T.C.
ONDOKUZ MAYIS UNIVERSITY
GRADUATE SCHOOL OF SCIENCES
NANOSCIENCE AND NANOTECHNOLOGY

INVESTIGATION ON THE EFFECT OF NANOMATERIALS ON THE MECHANICAL PROPERTIES OF THERMOPLASTIC COMPOSITES

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THESIS APPROVAL

"INVESTIGATION OF THE EFFECT OF MWCNT NANOMATERIALS ON THE MECHANICAL PROPERTIES OF LPET/GF THERMOPLASTIC COMPOSITES" thesis study, prepared by Ali Al-darkazali, has been accepted by the jury given below on the date 04../..12./2017 as a Master thesis in the Graduate School of Science/ Department of Nanoscience and Nanotechnology at Ondokuz Mayıs University.

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ETHICAL DECLARATION

I declare that all the information in this thesis is accurate and prepared in accordance with the thesis writing rules of Ondokuz Mayis University, Graduate School of Science. I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

Ali Al-darkazali

ABSTRACT

Master's Thesis

INVESTIGATION OF THE EFFECT OF MWCNT NANOMATERIALS ON THE MECHANICAL PROPERTIES OF LPET/GF THERMOPLASTIC COMPOSITES

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In recent times, studies regarding nanotechnology have become popular and substantial in contribution terms to the multidisciplinary research fields. The ever-expanding desire for improved properties of thermoplastic matrix composite materials especially for light-weight structures and multifunctional characteristics has highly shifted the focus of researchers and investigators on using nanomaterials as an assistant factor for strengthening these thermoplastic composites. Carbon nanotubes (CNTs) are famous for their outstanding properties in terms of their exceptional lightness, high aspect ratio, strength and stiffness and additional multi-functional characteristics. For these reasons the usage of these nanotubes could create remarkable property enhancements and hence improving the mechanical properties of the materials that incorporated with these nanoscale materials.

Within this research, Multi-Walled Carbon Nanotubes (MWCNTs) were incorporated with thermoplastic polymer and reinforcement fibers to fabricate composite materials with improved mechanical properties. Commingled fibers (low melting point polyethylene terephthalate fiber/glass fiber) were used in Non-Crimp Fabric (NCF). NCFs were coated with different weight percentages of MWCNTs (0.7 wt%, 0.9 wt% and 1.1 wt%) in order to produce thermoplastic composites using hot-press technique. Samples were prepared for each percentages with different directions such as 0°, 45° and 90°. The fabricated specimens were tested against tensile and three-point flexural loadings. Specimens with 0.9 wt% MWCNTs in 45° direction showed the highest values of tensile and flexural properties with an improving of about 8% and 33% in tensile and flexural modulus and about 3% and 65% in tensile and flexural strength compared to specimens without MWCNTs in 45° direction.

Keywords: polymer matrix, Carbon Nanotube (CNT), commingled fibers, non-crimp fabric, thermoplastic composites, tensile and three-point flexural tests.

ÖZET

yüksek lisans tezi

ÇDKNT NANOMALZEMELERİN LPET/CE TERMOPLASTİK KOMPOZİTLERİN MEKANİK ÖZELLİKLERİ ÜZERİNE ETKİSİNİN İNCELENMESİ

Ali AL-DARKAZALI

Ondokuz mayıs üniversitesi

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Nanobilim ve Nanoteknoloji Bölümü

Danışman: Asst. Prof. Dr. İbrahim İNANÇ

Son zamanlarda, nanoteknoloji ile ilgili yapılan disiplinlerarası çalışmalar ve araştırmalar diğer alanlara çok büyük katkılarda bulunduklarından dolayı çok popüler ve önemli hale geldiler. Hafif yapılar ve çok fonksiyonlu yapılarda kullanılan termoplastik matris kompozit malzemelerin geliştirilmiş özelliklerine duyulan ve sürekli artan talep, araştırmacıların odağını nanomalzemeleri bu termoplastik bileşiklerin güçlendirilmesi için bir yardımcı faktör olarak kullanmaya yöneltti. Karbon nanotüpler (KNT'ler), olağanüstü hafifliği, yüksek en boy oranı, mukavemeti ve sertliği ve çok fonksiyonlu özellikleri açısından üstün özellikleri ile ünlüdür. Bu nedenlerden ötürü, bu nanotüplerin kullanılması olağanüstü iyileştirmeler yaratabilir ve dolayısıyla nanomalzemelerle birleştirilen malzemelerin mekanik özelliklerini geliştirir. Bu araştırmada, çok duvarlı karbon nanotüpleri (ÇDKNT), gelişmiş mekanik özelliklere sahip kompozit malzemeleri imal etmek için termoplastik polimer ve takviye lifleri ile birleştirildi. Karıştırılmış lifler (düşük erime noktalı polietilen tereftalat (LPET) elyaf / cam elyafı (CE)) Kıvrımsız

Kumaş (KK) kullanıldı. KK'ler, sıcak-pres tekniği kullanılarak termoplastik kompozitleri üretmek için farklı ÇDKNT ağırlık yüzdeleri ile (ağırlıkça % 0.7, % 0.9 ve % 1.1) kaplandı. Numuneler, her yüzde için 0°, 45° ve 90° gibi farklı yönlerde hazırlandı. Hazırlanan numuneler çekme ve üç noktalı eğilme yüklerine karşı test edilmiştir. 45° yönünde ÇDKNT'den ağ. % 0.9 içeren numuneler,en yüksek gerilme ve eğilme değerleri göstermiştir; ÇDKNT katkılanmamış 45° yönünde hazırlanmış refarans numunelere kıyasla gerilme ve eğilme modülünde yaklaşık % 8 ve % 33 oranında ve çekme ve eğilme mukavemetinde yaklaşık % 3 ve% 65 oranında iyileşme göstermiştir.

Anahtar kelimeler: polimer matris, karbon nanotüp, karıştırılmış lifler, kıvrımsız kumaş, termoplastik kompozitler, çekme ve üç-nokta eğime testi.

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Ali AL-DARKAZALI

ABBREVIATIONS

CNT	Carbon Nanotube
DWCNT	Double-Walled Carbon Nanotube
MWCNT	Multi-Walled Carbon Nanotube
NCF	Non-Crimp Fabric
PET	Polyethylene Terephthalate
LPET	Low Melting Polyethylene Terephthalate
PP	Polypropylene
GF	Glass Fibers
RTM	Resin Transfer Molding
GFRP	Glass-Fiber-Reinforced Polymers
TPNR	Thermoplastic Natural Rubber
MMC	Metal Matrix Composite
CNC	Ceramic Matrix Composite
PMC	Polymer Matrix Composite
0-D	Zero Dimensional
1-D	One Dimensional
2-D	Two Dimensional
CVD	Chemical Vapor Deposition
LCD	Liquid Crystal Displays
ASTM	American Society for Testing and Materials

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Chapter 1

Introduction

The necessity for obtaining composite materials, which they are characterized with high strength and stiffness, has pushed scientists and researchers to exploit nanomaterial in fabrication process of composites [1, 2]. Multi-Walled Carbon Nanotubes (MWCNTs), [3, 4] a cylindrical nanostructure with diameter in nanometer scale, are famous with their superb properties, in terms of thermal conductivity [5], electrical conductivity, modulus and strength [6, 7]. Two main reasons are accountable for the unique properties of the CNTs [8], one is the interlocking type of the carbon-to-carbon covalent bonds and the second one is the reality that every single carbon nanotube is one molecule, which means no weak spots can be found in the tube structure that could weaken the tube [9,10]. Thus, the incorporation of the nanotubes with the matrix can bring a remarkable improvement to the fabricated composites [11].

At the present time, thermoplastic materials are widely used around the globe in different applications, covering various sectors, such as aeronautic industry, automobile industry, sport and recreation and many other sectors and applications [12]. Thermoplastics as matrix are replacing metals in most occasions in producing composite materials due to the specifications accompanied by them, such as the light weight, the relatively low cost and the recyclability [13]. In order to overcome the high viscosity issue possessed by the thermoplastics polymers, they were produced in the form of fibers. And the thermoplastic polymers were commingled with the reinforcement fibers (also known as commingled yarns) and knitted to form a fabric structure [14]. The commingled fibers technique are featured with the homogeneous distribution of the matrix and reinforcement fibers over the composite cross section. And it raises the properties of the thermoplastic composites to their upper limit [15]. The commingled fibers are usually organized in the form of the Non-Crimp Fabric (NCF) in order to fabricate the composite materials. The Non-Crimp Fabric (NCF) is a fabric type that consists of more than one layer with the different orientation of the fibers. The layers of the NCFs were stitched together by using the stitch

fibers. Thus, the NCFs can be formed in the biaxial (0°/90° or ±45°), triaxial (0°/+45°/-45°) and quadraxial fabrics (0°/+45°/-45°/90°), depending on the orientation of the fibers in the layers.

