingredients weighted and send to the mixer at determined proportions. Glass is melted at 1260 °C after the mixing process. The molten glass is spunied from the bushings which is made from the alloy of platinum and boron. The fiber form of the glass is winded at 20-25 m/s (Cam Elyaf Sanayii A.Ş., 2004).



Figure 2.15 Glass fiber roving

After these processes, the fibers cooled with air and water. The glass fibers coated with a material to protect from environmental effects and to make compatible fibers with matrix. The coating material differs depending on the matrix material.

Cam Elyaf A.Ş. manufactures glass fiber in TURKEY. It manufactures different types of E glass fiber for various applications.



Figure 2.16 Glass fiber manufacturing processes (Peters, 1998)

2.2.2 Carbon (Graphite) Fiber

Carbon fibers have been obtained by inadvertently from nature cellulose fibers such a cotton or linen for thousands of years. Modern carbon fibers were first introduced in about 1967 as a result of independent development work in UK and Japan and are much stiffer than glass with comparable strength (Bond, 2005).

Carbon fibers have outstanding properties. It can operate at high temperatures and has high mechanical, electrical and thermal properties. It competes with steel and the electrical and thermal conductivities exceed the competing materials.

Carbon fibers have high tensile strength/density (σ/d) and Elasticity modulus/density (E/d) ratios, which make carbon fibers unique.

The carbon and graphite fibers are manufactured using similar materials. The fibers were first produced from a polymeric fiber precursor and poly-acrylonitrile (PAN) which is produced for textile applications, as well.

Carbon fibres are long bundles of linked graphite plates, forming a crystal-like structure layered parallel to the fiber axis. These linked bundles increased the anisotropic structure of carbon fiber and increased the mechanical properties. The structure of the carbon fibers is shown in Figure 2.17. The properties of different carbon fiber types are listed in Table 2.5.



Figure 2.17 Structure of carbon fiber (Bond, 2005)

Supplier/	Fiber Type	Tensile	Elastic	Fracture	Density	σ_t/ρ	Ε/ ρ
Fiber name		Stength σ_t	Modulus F (CPa)	Elong.	$\rho(kg/m^3)$	(10 ⁶	(10 ⁶
I wer name		(GI a)	E (GI a)	(70)		m^2/s^2)	m^2/s^2)
	Pitch Type						
Amoco							
/Thornel	P100	2.2	690	0.3	2150	1.02	321
	P120	2.4	830	0.3	2150	1.11	386
Petoca							
/Carbonic	HM50	2.8	490	0.6	2000	1.40	245
	HM60	3.0	590	0.5	2000		
	HM80	3.5	790	0.4	2000	1.75	395
	Pan Type						
Amoco/	T-300	3.45	231	NA	1760	1.96	131
Thornel	T-50	2.9	390	NA	1810	1.60	215
	T-40	5.65	290	NA	1810	3.12	160
Akzo /							
Fortafil	F-5 (c)	2.76	345	NA	1800	1.53	192
	F-3 (c)	3.80	227	NA	1700	2.24	133
RK Fibers/ RK	RK30	>3.0	230	NA	1780	1.68	129
	RK25	>2.5	230	NA	1780	1.40	129
Toray/							
Torayca	M46J	4.2	436	0.5			
	Т300	3.5	230	1.2	1750	1.71	143
	T800	5.5.	294	2.0			
Toho/							
Besfight	ST1	3.6	240	1.5	1800	2.00	160
	ST2	4.0	240	1.5	1800	2.00	160
	ST3	4.4	240	1.8	1800	2.38	133
	Metals						
	Aluminum	0.172	73	NA	2720	0.063	27
	Titanium	0.324	110	NA	4500	0.072	24
	Steel	0.414	199	NA	7860	0.052	25

Table 2.5 Carbon fibers and properties (Peters, 1998)

Carbon fibers (Figure 2.18) are obtained by two different raw materials. They are poly-acrylonitrile (PAN) and pitch.

The first manufacturing process of the carbon fiber is hot stretching of the polyacrylonitrile (PAN) (Figure 2.19). The molecules are induce molecular alignment and then stabilized and oxidized under tension, at about 250°C. This removes some hydrogen and cross-links. In this process PAN losses half of its weight (Mazumdar, 2002). The oxidized fiber is heated in an inert atmosphere for carbonization at 1000 -1600°C. The PAN loses remaining hydrogen and nitrogen atoms at this process. If the carbonized fibers heated to 1800-2500 °C, graphitizing happens. This process is used also making for graphite fibers and high modulus fibers.

The process is unique in that the graphite crystallites are nucleated from the hexagonal ring structure of the oxidized fiber. This means that the graphite hexagonal basal planes are always aligned along the fiber axis.



Figure 2.18 Carbon fiber roving



Figure 2.19 Carbon (Graphite) fiber manufacturing using Polyacrylonitrile (PAN)

Another process to get carbon fiber is using pitch as raw material (Figure 2.20). Pitch, as PVC, coal tar or petroleum asphalt is spun into a filament from either a simple melt or from a liquid crystal 'mesophase' melt of aromatic chain structures. The tension is applied to the filaments if they obtained from simple melt process. The fibers are manufactured in the same processes; oxidation, carbonization and graphitizing which are used in PAN carbon fiber manufacturing.



Figure 2.20 Carbon (Graphite) fiber manufacturing using pitch

The temperatures applied in the graphitizing process acts an important role on to the properties of the carbon fibers. This temperature can be changed for the needs from the carbon fiber. Figure 2.21 shows the changing of the elasticity (Young) modulus and tensile strength depending on the graphitizing temperature.



Figure 2.21 Young modulus and tensile strength depending graphitizing temperature (Bond, 2005)

2.2.3 Aramid Fiber

Aramid, the organic reinforcing fiber is used in advanced composite since the early 1970s. Aramid fibers are obtained by the aromatic polyamide (poly-para-phenylene-terephthalamide PPTA). The expression of aramid comes from the "ar"-omatic poly-"amide".

The US Federal Trade Commission defines an aramid fiber as "a manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings" (Peters, 1998).

Aramid fibers have two different types called para-aramid (Figure 2.22) and metaaramid (Figure 2.23).



Figure 2.22 Molecule of Para - aramid fiber (Peters, 1998)



Figure 2.23 Molecule structure of Meta - aramid fiber (Peters, 1998)

The first commercial para-aramid synthesized by DuPont in 1965. The aramid called by Kevlar. There are several companies also producing aramid fibers. Aramid

fibers provide the highest tensile strength-to-weight ratio among reinforcing fibers. They provide good impact strength and have low density. This makes them useful reinforcing materials for the ballistic protection applications. Like carbon fibers, they provide a negative coefficient of thermal expansion. Aramid fibers have good chemical and flame resistance. The disadvantage of aramid fibers is that they are difficult to cut and machine. Another disadvantage is its cost.

Aramid fibers (Figure 2.24) are produced by extruding an acidic solution (a proprietary polycondensation product of terephthaloyol chloride and p-phenylenediamine) through a spinneret. The solution is then extruded through small die holes (bushings) in a process known as solution spinning. During the drawing operation, aramid molecules become highly oriented in the longitudinal direction. Aramid fibres generally are not treated with a size if they are to be used in a composite. The high aromatic content of the polymer gives good thermal and strength properties and the liner nature of the bonding as well as the intermolecular hydrogen bonds give high rigidity (Table 2.6).



Figure 2.24 Aramid fiber roving

Fiber	Туре	Tensile Strength σ_t (GPa)	Tensile Modulus E (GPa)	Elongation at break (%)	Density ρ (g/cm ³)
DuPont/Kevlar 49	Para- aramid	3000	112	2.4	1.44
Akzo/Twaron HM	Para- aramid	2800	103	2.5	1.45
Teijin/Technora	Para- aramid	3440	73	4.6	1.39
DuPont/Nomex	Meta- aramid	596	11.6	28	1.38
Teijin/Teijinconex	Meta- aramid	650-800	8–12	20-30	1.38

Table 2.6 Aramid fiber and properties (Peters, 1998)

CHAPTER THREE

PRODUCTION TECHNIQUES OF COMPOSITE MATERIALS

Composite material is a very common expression and it contains different matrices and reinforcements. Therefore production techniques of the composite materials differ depending on the type of matrix and reinforcement to be used.

The main subject of this study is production techniques of the thermoplastic composite materials. There are different production techniques for the thermoplastic composite material. The differences come from especially the form of the reinforcements. Discontinuous and continuous fiber reinforced production techniques have great differences. Discontinuous reinforcements can be processes by using many production process but specialized processes needed to make continuous fiber reinforced thermoplastic composite.

The continuous fiber reinforced thermoplastic prepreg production techniques were described in this chapter. Then the composite part manufacturing processes with using these prepreg is explained.

3.1 Continuous Fiber Reinforced Thermoplastic Prepreg Production Techniques

There are three different techniques used for production of prepreg in practical applications. These techniques are;

- 1. Powder Impregnation,
- 2. Film Stacking,
- 3. Melt Impregnation.

The continuous fiber reinforced thermoplastic prepreg production techniques were explained below.

3.1.1 Powder Impregnation

In this production technique the powder form of thermoplastic material is impregnated with fabric or fiber reinforcement. The diameter of the powder thermoplastic is less than 5 μ m (Hancox, 1989).

The powder impregnation process which is developed by Klett & Edie (1999) is shown in Figure 3.1. The thermoplastic powder impregnated fibers called "Towpreg" in this process. Towpreg is different type of prepreg.



Figure 3.1 Powder Impregnation Process (Klett & Edie, 1999)

The powder impregnation process procedures are listed below;

- Tow spreading: To produce a flexible towpreg, the coating process must coat individual filaments in the tow. Pressurized air is applied to separate fiber filaments in the bundles,
- Powder deposition: Another critical area in this process is powder deposition. The static powder coating, vibrational coating or recirculating fluidized bed process was used in powder deposition chamber. During operation, dry pitch powder was fed into the chamber in a region of low air velocity and then fell toward a centrifugal fan.
- Powder Fusion: To get adherence between the powders to the individual filaments, the coated tow was passed through a tube furnace where it was

heated. If the temperature of the oven is excessively high, the powder completely melted and wet the fibers. The result is a stiff towpreg which could not be woven.

Towpreg is then used for different production techniques to produce composite parts.

3.1.2 Film Stacking

Film stacking (Figure 3.2) is another technique with which to prepare thermoplastic composites (Mayer, Wang & Neitzel, 1998; Bafna & Baird, 1991). In this case, fiber filaments arranged in sheet form are sandwiched between thermoplastic matrix polymer films. This assembly is then placed within a press where temperature transforms the film into a polymer melt. Pressure is then applied and forces the melt to impregnate the fiber filaments. Appropriate process conditions must be used in order to sufficiently reduce the matrix viscosity without thermally degrading the actual composite or de-align the fibrous reinforcement. Insufficient heat input and/or pressure will typically result in unwetted fiber and a high void content within the final material.



Figure 3.2 Film stacking process (Mazumdar, 2002)

After film stacking process, thermoplastic prepregs are used in compression molding process to make composite parts.

3.1.3 Melt Impregnation

Melt impregnation is another process to obtain continuous fiber reinforced unidirectional thermoplastic prepreg. The reinforcement material passes through the die which contain molten thermoplastic. Reinforcements are impregnated with thermoplastic matrix material in this die. This is the most common process to get continuous thermoplastic prepreg (Cano & Marchello, 1995; Lacroix, Werwer & Schulte, 1998; Moon, Um, Lee, Cho & Park, 1993).

To develop a melt impregnation system is one of the most important tasks in the present study. Through reviews on the existing design, it is concluded that a successful melt impregnation system should at least include a temperature controller and a well designed consolidation die. The schematic diagram for the process is shown at Figure 3.3. After the melt impregnation system is developed, both carbon and E-glass fiber reinforced unidirectional polypropylene prepregs are manufactured at this system.



Figure 3.3 Schematic diagram to melt impregnation process

For composite production techniques fully impregnation fiber to the matrix is the most critical point. Therefore increasing the impregnation depends on some parameters. These parameters are;

- 1. The viscosity of the matrix material,
- 2. Permeability of the reinforcement fibers,
- 3. The crystal structure of the thermoplastic,

These parameters have to be selected in line with matrix and reinforcement properties. The die geometry and temperature act important roles on these parameters and impregnation.

On the other hand, fiber content of the prepreg material has direct relationship with melt impregnation system. While fiber rovings are hauling from creel system, the cooling process has to be arranged not let the fiber separates from each. The cooling rate is calibrated with the hauling speed and thickness of the prepreg materials. Therefore, fiber content of the prepreg material is related with this thickness. Different tests are done using melt impregnation system which is developed. In the tests maximum fiber content is reached 75% however this fiber content is made problems during the fibers passing through in to the die. Lower fiber content is obtained by increasing the prepreg thickness which is caused hauling problems. According to these tests; the optimum fiber content is determined as 65-67% for production process. The figures of continuous E-glass and carbon fiber reinforced unidirectional polypropylene prepregs are shown in Figure 3.4.



Figure 3.4 Continuous E-glass and carbon fiber reinforced unidirectional polypropylene prepregs

3.2 Composite Parts Production with Continuous Fiber Reinforced Thermoplastic Prepreg

Continuous fiber reinforced thermoplastic prepreg have to be used in final process to make it end product. There are several processes which are used with continuous thermoplastic prepregs. These processes are "Thermoplastic Tape Winding", "Thermoplastic Pultrusion", "Hot Press Technique or Compression Molding".

Thermoplastic tape winding process is used to get cylindrical parts. For example high pressure vessels or pipes can be manufactured by thermoplastic winding process.

Thermoplastic pultrusion process is used in profile marketing. Profiles which have different sections can be made by this process.

The last common process is called hot press technique or compression molding. This process is used to make test samples also in this study.

3.2.1 Thermoplastic Tape Winding

Thermoplastic tape winding is used to make cylindrical composite parts. This process is also called as "Thermoplastic Filament Winding".

Thermoplastic prepreg tape is wound over the mandrel as shown in Figure 3.5. Towpreg can be used also instead of continuous fiber reinforced thermoplastic prepreg tape.

Cylindrical composite parts can be manufactured by thermoset winding process but thermoplastic tape winding has some superiority to thermoset winding. In thermoset winding, fibers pass in a resin bath before winding and after the winding the polymerization (curing) applied with autoclave. In thermoplastic tape winding the fibers have already impregnated with thermoplastic matrix. Therefore only heat and pressure applied on to the prepreg tapes during the winding. There is no need to use any curing process or resin bath.



Figure 3.5 Thermoplastic tape winding (Mazumdar, 2002)

The heat is supplied by IR sources in thermoplastic tape winding. Therefore dark color prepreg tapes are used to increase the heat absorption in thermoplastic tape winding technique.

3.2.2 Thermoplastic Pultrusion

This process is similar to the pultrusion process used with thermosets. Thermoplastic prepreg tapes or towpregs are pulled through a die to make the final product.

Thermoplastic pultrusion has some main divisions for the process. These are guidance system, pre-heating furnace, die, pulling system and cutting system. Thermoplastic prepreg tapes are guided to the pre-heating furnace. Thermoplastic prepreg tapes are heated before the entrance in to the die in pre-heating furnace. The temperature of the pre-heating furnace depends on the thermoplastic matrix material.

The schematic diagram for thermoplastic pultrusion process which is developed by Mota et al. (2000) is shown at Figure 3.6.



Figure 3.6 Thermoplastic pultrusion line (Mota et al., 2000)

Thermoplastic pultrusion die have two sections. The first section of the die is used for pressurize and consolidate thermoplastic prepreg tapes. This section is heated also during the process. The other section of the die cool the thermoplastic composite profile and calibrate the profile dimension. In the cooling section of the die mostly water is used. The thermoplastic profiles cut by cutting blades at the final desired length. The movement of fibers in this process is provided by pulling system. The advantages of the thermoplastic pultrusion are;

- 1. The thermoset pultrusion process is usually limited to polyester and vinyl Ester. However thermoplastic pultrusion can make by different thermoplastic matrices. (PP, PA, PPS, PEEK, TPE, PEI, etc.)
- 2. Thermoplastic pultrusion has reformability and repairability properties,
- 3. The process is environmentally friendly. Styrene emission does not occur,
- 4. The part can be recycled as other thermoplastic composite parts.

The disadvantages of the thermoplastic pultrusion are;

- 1. Thermoplastic pultrusion requires higher heat and pressure than thermosets,
- 2. The surface quality is inferior to thermoset,

- 3. Complex section shapes are difficult to produce because of high viscosity of thermoplastic,
- 4. Thermoplastic pultrusion process requires a high capital investment and the cost of initial raw materials are higher than for thermoset pultrusion.

3.2.3 Hot Press Technique or Compression Molding

In the hot press or compression molding technique thermoplastic prepregs are thermoformed by heat and pressure.

Prepregs are cut according to shape, size, and fiber orientation angle requirements. They are stacked in the desired fiber orientation and welded together to make sure do not move relative to each other during handling. After the prepregs are laid in the desired orientations, the laminated sheet is placed inside the mold. Before placing the laminate, a release agent is applied to the mold surface for easy removal of the molded part. The mold is then closed and placed between two heated platens of the compression molding equipment. The platens heated up to the softening temperature of matrix thermoplastic material. The pressure is also applied during the heating process to the mold platens. After the thermoforming the prepreg sheets the cooling process applied. This cooling process is used until the solidification occurred. After the cooling, mold is opened and the part is moved from the mold. The spherical compression molded composite part can be seen in Figure 3.7. The final process is trimming which is used to get end product dimensions.