Many researchers studied the different parameters of the commingled fibers that could affect the performance and properties of the composites. Long et. al. [16] studied the mechanical properties of the composites with the commingled yarn of the glass fibers/polypropylene filaments. They reported that the good mixture of the glass fibers/polypropylene filaments and the appropriate bulkiness of the glass fibers roving can increase the bending strength and bending modulus of the composites. Gilchrist et. al. [17] studied the fracture and fatigue performance of the textile composites with the commingled yarns. They investigated the mechanical properties of the novel warp knitted and unidirectional woven fabric composites with the commingled fibers of the glass fibers/polyethylene terephthalate fibers. After the performing of the tension, in-plane shear and flexure tests, they concluded that the warp knitted material was stiffer and marginally stronger when compared to the woven material. Demircan et. al. [18] investigated the effect of the various knitting techniques on mechanical properties of the biaxial weft-knitted thermoplastic composites. They found that the tensile, three-point bending and three-point bending impact properties of the thermoplastic composites with the commingled fibers could be improved by the changing of the knitting techniques.

Incorporation of the MWCNTs with the thermoplastic composites are expected to show the positive improvements in the mechanical properties of the composites especially in terms of the strength and stiffness, due to all the reasons mentioned above. Many research studies were conducted on the incorporation of CNTs with the polymeric matrix composites, most of them used the thermoset polymers as a matrix. Gojny et al. [19] reported the improvement in the modulus, tensile strength, fracture toughness and anisotropic electrical properties of the composites by adding 0.3 wt% MWCNTs. They used the resin transfer molding process in the production of the glass-fiber-reinforced polymers with carbon nanotube/epoxy matrix. Pilawka et. al. [20] reported the enhancements of the mechanical properties of the epoxy composites with carbon nanotubes. They found that the introducing of the carbon nanotubes in an epoxy matrix increased the mechanical strength of the thermoset composites. Gojny et. al. [21] studied

the influence of the different types of the carbon nanotubes on the mechanical properties of the epoxy matrix composites. They used single-walled, double-walled and multi-walled carbon nanotubes in their experiments. They found that the optimal improvement in the mechanical properties of the composites was achieved by using the double-walled carbon nanotubes.

Few research studies were done about the using of the thermoplastic polymers because of the high melt viscosity of the thermoplastics. In the thermoplastics, the dispersing of the nanostructures are relatively difficult. Sathyanarayana et. al. [22] conducted studies on the thermoplastic nanocomposites with CNTs. They found that the improvements in terms of the modulus and strength properties of the composites were achieved using CNTs in the polymers. Potschke et. al. [23] studied the melt mixing method to disperse carbon nanotubes into the thermoplastic polymers. They tried to overcome the dispersing issue of the nano materials. They found that the melt mixing process using the master-batch method is applicable and easily accessible for the small and medium-sized production. Tarawneh et. al. [24] investigated the mechanical properties of the thermoplastic natural rubber reinforced composites with the different types of the carbon nanotubes in terms of the purity, length and diameter. They reported that the tensile properties of the composites were improved with integrating of the MWCNTs when compared to the composites without MWCNTs. Vacha et. al. [25] studied the mechanical properties of the acrylonitrile butadiene styrene thermoplastic polymer matrix composites with carbon nanotubes. They found that the tensile strength, young's modulus and hardness of the composites were improved by using CNTs comparing to the composites without CNTs. The type of the bonding between the polymer and nanomaterials have a great effect on the properties of the thermoplastic composites. Wang et. al. [26] studied the carbon nanotube integrated composite materials. They conserved the superior properties of MWNTs in the composites through the using of the Kentera, a conjugate rigid rod polymer, poly (aryleneethynylenes). This conservation was a direct result of the non-covalent bonding interaction between the Kentera and MWNTs.

In the literature, the improvements in the modulus and strength properties of the composites were reported for both the CNTs integrated thermoset and thermoplastic composites. However, it was found no study on the integration of MWCNTs in the

thermoplastic composites fabricated from biaxial NCFs, which have commingled fibers of the Low melting point Polyethylene Terephthalate (LPET) polymer and Glass Fibers (GF). The purpose of this study is to characterize the mechanical properties of the MWCNTs integrated thermoplastic composites with the LPET/GF commingled fibers. Within this research, we investigated the tensile and flexural properties of the thermoplastic composites with the LPET/GF commingled fibers with the various weight percentages of the MWCNTs. We also investigated the mechanical properties of the thermoplastic composites in various directions (0°, 45° and 90°) in order to study the effect of the stitch and reinforcement fibers. The obtained results of our study can be used for the design of the new MWCNTs integrated thermoplastic composites.

Chapter 2

Composite Material

2.1 Definition

A composite material can easily be defined as the material resulted from the combination of two or more different constituent phases, which results in improved properties than those of the individual constituents used alone, and each one of the constituents retain their chemical, physical and mechanical properties. Two main phases can be distinguished in composite materials; matrix and dispersed phase. Matrix phase can be defined as the primary phase which have a continuous character and is usually ductile and less hard phase. This phase holds the dispersed phase and protect it, and moves the external loads to it. Dispersed phase is embedded in the matrix phase and it is usually stronger than the latter, that's why it also called reinforcement phase. Hence, composite materials properties are a function of the properties of the constituent phases, their relative quantity, and reinforcement phase geometry. Callister [27] mentioned that the reinforcement phase geometry refers to the size, concentration, distribution, orientation and Shape of the reinforcement. See Figure 2.1 for more details.

2.2 Classification

Composite materials are commonly classified to two distinct levels according to its constituents; reinforcement format and matrix type.

2.2.1 Reinforcement classification

The first common classification is based on the shape or form of the reinforcement phase. It divides into three main categories; particle reinforced, fiber reinforced and structural. Each one of these categories has at least two sub-categories which describe the format of the reinforcement. One of the most and common reinforcement is glass fibers. Figure 2.2

represents the classification according to the reinforcement format with an illustration sketch for each type.

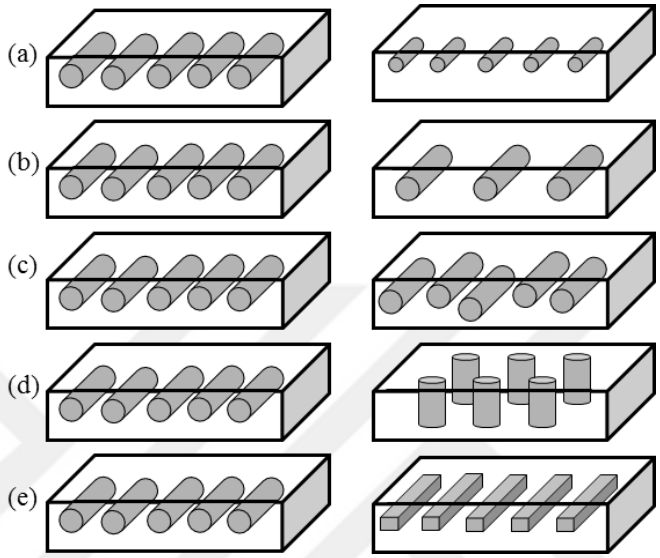

Figure 2.1. Reinforcement phase geometry. (a) Size, (b) Concentration, (c) Distribution, (d) Orientation and (e) Shape

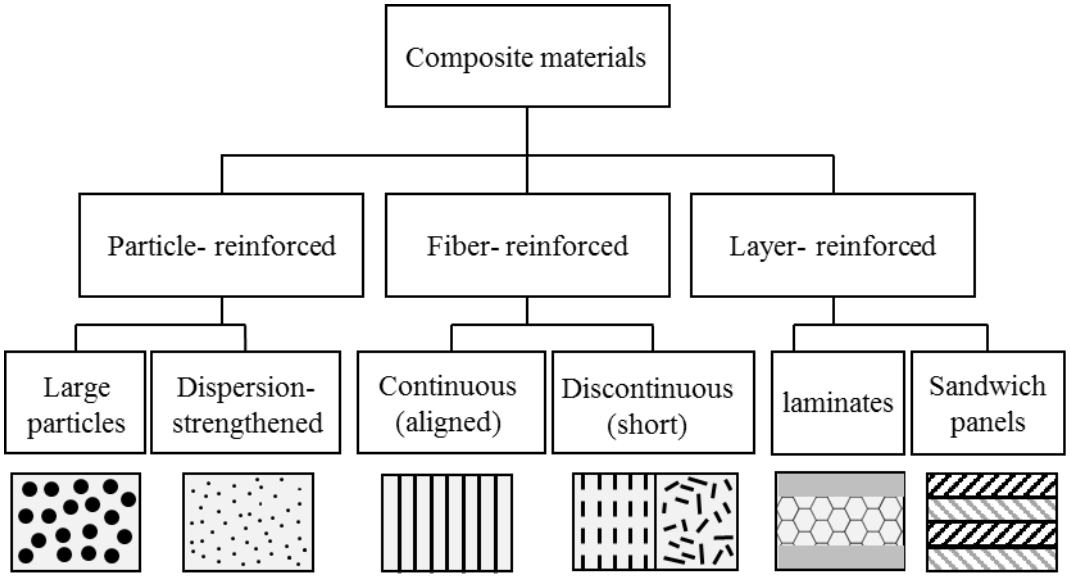

Figure 2.2. Composite classification according to the reinforcement format

2.2.2 Matrix classification

The second popular classification is usually made with respect to the matrix type. Mallick [28] studied the types of matrices in composite materials. He distinguished three main types of matrices: metal, polymer and ceramic as classified in Figure 2.3. He also mentioned that the main roles of the matrix in composite materials are: (1) to keep the fibers (or other reinforcing material geometries-e.g., particles, platelets, short fibers, or whiskers, etc.) in place, (2) to transfer stresses between the reinforcement, (3) to provide a barrier against an adverse environment, such as chemicals and moisture, and (4) to protect the surface of the reinforcement from mechanical degradation (e.g., by abrasion). Keeping the fibers separated decreases cracking and redistributes the load equally among all fibers a minor role in the tensile load-carrying capacity of a composite structure. Thus, the matrix contributes greatly to the properties of the composites. The ability of composites to withstand heat, or to conduct heat or electricity depends primarily on the matrix properties and type since this is the continuous phase. Therefore, the matrix selection depends on the desired properties of the composite being constructed.