Figure 3.7 Compression molded thermoplastic composite

There are two parameters that result in a good consolidated part. First, there should be good contact between adjacent layers to avoid delaminations and second, there should be sufficient heat and time for adhesion to take place at the interface.

Compression molding used to make test specimens in this study too. The Both carbon fiber reinforced unidirectional polypropylene prepreg tapes and E-glass fiber unidirectional polypropylene prepreg tapes are stacked together and molded. The mold is designed considering the heating and cooling capabilities. For this reason water cooling and electrical resistance heating are used in mold design. During compression molding process 12-15 bar pressure and 130 °C temperature applied on to the stacked tapes. The volumetric fiber content of the E-glass fiber unidirectional polypropylene prepreg and carbon fiber reinforced unidirectional polypropylene prepreg are 39.7% and %38.7 respectively. The steps of compression molding process are shown in Figure 3.8 and Figure 3.9.



Figure 3.8 Pressure –Temperature time profile for isothermal consolidation (Long, 2007)



Figure 3.9 Pressure –Temperature time profile for non-isothermal consolidation (Long, 2007)

CHAPTER FOUR

THEORIES FOR MECHANICAL AND THERMAL PROPERTIES OF CONTINUOUS FIBER REINFORCED THERMOPLASTIC COMPOSITES

4.1 Mechanical Properties of Continuous Fiber Reinforced Thermoplastic Composites

4.1.1 Tensile Properties

Tensile tests are used to determine the mechanical properties of the materials under static loads. Tensile test gives the fundamental mechanical properties of the materials.

Tensile tests are performed depending on the class of the testing material. The testing conditions such as dimensions of the sample, tensile test speed are also determined by the class of material. For continuous fiber reinforced thermoplastic composite, TS EN ISO-527 is used as a standard for tensile tests.

Tensile test is applied at certain speed and temperature at one axis of test specimen. During the test a tensile load is applied to the specimen until it fractures. The elongation and load is recorded in the form of a graphic. This graph (Figure 4.1) gives the mechanical properties and behavior of the test sample.



Figure 4.1 Stress-strain curve

Tensile test gives the properties of the test sample listed below;

a) <u>Tensile Strength (σ)</u>: One of the properties can be determined about a material is its tensile strength (σ). Tensile strength is the maximum stress that the material can support. Tensile strength may or may not equate to the strength at break. This all depends on what type of material is tested. Sometimes a material may be ductile when tested in a laboratory, but when placed in service and exposed to extreme cold temperatures, it may show transition to brittle behavior. For brittle materials, the tensile strength is a valid criterion for design.

$$\sigma = \frac{F_{\text{max}}}{A_o} \tag{4.1}$$

Here;

σ: Tensile Strength,F_{max}: Maximum load,

A_o: Original area.

b) <u>Elasticity (Young) Modulus (E)</u>: The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. This linear curve ends with the yielding point. The region after the yielding point called plastic region. If a specimen is loaded within this linear region, the material will return to its exact to same the condition if the load is removed. However at the point that the curve is no longer linear and deviates from the straight-line relationship, Hooke's Law no longer applies and some permanent deformation occurs in the specimen.

$$E = \frac{\sigma}{\varepsilon} \tag{4.2}$$

Here;

E: Elasticity (Young) Modulus,

ε: Strain.

- c) <u>Yield Strength (σ_y)</u>: A value called "yield strength" of a material is defined as the stress applied to the material at which plastic deformation starts to occur while the material is loaded. For the determining of yield strength most common method is using 0.2% off-set method. In this method the yield strength σ_y (0.2%) is found by drawing a parallel line to the elastic region. The point where parallel line intersects with the stress-strain curve is set as the yielding point.
- d) <u>Strain</u>: The amount of stretch or elongation is able to be found the specimen undergoes during tensile testing. This can be expressed as an absolute measurement in the change in length or as a relative measurement called "strain". Strain itself can be expressed in two different ways, as "engineering strain" and "true strain". Engineering strain is probably the easiest and the most common expression of strain used. It is the ratio of the change in length to the original length. True strain is similar but based on the instantaneous length of the specimen as the test progresses.

Engineering Strain
$$\mathcal{E} = \frac{l_f - l_o}{l_o} = \frac{\Delta l}{l_o} = (\text{Elongation/Initial gage length})$$
 (4.3)

True Strain
$$\varepsilon_t = \int_{0}^{\varepsilon} d\varepsilon = \ln\left(\frac{l}{l_o}\right) = \ln(1+\varepsilon)$$
 (4.4)

Where;

 l_o : original length of the gage section

l_f: final length

l: instantaneous length

4.1.2 Tensile Theories of Continuous Fiber Reinforced Composites

In this chapter the theoretical approaches for tensile properties of continuous fiber reinforced composite materials are given. The calculated mechanical properties and tests results are compared by using these approaches.



Figure 4.2 Continuous fiber reinforced composite

As it is shown on Figure 4.2 the reinforcements are arranged in one axis at continuous fiber reinforced composites. This axis is represented as "1" on Figure 4.2 and these composites are called as "unidirectional fiber reinforced composite". During the tensile tests, test samples are tested at this direction which gives the highest mechanical properties. For this reason, the theoretical approaches for unidirectional are given.

The elongation of the fibers and matrix materials are assumed that the same in continuous fiber reinforced unidirectional composite. This assumption is made considering the fibers and matrix has continuous adhesion with no void in composite structure. By this assumption the elongations;

$$\mathcal{E}_f = \mathcal{E}_m = \mathcal{E} \tag{4.5}$$

Here ε_f , ε_m and ε show the elongations of the fiber, matrix and composite respectively. Using these parameters and the constants Elasticity modulus of fiber (E_f) and matrix (E_m), stresses can be written as;

$$\sigma_f = E_f \times \varepsilon_f \tag{4.6}$$

$$\sigma_m = E_m \times \varepsilon_m \tag{4.7}$$

 σ_f shows the stress of fibers and σ_m shows the stress of the matrix material.

Considering that the load is shared by the matrix and fibers;

$$F_{total} = F_m + F_f \tag{4.8}$$

Here F_{total} is the total load and F_m , F_f are the load shared by matrix and fibers respectively. Using equation (4.1) F_{total} can be expressed in terms of area and stress.

$$F_{total} = F_m + F_f = \sigma \times A_{total} = \sigma_f \times A_f + \sigma_m \times A_m$$
(4.9)

$$\sigma = \sigma_f \times \frac{A_f}{A_{total}} + \sigma_m \times \frac{A_m}{A_{total}}$$
(4.10)

Equation (4.9) can be reformed as (4.10) by the volumetric fiber proportions.

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_f \times \boldsymbol{v}_f + \boldsymbol{\sigma}_m \times \boldsymbol{v}_m = \boldsymbol{\sigma}_f \times \boldsymbol{v}_f + \boldsymbol{\sigma}_m \times (1 - \boldsymbol{v}_f)$$
(4.11)

Here v_f shows the fiber content by volume and v_m shows the matrix content by volume. Using equations (4.5), (4.6) and (4.7) in (4.11), Elasticity modulus of the unidirectional fiber reinforced composite (E) can be written as equation (4.12);

$$E = \frac{E_f \times \varepsilon_f \times \upsilon_f}{\varepsilon} + \frac{E_m \times \varepsilon_m \times (1 - \upsilon_f)}{\varepsilon} = E_f \times \upsilon_f + E_m \times (1 - \upsilon_f) \quad (4.12)$$

Equation (4.12) is called "the rule of mixture" (Mallick, 2008).

Matrix elongates more than reinforcement at break in unidirectional fiber reinforced composite. Therefore; while matrix can elongate, the fibers fractured in composite structure. By these information and equation (4.12) the tensile strength of the composite can be expressed as;

$$\sigma_{Ltu} = \sigma_{fu} \times v_f + \sigma_m^{\ i} \times (1 - v_f)$$
(4.13)

Here, σ_{Ltu} is the unidirectional tensile strength of the composite. σ_{fu} is the tensile strength of the fiber and σ_m^{-1} is the tensile strength of the matrix where strain of the matrix equal to fibers strain at break.

4.2 Thermal Properties of Continuous Fiber Reinforced Thermoplastic Composites

4.2.1 Thermal Conductivity

Fiber reinforced plastic composite materials are considered as replacements for metals. The main factor is which they have better mechanical properties. The strength/weight and stiffness/weight ratios are higher than other metallic alloys. On the other hand, the thermal properties of the fiber reinforced plastic are important for some applications, especially which need thermal stability to composite material can operate.

One of the most important macroscopic thermal properties of composite materials is the effective thermal conductivity, which depends on the conductivities, relative amounts, geometries, and spatial distributions of the constituent phases.

The thermal conductivity of the continuous fiber reinforced composite is much lower than metals and it is anisotropic. These properties cause some difficulties to dissipate the heat in a composite part. For this reason mechanical and thermal properties should considered well, making an effective continuous fiber reinforced composite part.

Especially the composite materials which are used for electrical and electronic components are considered by thermal properties because during operation electronic systems produce a lot of heat. That heat must be dissipated in order to keep the elements at a temperature suitable for their reliable operation.

10°C increase in operating temperature of composite reduces the mean lifetime of the electronic devices by a factor of two (Tavman & Akıncı 2000). Therefore determining the thermal conductivity of the continuous fiber reinforced composite is important. The theoretical and experimental information are given in the following sections.

4.2.2 Thermal Conductivity Theories of Continuous Fiber Reinforced Composites

Thermal conductivity values change depending on to the fiber direction in continuous fiber reinforced composite materials. The differences come from anisotropic structure of the continuous fiber reinforced composite.

There are different existing theories for determining the thermal conductivity but tests samples are prepared as unidirectional and the models which are unidirectional ones are used.

Although there is a common equation used for determining the longitudinal thermal conductivity for unidirectional fiber reinforced composites, there are different approaches for transverse thermal conductivity.

Because of the geometrical disposition, the thermal conductivity in a direction perpendicular to the fiber axis or transverse to the fiber axis can not be obtained from a simple analytical expression.

The views for the transverse axis thermal conductivity are depending on in-plane shear field, the axial shear loading modulus, and elastic moduli model (McIvor, et al. 1990). In addition there are some studies for the effects of the fiber filaments shapes in matrix material to the thermal conductivity (Tai, 1998).

Springer and Tsai (1967) have found a theoretical equation for the thermal conductivity at transverse direction and this equation is similar to the equation which is found by McIvor et al., (1990).

As it is mentioned above there are two different thermal conductivity values for continuous fiber reinforced unidirectional composite materials. The longitudinal thermal conductivity is found by the following equation;

$$k_c = v_f \times k_f + (1 - v_f) \times k_m \tag{4.14}$$

lower bound of the thermal conductivity at transverse axis is found by classical (series model);

$$k_c = \frac{k_m \times k_f}{k_m \times v_f + (1 - v_f) \times k_f}$$
(4.15)

Here;

- k_c : Thermal conductivity of composite material,
- k_m : Thermal conductivity of matrix material,
- k_f : Thermal conductivity of reinforcement (fiber),
- v_f : Fiber ratio by volume.

Springer and Tsai (1967) used shear loading and heat transfer fundamentals and found out a semi-theoretical model for transverse thermal conductivity of unidirectional fiber reinforced composites. In this approach the fibers are assumed that in square form in matrix.

$$k_{c} = k_{m} \left\{ 1 - 2\sqrt{\frac{v_{f}}{\pi}} + \frac{1}{B} \left(\pi - \frac{4}{\sqrt{1 - (\frac{B^{2} \times v_{f}}{\pi})}} \times \tan^{-1} \left(\frac{\sqrt{1 - \frac{B^{2} \times v_{f}}{\pi}}}{1 + B\sqrt{\frac{v_{f}}{\pi}}} \right) \right) \right\}$$
(4.16)

Here;

$$B = 2\left(\frac{k_m}{k_f} - 1\right) \tag{4.17}$$

Thermal conductivity of unidirectional composite at transverse axis can be calculated using the equation 4.19. This equation is found by Halpin-Tsai using the in-plane field and boundary conditions (Progelhof, Throne & Ruetsch 1976).

$$k_{c} = k_{m} \left(\frac{1 + \xi \times v_{f} \times \eta}{1 - \eta \times v_{f}} - 1 \right)$$

$$(4.18)$$

Where
$$\eta = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + \xi}$$
 and $\xi = \sqrt{3} \times \log(\frac{a}{b})$ where a is the width, b is the thickness for

rectangular fibers and $\xi = 1$ for circular or square fibers.

Lewis-Nielsen modified the Halpin-Tsai equation to understand the effects of shape and orientation in two phase system (Progelhof et al., 1976).

$$k_{c} = k_{m} \left(\frac{1 + A \times \phi \times v_{f}}{1 - \phi \times v_{f} \times \psi} - 1 \right)$$
(4.19)

Where;

$$\phi = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A} \tag{4.20}$$

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right) \times \upsilon_f \tag{4.21}$$

The values of A and ϕ_m are found 0.5 and 0.82 from tables given Progelhof et al. (1976) respectively for uniaxially random oriented perpendicular fibers.
Table 4.1 A value for Lewis-Nielsen	n model according to dispersed phas	e and
direction of heat flow		

Type of dispersed phase	Direction of heat flow	Α
Cubes	Any	2.0
Spheres	Any	1.50
Aggregates of spheres	Any	(2.50/ φ _a)- 1
Randomly oriented rods	Any	1.58
Aspect ratio=2		
Randomly oriented rods	Any	2.08
Aspect ratio=4		
Randomly oriented rods	Any	2.8
Aspect ratio=6		
Randomly oriented rods	Any	4.93
Aspect ratio=10		
Randomly oriented rods	Any	8.38
Aspect ratio=15		
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

Table 4.2 $\,\phi_m$ value for Lewis-Nielsen model according to shape of particle and packing type

Shape of Particle	Type of Packing	φ _m
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Spheres	Random close	0.601
Rods or fibers	Uniaxial hexagonal close	0.907
Rods or fibers	Uniaxial simple cubic	0.785
Rods or fibers	Uniaxial random	0.82
Rods or fibers	Three dimensional random	0.52

CHAPTER FIVE

EXPERIMENTAL DETAILS

The determination of the macroscopic behavior of composite materials is one of fundamental and practical importance, particularly now, as new composites are being developed continually for the automotive and aerospace industries, electronic packaging, thermal insulation, and many other applications.

In this chapter, mechanical and thermal tests of the unidirectional thermoplastic composite made of prepreg tapes were examined.

After these tests, Scanning Electron Microcopy (SEM) photographs are investigated for both unidirectional E-glass and carbon fiber polypropylene composites.

5.1 Mechanical Tests

5.1.1 Tensile Tests

Tensile tests samples were prepared according to the TS EN ISO-527 and tested in the AG-50kNG Shimadzu Autograph Series tensile test machinery with a video extensometer system shown in Figure 5.1. For the tests, it was used at a constant cross-speed 2mm/min.

In this study the matrix material is fixed as polypropylene but two different fiber reinforcements are used for tensile tests. These reinforcements are E-glass fiber and carbon fiber. The glass fiber rovings are procured from "Cam Elyaf Sanayii A.Ş." and carbon fiber rovings are procured from Zoltek. The glass fibers are coated with aminosilane coupling agent to make compatible for polypropylene but carbon fibers are not compatible for polypropylene. E-glass fiber is impregnated with two different polypropylene (PP) types using melt impregnation process. These PP types are homopolymer polypropylene and random copolymer polypropylene. In addition different MAH-g-PP ratios are used which are 0%, 3% and 5%. MAH-g-PP is mixed PP before the production process for improving the adhesion between glass fiber and

PP. Carbon fibers are impregnated with only homopolymer PP matrix material. Although carbon fibers have not any bond coating for PP, different MAH-g-PP ratios are used to understand the effects of MAH-g-PP on tensile properties. The MAH-g-PP ratios are 0%, 3% and 5% PP. PP and MAH-g-PP are provided from Basell and ExxonMobil respectively.



Figure 5.1 Tensile test specimen and machinery

Equation (4.12) and (4.13) are show that the volumetric fiber ratio directly affects the mechanical properties of the composite materials. Therefore the volumetric fiber ratio are made almost equal for both carbon fiber and glass fiber reinforced thermoplastic composite to understand the effects of the reinforcing material.

Fiber content for the unidirectional carbon fiber reinforced PP composite is %56 by weight (wt) and the %65 (wt) for E-glass fiber reinforced PP composite.

Using the fiber content by weight, the volumetric fiber contents can be calculated. After volumetric ratios calculated, the elasticity modulus can be found theoretically by equation (4.12). For converting fiber ratio weight to volumetric;

$$w_{f} = \frac{d_{f} \times v_{f}}{\left[(d_{f} \times v_{f}) + (d_{m} + v_{m})\right]} = \frac{d_{f} \times v_{f}}{\left[(d_{f} \times v_{f}) + (d_{m} + (1 - v_{f}))\right]}$$
(5.1)

is generated and used. Here;

- w_f : Fiber content by weight,
- d_f : Density of fiber,
- v_f : Fiber content by volume,
- d_m : Density of matrix,
- v_m : Matrix content by volume.

E-glass fiber Polypropylene (PP) Prepreg;

The properties of the E-glass fiber and polypropylenes are given at Table 5.1. Using these properties, the theoretically elasticity modulus of E-glass fiber reinforced PP composites calculated by equation (5.1) and (4.12).