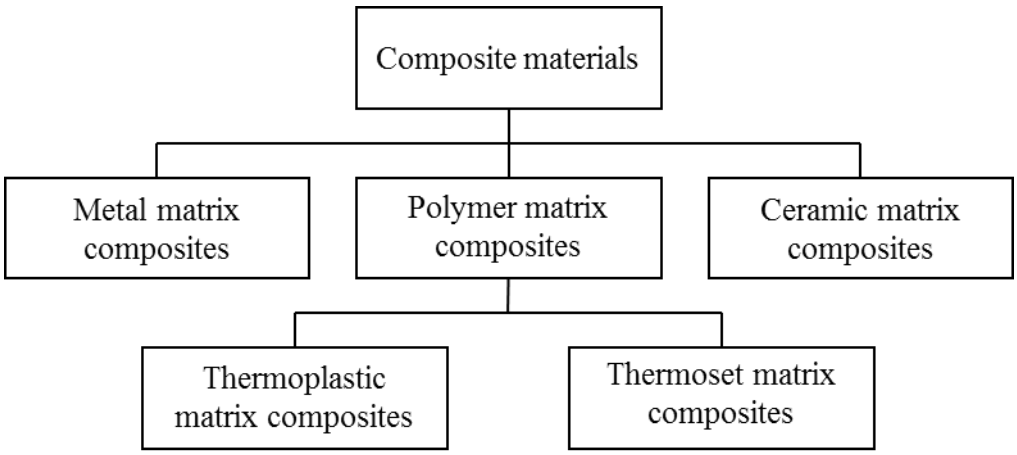

Figure 2.3 Composite classification according to the matrix type

Metal Matrix Composites (MMC) are the material that employ metals as a matrix and the reinforcement could be also metal or other type of material (e.g. ceramic). It has an intermediate working temperature range between 200 - 800 °C. Metal matrices provide

electrical conductivity, ductility, high strength, and high stiffness. However, due to their relatively higher density and processing complexity as compared to polymer matrices, they are less commonly used.

Ceramic matrix composites (CMC) consists of a ceramic matrix with reinforcement of different type. It used for high temperature applications. CMCs offer low density, high hardness and superior thermal and chemical resistance. Disadvantages include brittleness and the high processing temperature that could result in complexity in manufacturing and hence expensive processing.

Polymer matrix composites (PMC) are composites with polymeric matrix. Polymers are chemical compound in which the molecules are bonded all together in a relatively long repeating chains. The type of molecules they're made up of and how they're put together determine the type of the polymer. This type of composites are used in applications of relatively low working temperature of 250°C or lower. These materials are used in the greatest diversity of composite applications, as well as in the largest quantities, mainly due to their light weight, ease of fabrication, and lower cost comparing to the other types beside many other advantages.

2.3 Thermosets and thermoplastic polymers

There are two essential types of polymer matrices: thermoset polymers and thermoplastic polymers. Nijssen [29] studied the effect of matrix type on the properties of polymer composites. He also mentioned the differences between the two types. Table 2.1 shows the main differences between thermosets and thermoplastics.

Thermosets can be defined simply as the materials that undergo a chemical reaction (cure) and convert from a liquid state to a solid state. In its uncured form, the material has very small, unlinked molecules (known as monomers). Adding a second material (catalyst) and/or heat or some other activating factors will start the chemical reaction in these monomers. During this reaction the molecules cross-link and form considerably longer molecular chains, resulting the thermoset liquid to convert into a solid state. This conversion is characterized of being permanent and irreversible. Therefore, if the thermoset exposed to high heat, it will degrade, not melt. This is because these materials

typically degrade at a temperature below where it would be able to melt. Examples of thermosets are Epoxy and Polyester.

Thermoplastics, in a basic definition, are melt-processable plastics (materials that use heat in its processing). When the plastic exposed to a specific heat and bring the temperature of the plastic above its melt point, the plastic converted into liquid (softens enough to be processed). Removing the heat source would cause the temperature of the plastic dropping off to a limit below its melt point, the plastic starts solidifying (or freezing) back into a glass-like solid. This operation is repeatable, with the plastic melting and solidifying as the temperature climbs above and drops below the melt temperature, respectively. Anyway, the thermoplastic would be increasingly exposure to ruin in its molten state, so there is a specific limit to the number of times that this reprocessing can happen before material characteristics begin to deteriorate. Many thermoplastic polymers are addition-type, capable of yielding very long molecular chain lengths (very high molecular weights). Examples about thermoplastics are: polypropylene and polyethylene terephthalate.

Table 2.1. Comparison between thermosets and thermoplastics

Thermosets	Thermoplastics
Chains are cross-linked with each other	Chains have low amount of cross-linking
Hard and brittle	Ductile
Heat has no softening effect	Soften when exposed to heat
Better chemical resistance	Lower chemical resistance
Unrecyclable	Recyclable
Lower fabrication temperature	High fabrication temperature
Long cure cycle	Short cure cycle
Example: Epoxy	Example: Polypropylene

2.4 polyethylene terephthalate.

Polyethylene Terephthalate (PET) is a thermoplastic polymer from the family of polyesters, characterized mainly with its strength, stiffness and dimensional stability that absorbs very little water. PET is spun into fibers for permanent-press fabrics, blow-molded into disposable beverage bottles, and extruded into photographic film and magnetic recording tape beside many other applications. The production of PET is done by the polymerization of ethylene glycol and terephthalic acid. Ethylene glycol is a liquid without a color obtained from ethylene, and terephthalic acid is a crystalline solid obtained from xylene. When both of these materials exposed to heat together under chemical catalysts presence, ethylene glycol and terephthalic acid produce PET in the a molten form, viscous mass that can be spun directly into fibers form or converted to solid state as a plastic for later processing. Water is also produced as a by-product in this process. The reaction between the ethylene glycol and terephthalic acid can be seen in Figure 2.4

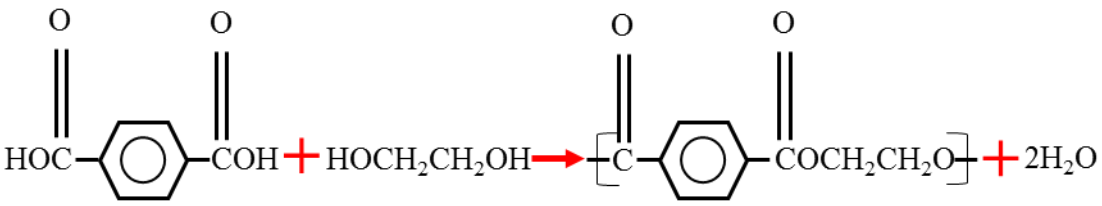

Figure 2.4. Ethylene glycol and terephthalic acid reaction and result

The existence of a large aromatic ring in the PET repeating units gives the polymer notable stiffness and strength, particularly when the polymer chains are aligned with one another in an organized order by drawing (stretching). PET is made into a high-strength plastic that can be shaped by all the common methods employed with other thermoplastics. It can be extruded in a film form and used as magnetic recording tape and photographic film, also the molten form of PET can be blow-molded into transparent containers of high strength and rigidity that are also virtually impermeable to gas and liquid. In this form, PET has become widely used in carbonated-beverage bottles and in

jars for food processed at low temperatures. The low softening temperature of PET is approximately 70 °C (160 °F) prevents it from being used as a container for hot-filled foods or in any application that required working temperature above this temperature. PET is one of the most used recyclable thermoplastic. Bottles and containers made from PET are commonly recycled by melting them down and spun into fibers for fiberfill or carpets. Awaja et. al. [13] studied recycling of PET. They concluded that when PET is collected in an appropriately pure state, it can be recycled into its original uses, using certain and specific methods in breaking down the polymer chains into its chemical precursors for resynthesizing into PET.