Properties	E-glass fiber	Carbon fiber	Random copolymer PP	Homopolymer PP
Density (g/cm ³)	2.54	1.81	0.90	0.90
Modulus of elasticity (GPa)	72	242	1.2	1.9
Tensile strength (MPa)	2600	3800	30	40
Thermal conductivity	5.0	6.4	0.20	0.20

 w_f : 0.65

 d_f : 2.54 g/cm³

 v_f Fiber content by volume,

 d_m : 0.90 g/cm³

 v_m : Matrix content by volume,

$$0,65 = \frac{2,54 \times v_f}{\left[(2,54 \times v_f) + (0,90 + (1 - v_f))\right]}; v_f = 0,397, (v_f \% 39,7)$$

Using this content ratio with equation (4.12) elasticity modulus of E-glass fiber reinforced random copolymer PP composite can be calculated as;

$$E_{g1} = E_f \times v_f + E_m \times (1 - v_f) = 72 \times 0,397 + (1 - 0.397) \times 1,2 = 29,31$$
 GPa

Elasticity modulus of E-glass fiber reinforced homopolymer PP composite can be calculated as;

$$E_{g2} = E_f \times v_f + E_m \times (1 - v_f) = 72 \times 0,397 + (1 - 0.397) \times 1,9 = 29,73$$
 GPa

These theoretical values are compared with the tensile tests results. After these theoretical calculations, tensile tests are applied. Tensile test specimens are prepared according to the TS EN ISO-527 and it is shown at Figure 5.2.



Figure 5.2 Tensile test specimen dimensions

		Dimensions (mm)
L ₃	Total length	≥ 150
L ₁	Narrow rectangular section between radius	60± 0.5
R	Radius	≥60
b ₂	Width at the end	20±0.2
<i>b</i> ₁	Width of narrow rectangular	10±0.2
h	Thickness	2-10
L _o	Test length	50±0.5
L	Length between the test machinery gabs	115±1

Table 5.3 Tensile test specimen dimensions

Three test specimens are used in this study for each case and they are produced using compression molding. The test results are shown by tables and graphs below.



Figure 5.3 Tensile test graphs of E-glass fiber reinforced Random Copolymer PP (%0 MAH-g-PP) unidirectional composite



Figure 5.4 Tensile test graphs of E-glass fiber reinforced Homopolymer PP (%0 MAH-g-PP) unidirectional composite



Figure 5.5 Tensile test graphs of E-glass fiber reinforced Random Copolymer PP (%3 MAH-g-PP) unidirectional composite



Figure 5.6 Tensile test results of E-glass fiber reinforced Homopolymer PP (%3 MAH-g-PP) unidirectional composite



Figure 5.7 Tensile test results of E-glass fiber reinforced Random Copolymer PP (% 5 MAH-g-PP) unidirectional composite



Figure 5.8 Tensile test results of E-glass fiber reinforced Homopolymer PP (%5 MAH-g-PP) unidirectional composite

Material	MAH-g-PP	Test no	Yield	Max.	Elastic	Max.
	(%)		stress	Stress	Modulus	Strain
			(MPa)	(MPa)	(GPa)	(%)
		1	260.44	349.26	20.30	1.81
osites	0%	2	348.67	254.42	21.32	1.79
comp		3	271.36	311.51	18.38	1.82
ner PP		Average	293.06	305.06	20.0	1.80
polyn		1	169.53	353.92	25.96	1.42
lom cc	3%	2	-	400.24	28.20	1.42
l Rand	Rand	3	-	410.40	29.70	1.31
forced		Average	169.53	388.18	27.95	1.38
er rein		1	431.17	454.41	33.49	1.55
E-glass fibe	5%	2	-	688.42	35.01	2.08
		3	566.56	606.98	39.65	1.53
		Average	498.86	583.27	36.05	1.72

Table 5.2 Tensile test results of E-glass fiber reinforced Random Copolymer PP (0%, 3% and 5% MAH-g-PP) unidirectional composite

Material	MAH-g-PP	Test no	Yield	Max.	Elastic	Max.
	(%)		stress	Stress	Modulus	Strain
			(MPa)	(MPa)	(GPa)	(%)
		1	430.00	453.50	25.52	1.92
ites	0%	2	186.12	348.51	23.47	1.64
isoduu		3	176.24	327.13	23.91	1.42
. PP cc		Average	264.12	376.28	24.3	1.66
olymer		1	308.89	485.59	29.89	1.63
omope	3%	2	486.46	532.58	28.50	1.97
ced H	Eed Ho	3	442.70	478.28	29.31	1.73
einford		Average	412.68	498.82	29.23	1.77
iber re		1	445.24	518.78	33.67	1.62
lass f	5%	2	531.00	572.26	32.90	1.87
E-g		3	-	537.41	37.54	1.51
		Average	488.12	542.81	34.70	1.67

Table 5.3 Tensile test results of E-glass fiber reinforced Homopolymer PP (0%, 3% and 5%MAH-g-PP) unidirectional compositeMAH-g-



Figure 5.9 Tensile test specimen of E-glass fiber reinforced PP after test

These results are discussed in "Chapter Six - Results and Discussion".

Carbon fiber- Polypropylene Prepreg;

The properties of the carbon fiber and polypropylene are given at Table 5.1. Using these properties the theoretical elasticity modulus of continuous carbon fiber reinforced unidirectional PP composite calculated by equation (5.1.) and (4.12).

$$0,56 = \frac{1,81 \times v_f}{\left[(1,81 \times v_f) + (0,90 + (1 - v_f))\right]}; v_f = 0,387, (v_f \% 38,7)$$

Using this content ratio with equation (4.12) elasticity modulus of continuous carbon fiber reinforced unidirectional PP composite can be calculated as;

$$E_1 = E_f \times v_f + E_m \times (1 - v_f) = 242 \times 0.387 + (1 - 0.397) \times 1.9 = 94.82$$
 GPa

Tensile test specimens were prepared and tested similar with E-glass fiber reinforced unidirectional PP composite.



Figure 5.10 Tensile test results of carbon fiber reinforced Homopolymer PP (%0 MAH-g-PP) unidirectional composite



Figure 5.11 Tensile test results of carbon fiber reinforced Homopolymer PP (%3 MAH-g-PP) unidirectional composite



Figure 5.12 Tensile test results of carbon fiber reinforced Homopolymer PP (%5 MAH-g-PP) unidirectional composite

Material	MAH-g-PP	Test no	Yield	Max.	Elastic	Max.
	(%)		stress	Stress	Modulus	Strain
			(MPa)	(MPa)	(GPa)	(%)
		1	-	761.36	70.60	0.77
	0%	2	-	385.20	68.20	0.61
fes		3	-	408.16	77.96	0.44
mposit		Average	-	518.24	72.25	0.60
PP col		1	620.27	827.75	85.33	0.77
orced	3%	2	518.37	629.97	102.87	0.57
· reinfo		3	594.18	751.45	90.57	0.22
fiber		Average	577.60	736.40	92.93	0.52
arbon		1	436.20	681.75	129.20	0.67
Ű	5%	2	-	620.31	104.70	0.43
		3	-	586.30	108.61	0.58
		Average	436.20	629.45	114.17	0.56

Table 5.4 Tensile test results of carbon fiber reinforced PP (0%, 3% and 5% MAH-g-PP) unidirectional composite



Figure 5.13 Tensile test specimen of carbon fiber reinforced PP after test

5.1.2 Charpy Impact Tests

Charpy/Izod tests are used to determine impact strengths and toughness. However, in composites the crack often turns and runs parallel to the fibres until it finds a specimen edge. It has been shown that the impact energies of fiber reinforced composite are equal or higher than those of steel and aluminum, and the impact responses and damage mechanisms are complex and depend on a number of parameters including impact velocity, impact mass, impact angle, shape of striker, target geometry, and target material.

In Charpy test, the pendulum hammer in the apparatus is raised to a set height above the specimen and released; it will swing down and impact the specimen. Assuming the sample doesn't stop the hammer, the hammer will continue to swing after impact. Assuming that the pendulum pivot has relatively low friction, the energy is just the difference in the two heights times the weight of the hammer. The apparatus has a dial gauge that directly reads the impact energy. This energy absorbed by the specimen, as it breaks, can qualitatively be related to its fracture mode (ductile or brittle.) Ductile fracture, which involves substantial plastic deformation, would require much more energy than brittle fracture. Note that the fracture energy measured in a Charpy impact test is a relative energy and can only be used to compare dimensionally identical specimens; it cannot be easily used directly in engineering calculations.

The test specimens are prepared from E-glass, carbon fiber reinforced unidirectional random copolymer and homopolymer PP types with 0%, 3% and 5% MAH-g-PP. The test specimens are in dimensions of 10x10x50 mm which are unnotched and fiber contents by weight are 65% and 56% for E-glass, carbon fiber reinforced PP respectively. The test specimens are tested using universal Charpy impact test machinery (Figure 5.14). In figure 5.15 impact test specimens are shown after tests.



Figure 5.14 Charpy impact test machinery



Figure 5.15 Impact test specimens after tests (E - glass and carbon fiber reinforced PP composites)

Test results are listed at table 5.5 and these results are discussed at last chapter.

MAH-g- PP (%)	Impact test results (Joule)				
	E-glass fiber Random Co. PP	E-glass fiber Homopo. PP	Carbon fiber Random Co. PP	Carbon fiber Homopo. PP	
0	20.5	19.6	82	78.8	
3	23	19.1	86.5	82	
5	21	17	87	76.4	

Table 5.5 Impact test results of E-glass and carbon fiber reinforced PP (0%, 3% and 5% MAH-g-PP) unidirectional composite

5.1.3 Flexural Tests

One of the most common experiments to characterize materials in flexural conditions is the three-point bending test. Flexural loads are really a combination of tensile, compression and shear loads. When loaded as shown Figure 5.16, the upper face is put into compression, the lower face into tension and the central portion of the laminate experiences shear.



Figure 5.16 The loading due to flexure on a composite body

In this study, flexural specimens were machined from flat panels from unidirectional E-glass and carbon fiber reinforced polypropylene (Random Copolymer PP with 5% MAH-g-PP) composites. The dimensions of the flexural test specimens were 100x10x5 mm.

The three-point bend tests are performed at AG-50kNG Shimadzu Autograph Series test machinery running in compression mode (Figure 5.17). The center loading a cylindrical pin moved at a rate of 2 mm/min.



Figure 5.17 Flexural shear test of E-glass fiber reinforced PP

The maximum fiber stress at failure on the tension side of a flexural specimen is considered the flexural strength of the material. Thus, using a homogeneous beam theory, the flexural strength in a three-point flexural test is given by;

$$\sigma_{uf} = \frac{3P_{\max}L}{2bh^2}$$
(5.1)

Where; σ_{uf} denotes the flexural strength, P_{max} the maximum applied load that leads the specimen to rupture, L the support span, b the specimen width and h specimen thickness.

Flexural modulus is calculated from the initial slope of the load-deflection curve:

$$E_f = \frac{L^3}{4bh^3} \frac{\Delta P}{\Delta \delta}$$
(5.2)

Where; $\Delta P/\Delta\delta$ represents the slope of the load – defection curve; and E_f the flexural modulus.

The test results are listed at Table 5.6 and the graphs of the flexural tests are shown in Figure 5.18.



Figure 5.18 The graph of flexural tests

Specimen	Max. Load (N)	Yield stress (MPa)	Max. Stress (MPa)	Flexural Modulus (GPa)	Max. Strain (%)
E-glass fiber PP	2511.25	341.49	364.53	7.60	4.56
Carbon fiber PP	1486.87	190.33	202.41	13.63	2.10
E-glass fiber PE	1040.62	204.09	207.33	8.45	2.63

Table 5.6 Test results of flexural tests

5.2 Thermal Tests

5.2.1 Thermal Conductivity Tests

There are two kind of thermal conductivity test methods in practical applications. These are transient and steady methods classified in Table 5.7.

In this study, hot wire method which is a kind of transient thermal conductivity testing method was used. Tavman & Akıncı (2000) investigated transverse thermal conductivity of high density polyethylene reinforced with chopped strand glass fiber mat using hot wire technique.

Classification	Sub-classification	Remarks
	Absolute method	JIS A-1413 R-2616
Steady method	Reference method	ASTM C-177, C-518
	Ängstrom method	
	Flash method	ASTM D 2326
Transient method	Hot wire method	JIS R-2618
	QTM® method	

Table 5.7 Methods of measuring thermal conductivity

Infinitely slender heating wire is stretched axially through the center of a cylindrical specimen of infinite length and thickness as shown Figure 5.19. After constant power is supplied to this cylindrical heating wire, the increment of temperature can be calculated using equation (5.3) and (5.4), in which r is the distance of that point from the heating wire.



Figure 5.19 Principle of hot wire method

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial \gamma^2} + \frac{1}{\gamma} \frac{\partial T}{\partial t}$$
(5.3)

Here α is thermal diffusivity of specimen. When the calorific value is q (0.86RI²) per unit length and unit time and r is 0 the following equation can be formed as;

$$q = -2\pi\gamma\lambda\frac{\partial T}{\partial\gamma}$$
(5.4)

The solution of the equation (5.4) can be found as;

$$T = \frac{q}{4\pi\lambda} \int_{0}^{t} \frac{\exp(-\frac{\gamma^2}{4\alpha t})}{t} dt$$
(5.5)

When the $r/2\sqrt{\alpha t}$ <0.17 is obtained and the temperature of the heating wire is expressed t₁=T₁ and t₂=T₂ the following approximate equation found and the error 1% maximum.

$$x = q \frac{\ln(\frac{t^2}{t^1})}{4\pi(T_2 - T_1)}$$
(5.6)

The equation (45.6) is the basic expression for the hot wire technique and it is explained by a Figure 5.7. If nichrome or constantan wire diameter is less then 0.5 mm the condition $r/2\sqrt{\alpha t} < 0.17$ will be satisfied for almost all materials.

E-glass fiber Polypropylene (PP) Prepreg;

Using the properties of E-glass fiber and Polypropylene given at Table 5.1 the theoretical transverse thermal conductivities are calculated by equations which are found by Halpin-Tsai, Springer-Tsai, Lewis-Nielsen and classical models respectively for unidirectional E-glass fiber reinforced PP composites with %39.7 volumetric (65% wt) fiber ratio.

If the thermal conductivity at transverse axis is calculated by the equation Halpin-Tsai, first ξ and η have to be found out.

$$\xi = 1, \eta = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + \xi} = \frac{\frac{5}{0.20} - 1}{\frac{5}{0.20} + 1} = 0.923$$

$$k_{c} = k_{m} \left(\frac{1 + \xi \times v_{f} \times \eta}{1 - \eta \times v_{f}} - 1 \right) = 0.2 \left(\frac{1 + 1x0.397 \times 0.923}{1 - 0.923 \times 0.397} - 1 \right) = 0.431 W / m.K$$

Using equation (4.17) and (4.18) expressed by Springer-Tsai the transverse thermal conductivity is calculated as;

$$B = 2\left(\frac{k_m}{k_f} - 1\right) = 2\left(\frac{0.2}{5} - 1\right) = -1.92$$

$$\begin{split} k_{c} &= k_{m} \left\{ 1 - 2\sqrt{\frac{v_{f}}{\pi}} + \frac{1}{B} \left(\pi - \frac{4}{\sqrt{1 - (\frac{B^{2} \times v_{f}}{\pi})}} \times \tan^{-1} \left(\frac{\sqrt{1 - \frac{B^{2} \times v_{f}}{\pi}}}{1 + B\sqrt{\frac{v_{f}}{\pi}}} \right) \right) \right\} \\ &= 0.22 \left\{ 1 - 2\sqrt{\frac{0.397}{\pi}} + \frac{1}{-1.92} \left(\pi - \frac{4}{\sqrt{1 - (\frac{(-1.92)^{2} \times 0.397}{\pi})}} \times \tan^{-1} \left(\frac{\sqrt{1 - \frac{(-1.92)^{2} \times v_{f}}{\pi}}}{1 + (-1.92) \times \sqrt{\frac{0.397}{\pi}}} \right) \right) \right\} \\ &= 0.487W / m.K \end{split}$$

After the ϕ and ψ are calculated transverse thermal conductivity is calculated using Lewis-Nielsen equation 4.19;

$$\phi = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A} = \frac{\frac{5}{0.2} - 1}{\frac{5}{0.2} + 0.5} = 0.9411,$$

$$\psi = 1 + (\frac{1 - \phi_m}{\phi_m^2}) \times v_f = 1 + \left(\frac{1 - 0.82}{0.82^2}\right) \times 0.397 = 1.106$$

$$k_c = k_m \left(\frac{1 + A \times \phi \times v_f}{1 - \phi \times v_f \times \psi} - 1\right) = 0.2 \left(\frac{(1 + 0.5 \times 0.9411 \times 0.397)}{1 - 0.9411 \times 0.397 \times 1.106}\right) = 0.404W / mK$$

The last equation used to determine the transverse thermal conductivity is the simplest and basic one. Using this series model equation (4.16.) thermal conductivity determined as;

$$k_c = \frac{k_m \times k_f}{k_m \times v_f + (1 - v_f) \times k_f} = \frac{0.20x5}{0.20x0.397 + (1 - 0.397)x5} = 0.323W / m.K$$

After the theoretical values are calculated, the tests are applied to determine the differences. The basic steps for thermal conductivity tests were explained below.

While the thermal conductivity tests are applied, the calibration sample used to improve the test results. Because there could be deviations from the real thermal conductivity compared with the test results. Thermal conductivity of calibration sample is given by the thermal conductivity test machinery producer.



Figure 5.20 Shotherm QTM thermal conductivity meter

In test procedure, first calibration test sample tested with machinery (Figure 5.20) using a probe which is shown in Figure 5.21. The tested value is compared with the given reference value and found out the deviation ratio. This step of test procedure is made systematically to check the machinery.