2.5 Polypropylene

Polypropylene (PP) is a thermoplastic polymer from the polyolefin family, characterized mainly with its lightweight, Chemical resistant and Heat resistant. PP are available in different forms and shapes. It is molded or extruded into many plastic products or spun into fibers for employment in industrial and household textiles. PP built up by the polymerization of propylene monomers. Propylene is a gaseous compound obtained by the thermal cracking of ethane, propane, butane, and the naphtha fraction of petroleum. The chemical structure of propylene (CH_2=$CHCH_3$) shows that a single molecule of propylene contains a single pair of carbon atoms linked together by a double bond. Manufacturing process of PP includes subjecting the propylene monomers to heat and pressure in the presence of a catalyst system. Polymerization is achieved at relatively low temperature and pressure. According to the previous process, the double bond are break and thousands of propylene molecules linked together to form a chainlike polymer. The product yielded is translucent, but can be directly colored. Differences in catalyst and production conditions can be used to alter the properties of the plastic. The existence of methyl group (CH_3) in the propylene molecule allow different tacticity forms, but in practice only the isotactic form is marketed in significant quantities. Figure 2.5 shows the polymerization process of propylene and the chain structure of PP.

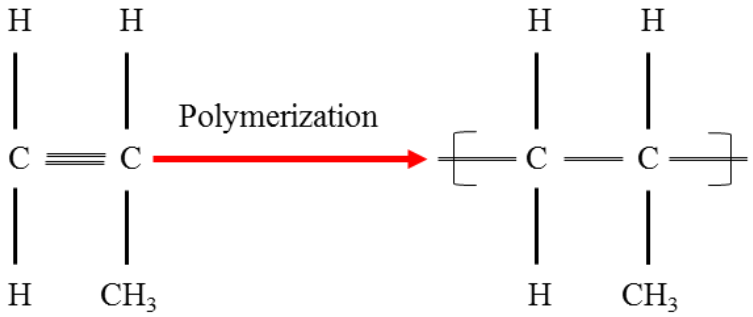

Figure 2.5 Propylene polymerization into polypropylene (PP)

Polypropylene is considered an important polymer with a very high growth rate, higher than the norm for such thermoplastics. This growth rate is partially because of the versatility of polypropylene, and hence the wide range of application areas.

2.6 Glass fibers

Glass fibers (Figure 2.6) can be represented as a material that consist of extremely fine filaments of glass, combined in yarn and woven into fabrics, used in masses as a thermal and acoustical insulator, or embedded in various resins to produce composite materials for boat hulls, fishing rods, and the like. Glass fibers are well-known for their remarkable attributes particularly in their strength, light weight and inertness that renders the composite containing them useful in a variety of corrosive environments.

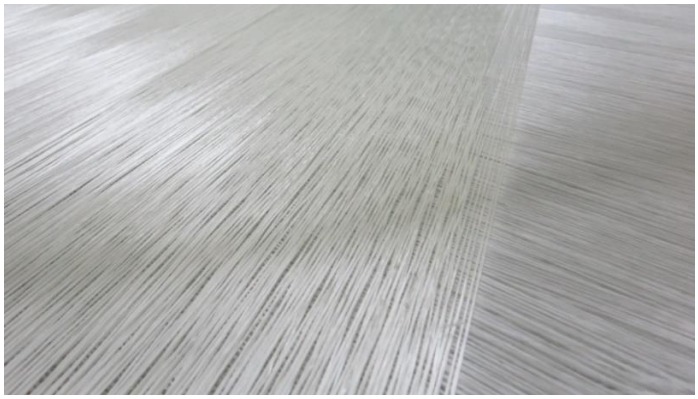

Figure 2.6 carbon fiber filaments

The process of manufacturing for glass fiber reinforcements begins with raw materials, which are basically minerals. Those minerals are mixed together based on the recipe of the glass formulation required. There are three main ingredients used for making the glass fibers; silicon dioxide (SiO_2), lime (calcium oxide or CaO) and aluminum oxide (Al_2O_3). The amount of each of the previous ingredient determines the type of the produced glass fibers, i.e. changing the mix of those components and other minerals will result in significantly different glasses. The first step in manufacturing process is melt down the mineral batch into a molten glass by using a furnace with a temperature of 1350 °C. Once completely molten, the liquid and homogeneous glass composition flows into heated refractory channels called the forehearth to feed the bushings. The bushings are mainly made of a platinum and rhodium alloy that contain small holes through which liquid glass flows. Then the glass turns into solid filaments form by cooling it rapidly. Figure 2.7 shows the manufacturing process of glass fibers. Additional coating processes take place for these filaments after solidification directly, using certain chemical components in order to give glass strands a good process-ability and adhesion with resins. Wallenberger [30] studied "commercial and experimental glass fibers". He investigated the properties of different types of glass fibers based on the percentages of raw materials during manufacturing. The main types of the produced glass fibers according to the amount of raw materials used are: E-glass (strength, electrical resistivity & lower cost), S-glass (high temperature application), C-glass (corrosive environments) and quartic (low dielectric). The high tensile modulus of E-glass (73 GPa) make it the most used glass on the market.

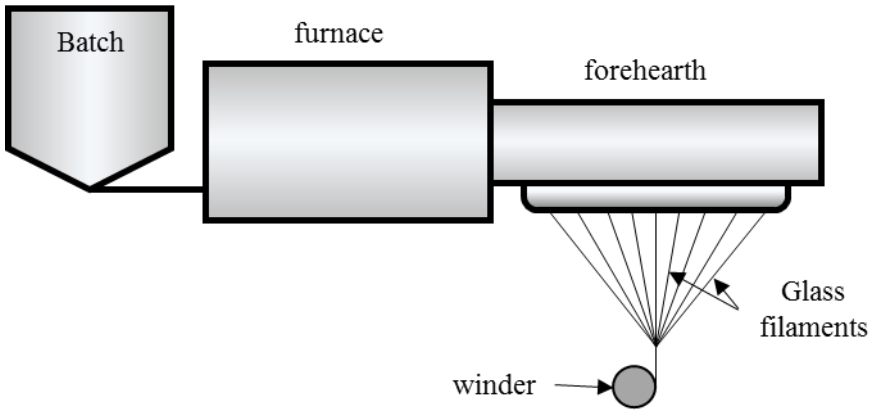

Figure 2.7. Manufacturing process of glass fibers

2.6 Commingled fibers

Commingled fibers are one of the possible preforms used for continuous fiber reinforced thermoplastic composites in order to solve the problem of high melt viscosity during impregnation and consolidation as the required steps for manufacturing of technical components. The preforms can be considered as 'dry' prepregs, in which the solid resin is physically divided and more or less evenly distributed among the reinforcement fibers. Thus, commingled fibers can be defined as a blend of reinforcement and matrix filaments within the tow (Figure 2.8), that provide a good material arrangement to overcome the high viscosity at melt of thermoplastic matrices. For this reason commingled fibers have the high potential for a homogeneous distribution of reinforcement material and matrix over the composite cross section that enables the matrix to achieve very short flow paths during manufacturing of the composite part, and makes a fast and complete impregnation of the reinforcement filaments possible. Commingled Fibers also enhance the ability to produce complex forms.

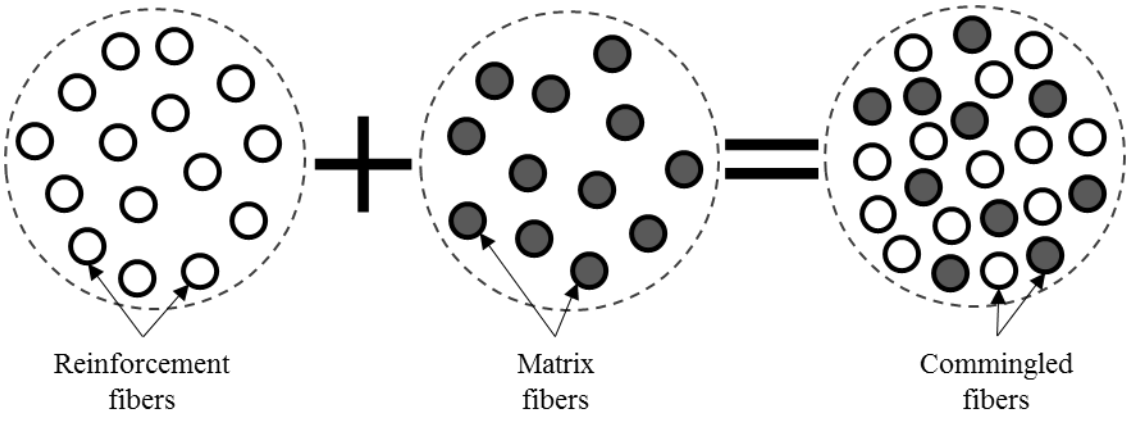

Figure 2.8. Structure of commingled fibers

2.7 Non-Crimp Fabric

Non-crimp fabrics (NCFs) have become increasingly popular during the recent years. The reason for this is that high quality composites can be manufactured both easier and cheaper with NCFs than with prepregs. NCFs can be considered as an attempt to provide

a compromise between the excellent mechanical properties but difficult handling of prepregs composites and the lower properties of easier to handle textiles [31]. NCFs can be defined as the fabric that consist of two or more plies or layers of unidirectional fibers, all stitched together with stitched fibers which usually made of thermoplastic material, to obtain a fabric with structural integrity. The classification of NCFs is based mainly on the fibers orientation in the layers. Thus, NCFs can be:

- Biaxial fabric (0°/90° or ±45°),
- Triaxle fabric (+45°/ 0°/-45°), and
- Quadraxial fabric (0°/+45°/-45°/90°).

Figure 2.9 represents an example of NCF with 2 layers of the following orientations: (+45°/-45°).

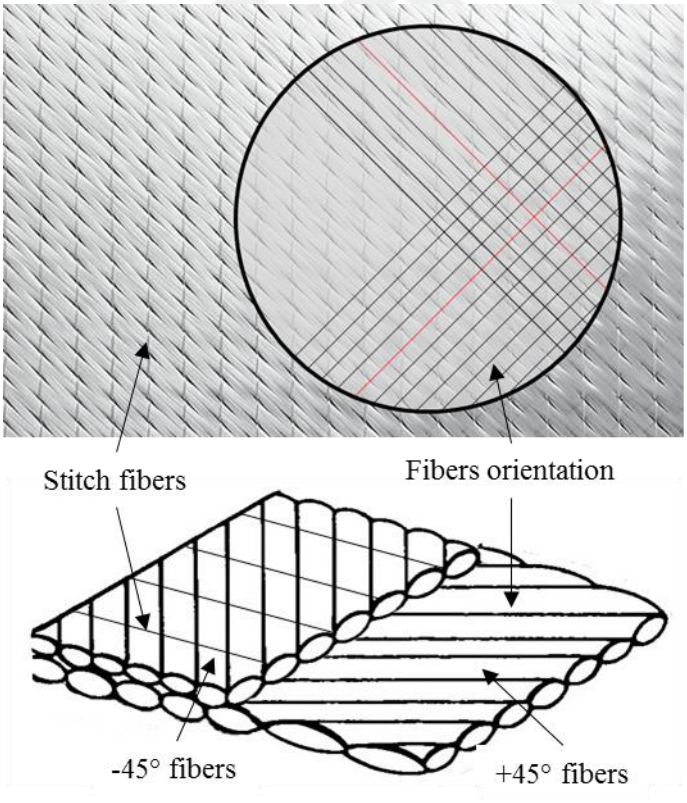

Figure 2.9. Biaxial fabric of (+45°/-45°) orientation

Chapter 3

Nanotechnology and Nanoscience

3.1 Introduction

The terms nanotechnology and nanoscience have become popular and gained great importance and attention because of the potential applications in various areas such as chemical and textile industries, materials industry, medical diagnostics, and other related field and technology areas. Thus, nanotechnology has the potential to solve problems related to human civilizations, pertaining to both basic needs and aspirations for a comfortable life.

The concept of a ‘‘nanometer’’ was first mentioned by Richard Zsigmondy, the 1925 Nobel Prize Laureate in chemistry. He coined the term nanometer explicitly for characterizing particle size and he was the first to measure the size of particles such as gold colloids using a microscope. Modern nanotechnology was the brain child of Richard Feynman, the 1965 Nobel Prize Laureate in physics [32]. During the 1959 American Physical Society meeting at Caltech, he presented a lecture titled, ‘‘There’s Plenty of Room at the Bottom’’, in which he introduced the concept of manipulating matter at the atomic level. It is for these reasons that he is considered the father of modern nanotechnology. In recognition of this reality, the national investments and enormous support has been started for studies in the area of nanoscience and Nano engineering to reap nanotechnology’s potential social and economic benefits.

3.2 Definition

The expression “Nano” is originally took from the Greek word “Nanos”, meaning dwarf (an expression used for abnormally short person). Nanotechnology generally can be defined as the science and engineering of fabricating and investigating materials, structures, and devices on a nanometer scale, and nanometer scale includes scales from 1 nm to 100 nm [33]. Scientifically, nanometer represents a remarkable small value equal

to one thousandth of a micrometer, one millionth of a millimeter, and one billionth of a meter (i.e. 10^{-9}). Following examples can provide better understanding of the sense of Nano scaled objects: water molecules have an average size of about 0.1 nm, the minimum size that can be seen by a human is 10,000 nm, the average diameter of a single hair is about 80,000 nm while the normal human body height is about 180 cm that equals to 1.8 billion nm, Figure 3.1 illustrates the nano-, micro-, and macro scale regimes, the size of some typical features, and an overall size comparison.

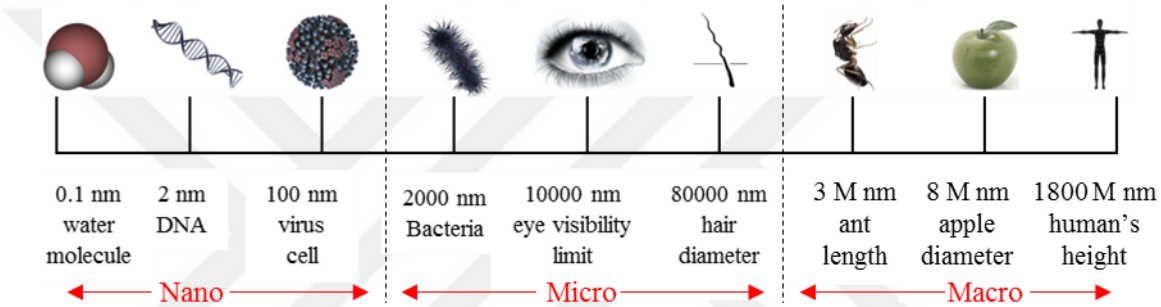

Figure 3.1 size comparison

At nanoscale, the behavior is not necessarily expected from that observed at large size scales. The laws of physics work somewhat in another way at this scale; the classical mechanics that we encounter in everyday life give way to quantum mechanics. Reducing at least one of the dimensions of any type of material below 100 nm would result in changing in mechanical, thermal, optical, magnetic and other properties at a variety of levels. Thus within the same material one can get a range of properties.

3.3 Nanomaterial

Nanomaterial is the cornerstones of nanotechnology and nanoscience. They can be defined as any substance that have at least one of the 3 dimensions in Nano scale. Nanomaterials have a relatively large surface area to volume ratio when compared to the same mass of material produced in a bulk form. This feature turns the material into more chemically reactive material, and affect their characteristics in terms of strength or

electrical properties. In order to clarify this concept; consider a cube has 2 cm length in sides, then the surface area of it would be 24 cm^2. Dividing the cube into 8 identical cubes would reduce the side length to 1 cm, but the total surface area of the 8 smaller cubes would equal to 48 cm^2. If each of these 8 cubes also divided into 10^{21} cubes, the side length would reduce to 1 nm and the total surface area would become 48 X 10^7 cm^2.

Nanomaterial ca be classified to three main categories according to the number of dimensions in the nanoscale as follows (Figure 3.2):

1- Zero dimensional (0-D): nanomaterial in this category have all of the 3 three dimensions in the nanoscale. These can have different shapes such as cubes and polygons, such as nanoparticles and quantum dots.

2- One dimensional (1-D): nanostructures have two dimensions in nanoscale. These include nanowires, nano-rods, and nanotubes. These materials are long (several micrometer in length), but with diameter of only a few nanometer.

3- Two dimensional (2-D): this type of nanomaterials have one dimension in the nanoscale. These include nano-films, nano-sheets or nano-walls. The area of the nano films can be large (several micrometer), but their thickness is very small (within nanometers scale).

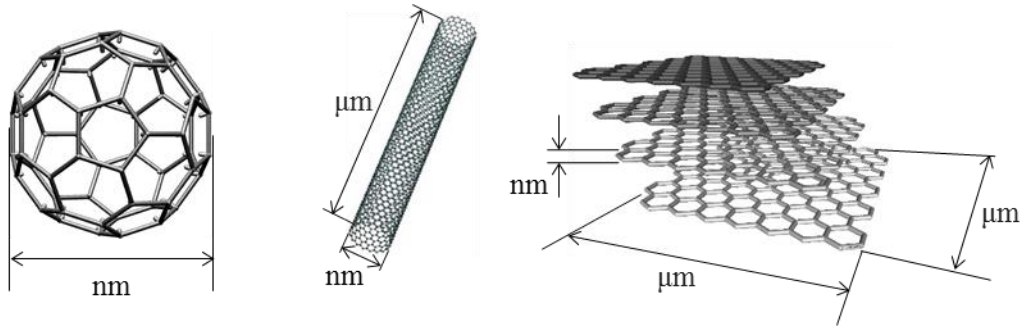

Figure 3.2 types of nanomaterials

3.4 Carbon nanotubes

Carbon is unique among the elements in its ability to form strongly bonded chains, sealed off by hydrogen atoms. Its unique properties are a direct results from the configuration of

electrons of the atom. Carbon atom has a set of 6 electrons, shared evenly between the 1s, 2s and 2p orbitals. For instance, the 2p atomic orbitals have the ability to hold up to six electrons. Hence, carbon is capable of making up to four bonds; however, the valence electrons, involved in chemical bonding, occupy both the 2s and 2p orbitals. The geometry and properties of carbon allotropes is determined from the number and nature of the bonds among the atoms.