Figure 5.21 Shotherm QTM thermal conductivity meter probe with test specimen under

After this step two test sample of each E-glass fiber is impregnated random copolymer and homopolymer PP composites specimens which have different MAH-g-PP ratios are tested. The MAH-g-PP ratios are 0%, 3% and 5% which is similar with tensile tests. Using the same MAH-g-PP ratios is used for understanding the relation between the thermal and mechanical properties. Besides, effects of different MAH-g-PP ratios on to the thermal conductivity are examined as well.

All thermal test specimens are compression molded under heat and pressure in dimensions 18x50x100 mm. During the tests both side of the samples are tested to get uniform thermal conductivity results. The test results of continuous E-glass fiber reinforced PP composites specimens are listed at Table 5.8 and 5.9. These results are corrected using calibration sample. Calibration sample is tested at beginning, middle and end of the tests.

Material	MAH-g-PP	Test sample	Initial	Average	Thermal
	(%)		Temp.	Temp.	conductivity
			$(T_i \ ^\circ C)$	(T _{av} °C)	(W/mK)
osites	0%	1	28	47	0.396
			30	48	0.402
			30	48	0.390
			30	48	0.403
		2	30	48	0.411
			30	49	0.400
			29	47	0.403
			30	48	0.405
omp		Average	29.6	47.85	0.400
PP c	3%	1	28	46	0.445
ner			29	46	0.428
E-glass fiber reinforced random copolyn			28	45	0.418
			29	47	0.408
		2	28	46	0.417
			30	46	0.454
			29	46	0.444
			29	46	0.420
		Average	28.75	46	0.43
	5%	1	25	41	0.426
			25	42	0.454
			27	25	0.422
			27	44	0.457
		2	26	45	0.435
			27	44	0.445
			28	47	0.449
			29	45	0.448
		Average	26.75	41.6	0.442

Table 5.8 Thermal conductivity test results of E glass fiber reinforced Random Copolymer PP composite

Material	MAH-g-PP	Test sample	Initial	Average	Thermal
	(%)		Temp.	Temp.	conductivity
			$(T_i \ ^\circ C)$	$(\mathbf{T}_{\mathbf{av}} \circ \mathbf{C})$	(W/mK)
osites	0%	1	27	43	0.401
			28	44	0.408
			29	45	0.394
			29	45	0.410
		2	30	46	0.400
			30	46	0.417
			27	46	0.4405
			28	47	0.410
duo		Average	28.5	46.1	0.406
E-glass fiber reinforced random copolymer PP c	3%	1	26	43	0.486
			27	44	0.445
			27	45	0.459
			27	45	0.450
		2	27	46	0.462
			27	46	0.460
			28	46	0.455
			28	47	0.464
		Average	27.1	45.25	0.46
	5%	1	28	44	0.481
			29	45	0.510
			29	45	0.505
			29	46	0.520
		2	29	44	0.496
			30	45	0.505
			30	46	0.487
			30	46	0.480
		Average	29.25	45.1	0.498

Table 5.9 Thermal conductivity test results of E glass fiber reinforced Homopolymer PP composite

Carbon fiber Polypropylene (PP) Prepreg;

Carbon fiber reinforced homopolymer PP composites with %38.7 volumetric (56% wt) fiber content is used for transverse thermal conductivity tests. After the tests, test results are compared with theoretical models used in E-glass fiber reinforced PP too.

Using the properties of carbon fiber and Polypropylene given at Table 5.1 the theoretical transverse thermal conductivities are calculated by Halpin-Tsai, Springer-Tsai, Lewis-Nielsen and series (classical) models.

If Halpin-Tsai model is used, first η is needed for $\xi=1$.

$$\xi = 1, \eta = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + \xi} = \frac{\frac{6.4}{0.20} - 1}{\frac{6.4}{0.20} + 1} = 0.94$$

Using this value, transverse thermal conductivity of continuous carbon fiber reinforced PP composite is found as;

$$k_c = k_m \left(\frac{1 + \xi \times v_f \times \eta}{1 - \eta \times v_f} - 1 \right) = 0.2 \left(\frac{1 + 1.x \cdot 0.387 \times 0.94}{1 - 0.94 \times 0.387} - 1 \right) = 0.428 W / m.K$$

Another model which is expressed by Springer-Tsai is used and the transverse thermal conductivity is calculated from equation (4.17) and (4.18);

$$B = 2\left(\frac{k_m}{k_f} - 1\right) = 2\left(\frac{0.2}{6.4} - 1\right) = -1.937$$

$$k_{c} = k_{m} \left\{ 1 - 2\sqrt{\frac{\nu_{f}}{\pi}} + \frac{1}{B} \left(\pi - \frac{4}{\sqrt{1 - (\frac{B^{2} \times \nu_{f}}{\pi})}} \times \tan^{-1} \left(\frac{\sqrt{1 - \frac{B^{2} \times \nu_{f}}{\pi}}}{1 + B\sqrt{\frac{\nu_{f}}{\pi}}} \right) \right) \right\}$$
$$= 0.2 \left\{ 1 - 2\sqrt{\frac{0.387}{\pi}} + \frac{1}{-1.937} \left(\pi - \frac{4}{\sqrt{1 - (\frac{(-1.937)^{2} \times 0.387}{\pi})}} \times \tan^{-1} \left(\frac{\sqrt{1 - (\frac{(-1.937)^{2} \times 0.387}{\pi}}}{1 + (-1.937) \times \sqrt{\frac{0.387}{\pi}}} \right) \right) \right\}$$
$$= 0.484W/mK$$

Using Lewis-Nielsen model (equation 4.19), first φ and ψ are calculated;

$$\phi = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A} = \frac{\frac{6.4}{0.2} - 1}{\frac{6.4}{0.2} + 0.5} = 0.9538,$$

$$\psi = 1 + (\frac{1 - \phi_m}{\phi_m^2}) \times v_f = 1 + \left(\frac{1 - 0.82}{0.82^2}\right) \times 0.397 = 1.1036$$

Transverse thermal conductivity is calculated as,

$$k_c = k_m \left(\frac{1 + A \times \phi \times v_f}{1 - \phi \times v_f \times \psi} - 1 \right) = 0.2 \left(\frac{(1 + 0.5 \times 0.9538 \times 0.387)}{1 - 0.9538 \times 0.397 \times 1.1036} \right) = 0.4W / mK$$

The last model is series model and this model is given transverse thermal conductivity as;

$$k_{c} = \frac{k_{m} \times k_{f}}{k_{m} \times v_{f} + (1 - v_{f}) \times k_{f}} = \frac{0.2x6.4}{0.2x0.387 + (1 - 0.387)x6.4} = 0.32W / m.K$$

which is also lower value for all models.

The transverse thermal conductivity test results of continuous carbon fiber reinforced PP specimens are listed at Table 5.10. These results are corrected with calibration sample during the tests too.

Material	Test sample	Initial	Average	Thermal
		Temp.	Temp.	conductivity
		$(\mathbf{T}_i \ ^\circ \mathbf{C})$	(T _{av} °C)	(W/mK)
orced PP composites		29	44	0.573
		30	46	0.595
	1	30	45	0.575
		31	46	0.591
		32	46	0.588
		31	47	0.574
		29	45	0.560
reint		31	47	0.600
Zarbon fiber	2	31	46	0.595
		32	47	0.552
		32	47	0.562
		33	48	0.554
	Average	31	46.1	0.571

Table 5.10 Thermal conductivity test results of carbon fiber reinforced PP

Test results and calculated theoretical values are compared at last chapter for both E-glass and carbon fiber reinforced PP composites.

5.3 Scanning Electron Microcopy (SEM) Analysis

The surfaces and section of the prepreg samples are investigated by using a Scanning Electron Microscope (SEM) in order to observe fiber distribution in composite and interface interaction between fiber and polymer. The SEM photographs are taken at different magnifications using JEOL JSM 6060 (Figure 5.22) SEM machinery.



Figure 5.22 Scanning Electron Microscope (SEM)

SEM photographs are useful for understanding the morphologies and adhesion in composite structures. The adhesion between the matrix and reinforcement can be examined from dendrite structure on photographs. The adhesion is directly proportional to dendrite structure between matrix and reinforcement.

Both E-glass and carbon fiber reinforced polypropylene prepreg are used for SEM photographs. Besides two different E-glass fiber reinforced polypropylene prepreg is supplied which are already market and they are compared with E-glass fiber reinforced polypropylene prepreg which is manufactured in this study using SEM photographs. These products SEM photographs are shown in Figure 5.24 and 5.25.

Figure 5.23 and 5.26 illustrates the unidirectional E-glass and carbon fiber polypropylene prepreg. The unidirectional structures of the prepregs are seen more clearly from these figures.