The observation of carbon nanotubes (CNT) in 1991 done by Lijima [34] using a transmission electron microscope (Figure 3.3), opened up a new era in materials science. These extraordinary structures have an array of fascinating electronic, magnetic and mechanical properties. For example, carbon nanotubes are at least 100 times stronger, and six times lighter than steel. Thus, the addition of carbon nanotubes to any material would strengthen it and enhance other properties.

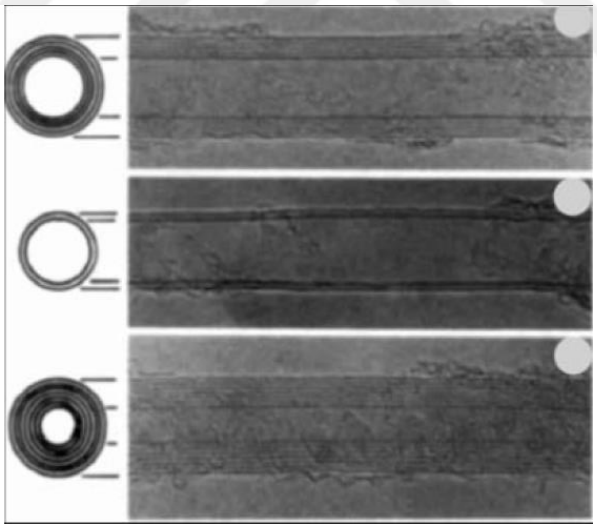

Figure 3.3 the first CNT's observed by Lijima using transmission electron microscope

A carbon nanotube is a tube-shaped material, made of rolled-up graphene layers, having a diameter measuring on the nanometer scale and few micrometers in length. The unique properties possess by carbon nanotubes are a consequence of the nature of bonding among atoms and the extreme aspect ratios.

Various structures can be seen in carbon nanotubes, differing in length, thickness, and number of layers. Depending on how the graphene has rolled-up, the characteristics of nanotubes can be determined, causing it to act either as a metallic or as a semiconductor. Carbon nanotubes mainly classified into two types, single walled carbon nanotubes (SWCNT) which is formed from rolling-up single layer of graphene, and multi walled carbon nanotubes (MWCNT) which formed from rolling-up multiple layers of graphene as illustrated in Figure 3.4.

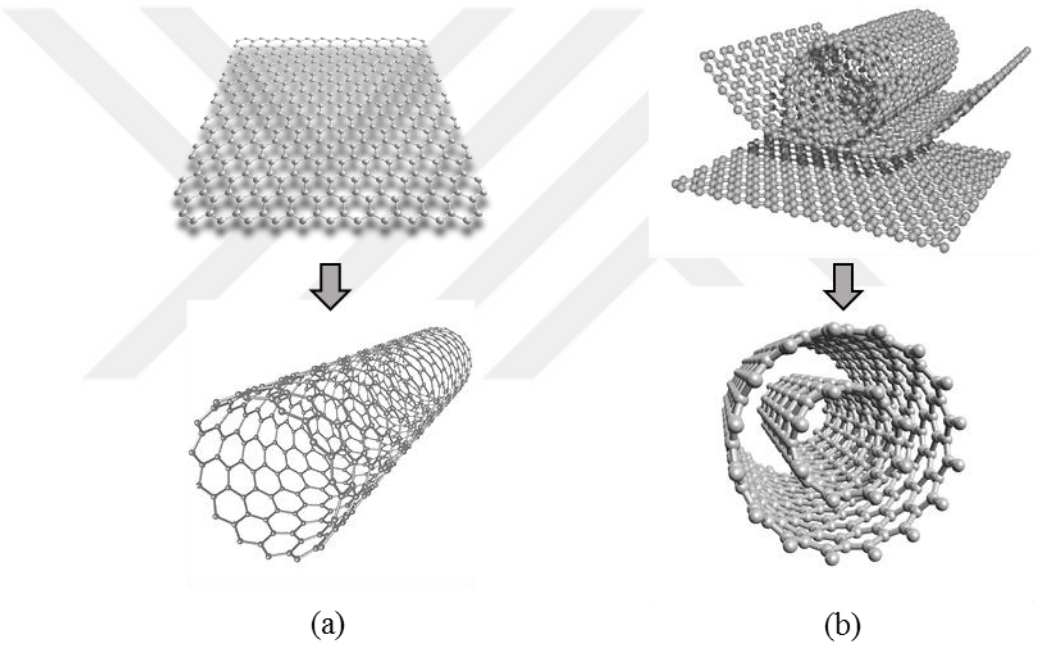

Figure 3.4 (a) single graphene layer rolled-up to form SWCNT, (b) Multi graphene layers rolled-up to form MWCNT.

The choice of rolling axis relative to the hexagonal network of the graphene sheet (Figure 3.5) and the radius of the closing cylinder allows for different types of CNTs, which vary from insulating to conducting. .Figures 3.6a, 3.6b and 3.6c, show CNTs of three different types: armchair, zigzag, and chiral respectively.

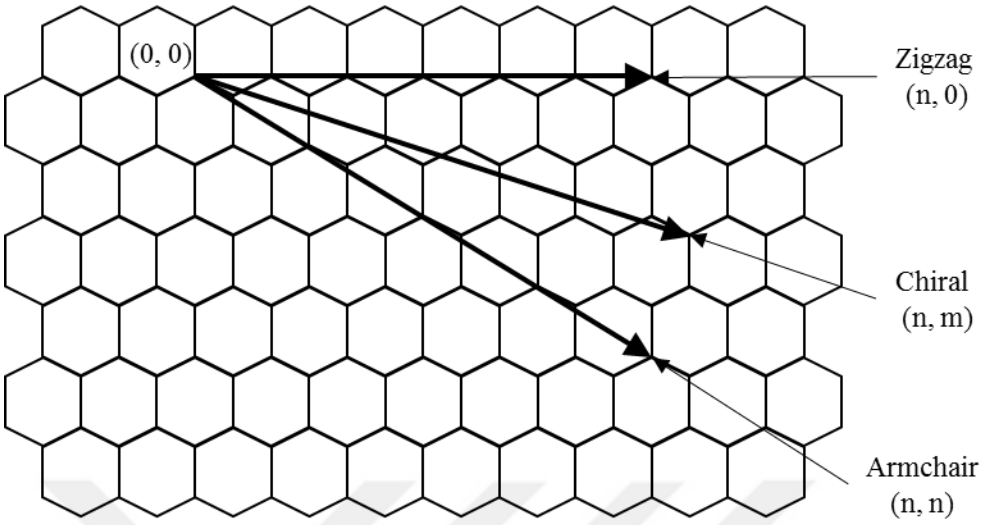

Figure 3.5 the graphene sheet labeled with the integers (n, m). The diameter, chiral angle, and type can be determined by knowing the integers (n, m) [30 of 1].

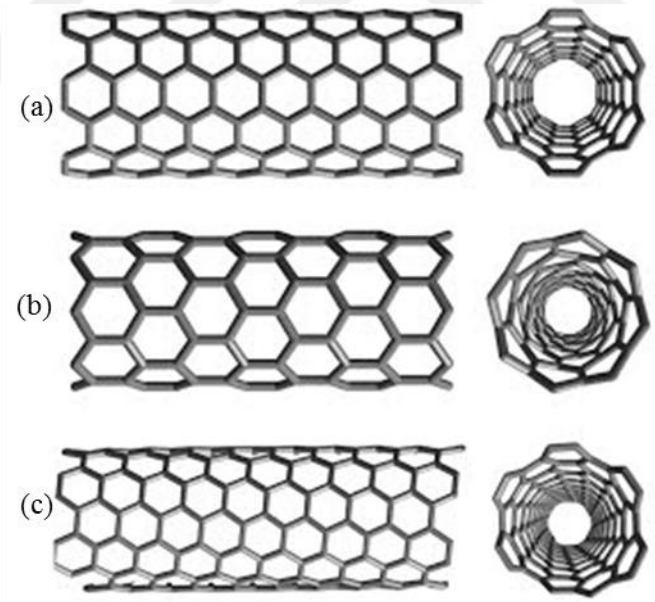

Figure 3.6 three rolling types of CNT's (a) armchair, (b) zigzag, and (c) chiral

3.5 Mechanical properties of Carbon nanotubes

The extraordinary mechanical properties of carbon nanotubes make them the filler material of choice for composite reinforcement. The nature of bonding between carbon-

carbon atoms in a carbon nanotube is the main reason for their distinct properties. Rolling up a graphene sheet on a nanometer scale has dramatic consequences on the electrical properties, also the diameter of the resulted tube has a big effect on the mechanical properties of these materials. Theoretically, the mechanical properties of carbon nanotubes in terms of strength and stiffness are better than any known material. Yakobson simulation studies [35] and Falvo experiments [36] showed a fabulous "bend, don't break" response of individual single walled carbon nanotube to large transverse deformations.

Multi-wall carbon nanotubes and single-wall carbon nanotube bundles may be stiffer in bending compared to tensile strength because in tension, bundles are weaker due to slip in shear of individual nanotubes. The stress–strain curves suggest that the load is carried primarily by single-wall carbon nanotube on the exterior surface of the tubes, from which breaking strengths from 13 to 52 GPa were revealed in the studies of Yu et. al. [37]. On the other hand, the mean value of tensile modulus was 1 TPa, and the result is consistent with near-ideal behavior. With the same method, tensile strength of multi-wall carbon nanotubes were measured between 11 and 63 GPa and Young's modulus between 0.27 – 0.95 TPa. On a density-normalized basis the nanotubes look much better for reinforcement; because, the modulus and strength are, 19 and 56 times better than steel, respectively [38].

3.5.1 Elastic modulus of carbon nanotube

Knowing the modulus of elasticity (Young's Modulus) of a material is the first step towards its use as a structural element for different applications. Young's modulus is a numerical constant that describe the elastic properties of a solid undergoing tension or compression in only one direction within elasticity zone. This modulus can be obtained by dividing the stress by the strain. Wong et al. in 1997 researches showed modulus of MWNTs of (1.28 TPa). In 1998, Treacy et al. [39] reported an elastic modulus for single walled carbon nanotube of 1.25 TPa. Other new studies showed close results to the previous studies for different type of carbon nanotube, with more accuracy comparing to the previous studies.

3.6 Carbon nanotubes synthesis methods

Every time you light a matchstick, you are making carbon nanotubes. The problem is that there are only small number of them with big differences in their shape, and they are mixed up with other form of carbon and hence they are not useful. The focus of carbon nanotube synthesis is in making a considerable quantity of pure nanotubes with minimal contamination and controlled shape. Synthesizing nanotubes with symmetric or semi-symmetric width and length require a huge deal of efforts. Hence, diameter and length cannot controlled very well when using high volume synthesis methods. Szabo et. al. [40] studied synthesis methods of carbon nanotubes and related materials. They referred to the main CNTs synthesis techniques and the progresses made in this field. So far, arc discharge, laser ablation, and chemical vapor deposition (CVD) are the three main methods for the production of carbon nanotubes. Following are brief about each of these three methods:

3.6.1 Arc Discharge

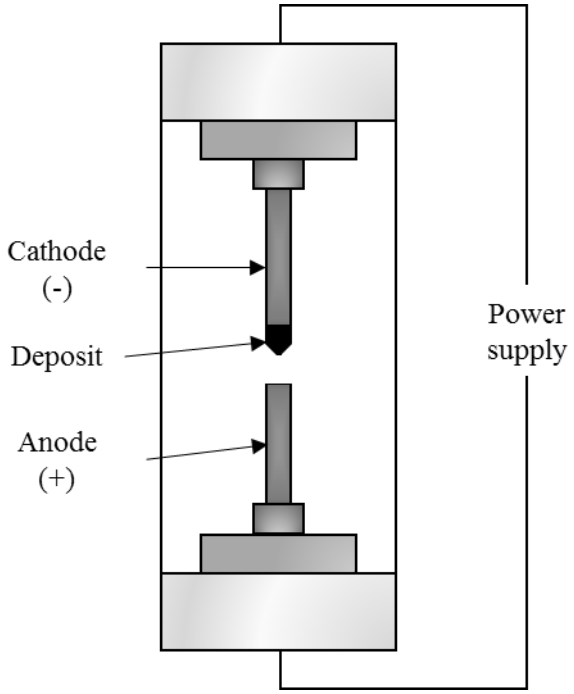

Figure 3.7 arc discharge apparatus used in synthesizing CNT's

The apparatus of the arc discharge method consists of an enclosure that is filled with some inert gas (like helium or argon) at low pressure (between 50 and 700 mbar) with two graphite rods that placed inside it (Figure 3.7). The carbon rods act as electrodes which are kept at different potentials. Both the anode and cathode are moved close to each other, until an arc generates and the electrodes are kept at the distance of 1 mm for the whole duration of the process that takes about one minute. After the de-pressurization and cooling of the chamber the nanotubes together with the by-products, can be collected. Most nanotubes deposit on the cathode. Arc-evaporation with pure graphite electrodes produces mainly multi-wall nanotubes, although single-wall nanotubes can be made by this method by doping the anode with a metal catalyst such as cobalt or nickel. When optimized, this method can turn roughly 30% of the carbon into carbon nanotubes.

3.6.2 Laser Ablation

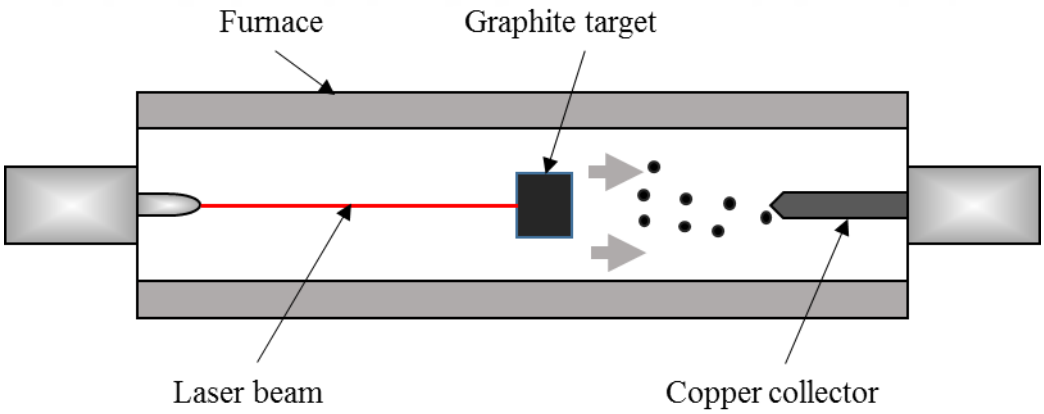

Figure 3.8 Laser ablation method for synthesizing CNT's

Laser ablation works through the same mechanism as arc discharge, but instead of producing heat through electrical discharge a laser is used (Figure 3.8). A focused and powerful laser is used to ablate a carbon target which is placed in a tube-furnace heated to 1200°C. During the process some inert gas like helium or argon flows through the chamber to carry the grown nanotubes to the copper collector. After the cooling of the

chamber the nanotubes and other side-products can be collected. The additional benefit of this is that the temperature and pulse times can be precisely controlled. Because of these strict controls the parameters of the CNTs can be finely tuned and up to 70% of the carbon can be turned into CNTs.

3.6.3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) method consider to be the most common and the easiest way to synthesis carbon nanotube in the laboratory (Figure 3.9). In this method, a covered substrate with a metal catalyst, like iron, cobalt or nickel is placed inside a heated chamber of temperature around 750 °C. CVD uses a carbon-rich gas feedstock, such as acetylene or ethylene. The gas is passed over the substrate with the catalyst and carbon atoms dissociate from the gas molecules rearranging on the surface to form nanotubes and fullerenes. This allows nanotubes to be synthesized continuously, making the technique ideal for scaling up to large manufacturing volumes.

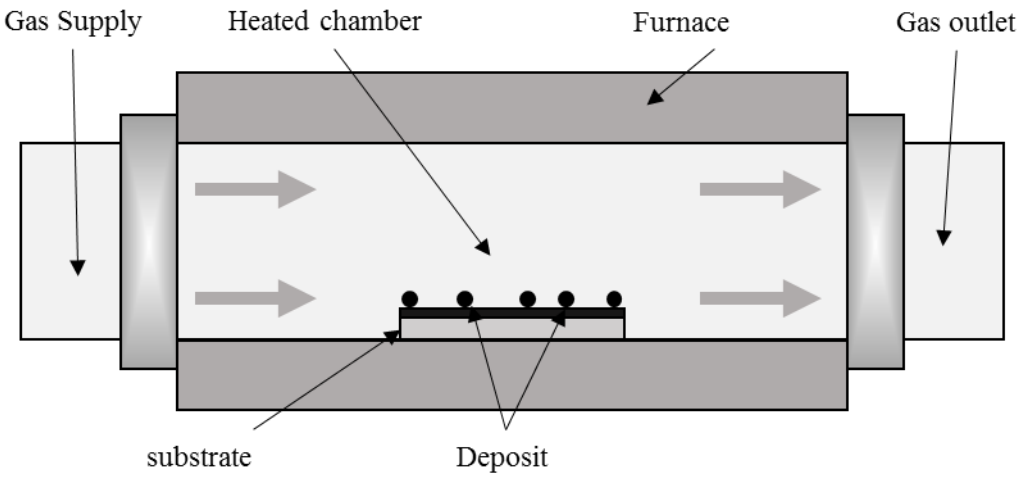

Figure 3.9 chemical Vapor Deposition (CVD) method in synthesizing CNT's

3.7 Application areas of carbon nanotubes

Because of its remarkable electronic and mechanical properties, carbon nanotubes are one of the best candidate materials for uses in various industrial applications. Carbon nanotubes possess remarkable high tensile strength. This is important one to make them valuable components for mechanically reinforced composite materials. Furthermore, the high aspect ratio (length to radius ratio) and high conductivity of carbon nanotubes makes them excellent for conducting composites. Nanotube composites were first used for electrostatically applying paint onto car components by Baughman et al. They have a much better surface finish compared with the previously used carbon black or carbon fiber composites. Carbon nanotubes also used in field emission display: Carbon nanotubes can emit electrons from the end of them like a small cannon when a nanotube is put into an electric field. If those electrons are allowed to bombard a phosphor screen then an image can be created. The advantages of carbon nanotube screen over liquid crystal displays (LCD) are based upon a low power consumption, intense brightness, wider viewing angle, fast rate response, and a wider operating temperature range.