Figure 5.23 SEM photographs of unidirectional E-glass fiber PP composites



Figure 5.24 SEM photographs of unidirectional E-glass fiber PP obtained from market (product-1)



Figure 5.25 SEM photographs of unidirectional E-glass fiber PP obtained from market (product-2)



Figure 5.26 SEM photographs of unidirectional carbon fiber PP composites

CHAPTER SIX

RESULTS AND DISCUSSION

Results of this study can be discussed in two sections as thermal and mechanical properties. Glass fiber and carbon fiber polypropylene prepreg composite were used in this study and they gave us different thermal and mechanical behaviors. If the tensile tests and theoretical results are compared the differences are seen.

The theoretical elasticity modulus of glass fiber reinforced Random copolymer PP is calculated as 29.31 GPa and Homopolymer PP as 29.73 GPa by theoretical. On the other hand the test results of elasticity modulus are represented in Figure 6.1.



Figure 6.1 Changing of elasticity modulus depending on MAH-g-PP ratio for E-glass fiber reinforced PP

Figure 6.1 shows that E-glass fiber adhesion with PP increases using MAH-g-PP for both Random copolymer and Homopolymer types. The theoretical elasticity modules show similarities with 3% MAH-g-PP added specimens.

It can be seen from the graphs that E-glass fiber reinforced Homopolymer is more rigid than Random copolymer until the 5% MAH-g-PP added to Random copolymer PP. Although there is not any parameter for matrix modification parameter in rule of mixture, it is understood from test results that modification PP with MAH-g-PP is increased the modulus of elasticity value.

Tensile stress is increased with adding MAH-g-PP as well for E-glass fiber (Figure 6.2). Homopolymer PP shows good mechanical properties for 0% and 3% MAH-g-PP added specimens however tensile stress of Random copolymer PP which is 5% added MAH-g-PP is higher than Homopolymer PP.



Figure 6.2 Changing of tensile stress depending on MAH-g-PP ratio for E-glass fiber reinforced PP

MAH-g-PP addition in PP results in loss of ductility, increased stiffness, leads to higher values of tensile strength and modulus.

On the other hand carbon fiber-PP has 94.82 GPa elasticity modulus by theoretically. This value is similar with 3% MAH-g-PP added carbon fiber reinforced PP specimen which has 93 GPa elasticity modulus (Figure 6.3).



Figure 6.3 Changing of elasticity modulus depending on MAH-g-PP ratio for carbon fiber reinforced PP

Although adding 5% MAH-g-PP to carbon fiber reinforced PP is increased modulus of elasticity, it is decreased the tensile stress (Figure 6.4). Therefore the MAH-g-PP ratio has to be selected depending on the application where tensile stress or rigidity needed. Besides the optimum MAH-g-PP ratio can be determined using different ratios between 3% and 5% for getting the maximum mechanical performance for elasticity modulus and tensile stress at the same time.



Figure 6.4 Changing of tensile stress depending on MAH-g-PP ratio for carbon fiber reinforced PP

However, carbon fibers used in this study are not directly compatible for polypropylene; MAH-g-PP increases the mechanical properties. The mechanical properties of carbon fiber reinforced polypropylene composites may be increased if the carbon fibers are coated with coupling agent to make compatible for polypropylene.

Impact energy absorption is an important factor in studying the impact properties of materials. The impact performance of materials can be determined and compared from an impact test by keeping the specimen shape and boundary condition unchanged.

The Figure 6.5 illustrates that 5% MAH-g-PP is decreased absorbed energy and make prepreg materials more brittle except carbon fiber reinforced random copolymer PP composite. On the hand, homopolymer PP shows more brittle properties than random copolymer for both E-glass and carbon fiber reinforced specimens.

If the test specimens are examined after tests, the failure mode of carbon fiber reinforced PP is preferable to the E-glass fiber reinforced PP since after the impact carbon fiber reinforced PP still has strength to resist a higher impact load and to prevent the penetration of the striker head. Although E-glass fiber reinforced PP composite specimens are delaminated after the impact test, carbon fiber reinforced PP composite specimens are only delaminated from the edges.



Figure 6.5 Changing of impact energy depending on MAH-g-PP ratio for E-glass and carbon fiber reinforced PP

Flexural strength is the ability of the composite material to withstand bending forces applied perpendicular to its longitudinal axis. When the flexural tests results are examined, it is seen that E-glass fiber reinforced PP composites have higher load carry capacity than carbon fiber reinforced PP. Carbon fiber reinforced PP is more brittle than E-glass fiber reinforced PP although they have almost the same fiber contents. In addition, this brittle structure of carbon fiber reinforced PP composite decreased the deflection. Although carbon fiber reinforced PP specimen is deflected 5.85 mm. This is expected before the tests because E-glass fiber has higher elongation at break value

than carbon fiber. In addition, this poor shear strength of carbon fiber reinforced polypropylene, reinforced with high modulus fibers in particular, is generally attributed to a lack of bonding at the fiber-matrix interface (Kim & Mai, 1998).

In summary; if all mechanical tests are examined totally, the results which are listed below are found,

1- The maximum tensile strength is obtained using 5% MAH-g-PP with Random Copolymer PP for unidirectional E-glass fiber reinforcements and 3% MAH-g-PP Homopolymer PP for unidirectional carbon fiber,

2- The maximum elasticity modulus is obtained using 5% MAH-g-PP with Random Copolymer PP for unidirectional E-glass fiber reinforcements and 5% MAH-g-PP Homopolymer PP for unidirectional carbon fiber,

3- The maximum impact properties are found using 3% MAH-g-PP with Random Copolymer PP for unidirectional E-glass fiber reinforcements and 3% MAH-g-PP Random Copolymer PP for unidirectional carbon fiber.

4- E-glass fiber reinforced PP composite is lower mechanical properties than carbon fiber reinforced except flexural tests however E-glass fiber reinforced PP has a higher ductility than carbon fiber reinforced PP for all specimens.

If thermal conductivity test results are examined, Lewis-Nielsen model is found most adequate theoretical model for both unidirectional E-glass fiber reinforced random copolymer and homopolymer polypropylene for 0% MAH-g-PP. Adding MAH-g-PP increases transverse thermal conductivity for all specimens and changes the adequate model. Although Halpin-Tsai model gives almost the same value for 3% MAH-g-PP for E-glass fiber reinforced random copolymer PP, Springer-Tsai is more proper when MAH-g-PP ratio is increased to %5.

On the other hand, MAH-g-PP increases transverse thermal conductivity of homopolymer more than random copolymer polypropylene. However this difference is only 10% maximum. The test results and calculated values are listed at Table 6.1.

Besides the thermal conductivity test results are graphed depending on to the MAHg-PP ratio is shown Figure 6.6 as well.



Figure 6.6 Changing of transverse thermal conductivity depending on MAH-g-PP ratio for E-glass reinforced random copolymer and homopolymer PP

		Therm	al Conductivity (W/mK)	
		Carbon fiber PP	E-glass fiber reinforced	E-glass fiber reinforced
			Rand. Co. PP	Homopo. PP
Calculated results	Series model	0.320	0.323	
	Halpin-Tsai model	0.428	0.431	
	Springer-Tsai model	0.484	0.487	
	Lewis-Nielsen model	0.400	0.404	
Test results	%0 MAH-g-PP	-	0.400	0.400
	%3 MAH-g-PP	-	0.430	0.460
	%5 MAH-g-PP	0.571	0.440	0.490

Table 6.1 Thermal conductivities of test specimens

Springer-Tsai model is resulted more proper for carbon fiber reinforced PP composite. The test result is found 0.571 W/mK for carbon fiber PP composite and calculated transverse thermal conductivity of unidirectional carbon fiber reinforced PP as 0.484 W/mK using Springer-Tsai model and which is % 15 differences with the test results average. The result of Halpin-Tsai model is 0.443 W/mK. The transverse thermal conductivity is found 0.320 W/mK from series model which is also the lower bound of the theoretically transverse thermal conductivity.

The experimental results show that the most adequate theoretically model is changed depending on MAH-g-PP ratios for unidirectional reinforced E-glass fiber reinforced PP, however, Springer-Tsai model is resulted more adequate for carbon fiber reinforced PP composite. From these results it is understood that different type of the fibers, contents and MAH-g-PP changes the adequate theoretical model. Therefore, other fiber contents and materials should be used to understand these models and optimize a theoretical model for transverse thermal conductivity calculations. The tests were applied at room temperature and constant fiber content for each composite but the adequate theoretically model may be changed depending on the room temperature and fiber content.

In accordance with SEM analysis it is observed that the thermoplastic matrices without compatibility with fibers show poor adhesion. The glass fibers-PP has a stronger interfacial adhesion than carbon fibers-PP. Carbon fibers were not well impregnated with matrix material and the fibers situated freely in prepreg material.

In addition E-glass fiber reinforced PP can be compared with other products in the market using SEM photographs. SEM photographs are showed that E-glass fiber reinforced PP prepreg which is developed in this study has higher quality than "Product 2" and is similar with "Product 1".

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