There is a wealth of other potential applications for carbon nanotubes, such as solar collection, nonporous filters, catalyst supports, gas and hydrogen storage, medical applications, coatings of all sorts and many other. There are almost certainly many unanticipated applications for this remarkable material that will come to light in the years ahead and which may prove to be the most important and valuable of all.

Chapter 4

Nanocomposites

Nanocomposites technology have become an important area of current researches and development. These high performance materials offer infrequent property combination and great potential for superb design. Their potential is so astonishing that they are useful in several areas and. The number of commercial applications of nanocomposites have been growing at a rapid rate. Okpala [41] mentioned in his study about nanocomposites that in less than two years, the worldwide production is estimated to exceed 600,000 tones and is set to cover the following key areas in the next five to ten years: Drug delivery systems, Anti-corrosion barrier coatings, UV protection gels, Lubricants and scratch free paints, New fire retardant materials, New scratch/abrasion resistant materials and Superior strength fibers and films.

4.1 Definition

The nanocomposite materials are an innovative product having Nano-sized structure fillers incorporated in the matrix. Typically, the structure is a matrix-filler combination where the fillers surround and bind together as discrete units in the matrix.

Cammarata [42] have mentioned in the book “Introduction to nanoscale science and technology” that most nanocomposites that have been developed and that have demonstrated technological importance have been composed of at least two phases, and can be microstructurally classified into three principle types: (a) Nano-layered composites composed of alternating layers of nanoscale dimension; (b) Nano- filament composites composed of a matrix with embedded (and generally aligned) nanoscale diameter filaments; (c) Nano-particulate composites composed of a matrix with embedded nanoscale particles. Figure 4.1 illustrates the three types on nanocomposites.

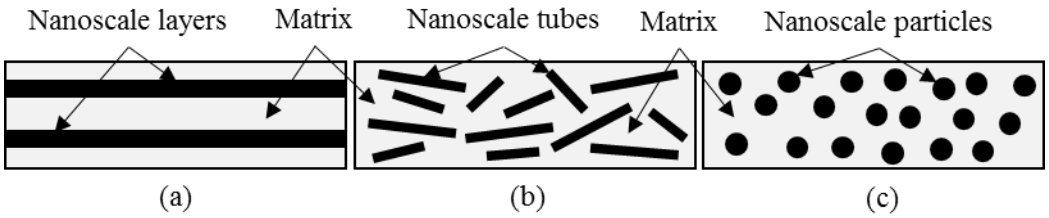

Figure 4.1. Classification of nanocomposites according to the nanostructures type

Another classification is available based on the matrix type. According to this classification, three types of nanocomposites can be distinguished: metal matrix nanocomposite, ceramic matrix nanocomposite and polymer matrix nanocomposite. This classification can be combined with the first one to give an accurate description for the nanocomposite.

4.2 Polymer matrix nanocomposite

The polymer matrix nanocomposites are composite materials with nanostructures embedded in a polymer matrix. This polymeric matrix can be thermoset or thermoplastic. Thermoset matrix become permanently hard through cross-linking when heated above glass transition temperature (Tg). Thus thermosetting polymers cannot be molded by softening. Instead, they must be fabricated during the cross-linking process. A thermoplastic polymer will soften when heated above the Tg and thus can be molded into a particular shape upon cooling. This process is repeatable, which makes thermoplastic materials reprocess-able and recyclable. The nanostructure shape, size and distribution in the polymeric matrix are of great importance for the final properties of the nanocomposites. Depending on the type of nanoparticles added, the mechanical, electrical, optical, and thermal properties of polymer nanocomposites can be altered. In the field of mechanical properties, the changes in modulus and strength depend strongly on the degree of interaction between the particle and the polymer.

Advantage of using nanoparticles as reinforcement is that their size is smaller than the critical crack length that typically initiates failure in composites. As a result, nanoparticles

provide improved toughness and strength. However, agglomeration of nanoparticles should be prevented at all costs. In fact, several investigations have shown that small levels of agglomeration can decrease the strain-to- failure by several tens of percent. Nanoparticles can also significantly affect Tg. Typically this occurs because nanoparticles influence the mobility of the polymer chains due to bonding between the particles and the polymer and bridging of the polymer chains between the particles.

4.3 Carbon nanotubes (CNTs) nanocomposites

Since the documented discovery of carbon nanotubes (CNT) in 1991 by Iijima [34] and the realization of their unique physical properties, including mechanical, thermal, and electrical, many investigators have seek to fabricate advanced CNT nanocomposite materials that exhibit one or more of these properties. Khare et. al. [43] in their review about Carbon Nanotube Based Composites talked about the enhanced interfacial bonding properties, mechanical performance, and electrical percolation of different CNTs based polymer nanocomposites. Several critical factors should be taken into consideration when using CNTs as fillers in polymeric matrices:

- CNTs uniform dispersion within the polymer matrix.
- CNTs Alignment in the nanocomposite.
- CNTs Interfacial bonding with the polymer matrix.

CNTs show smooth surfaces and intrinsic Van der Waals interactions, which tend to promote clustering when dispersed in a polymer matrix. If agglomeration occurs, the CNTs are less adhered to the matrix and will slip against each other under an applied stress, with drastic consequences for the mechanical properties. Thus, there are many method for despising CNTs, each has its own advantages and disadvantages. One of the famous techniques is ultrasonic dispersing method.

4.4 Ultrasonic dispersing of CNTs

CNTs, as mentioned earlier, are very cohesive. They are difficult to disperse into liquids, such as water, ethanol, oil, polymer or epoxy resin. Ultrasonic dispersing technique is an

effective method to obtain discrete – single-dispersed – CNTs. Vaisman et. al. [44] studied "The role of surfactants in dispersion of carbon nanotubes". They investigated different dispersing methods and concluded that ultra-sonication is a good method to decrease the nanotube agglomeration. In this method, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, with rates depending on the frequency. During the low-pressure cycle, high-intensity ultrasonic waves create small vacuum bubbles or voids in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a high-pressure cycle. This phenomenon is termed cavitation. Cavitation causes extreme effects locally that overcome the bonding forces between the nanotubes, and hence separate the tubes. Generally, CNTs are first premixed in the aqueous liquid by a standard stirrer (magnetic stirrer) and then homogenized using ultrasonic dispersing technique. Figure 4.2 shows the process of ultrasonic method.

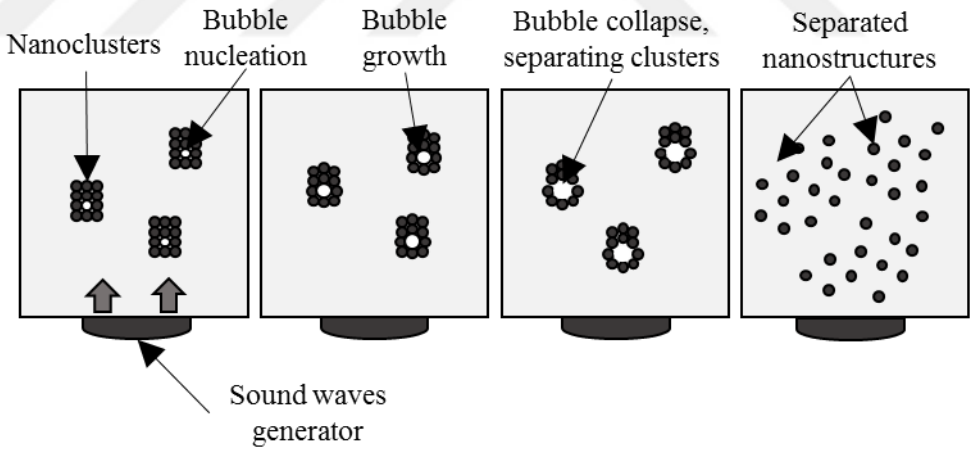

Figure 4.2. Ultrasonic dispersing method

Chapter 5

Experimental study and results of the matrix type

In this chapter, the effect of thermoplastic matrix type on the mechanical properties of the fabricated composites were investigated. Based on the results obtained from the study and experiments in this chapter, the best matrix between two types can be decided. The matrix with best mechanical properties would be considered for the second study, in which it would be incorporated with MWCNTs.

5.1 Composite constituents

The PP composite plates are fabricated from biaxial Non-Crimp Fabric (NCF) of commingled fibers of Polypropylene (PP) thermoplastic polymer as a matrix and Glass Fibers (GF) as a reinforcement. The NCF consists of two layers of fabric with different orientation of fibers. The total weight of the PP NCF is 749 gr/m^2.

The LPET composite plates are also fabricated from biaxial Non-Crimp Fabric (NCF) of commingled fibers with GF as reinforcement, but they use Low Melting Point Polyethylene Terephthalate (LPET) as a matrix instead of the PP. The LPET NCF consists of two of different fiber orientation layers and has a total weight of 763 gr / m^2.

The structure of commingled fibers of both of PP and LPET with GF is similar to each other as can be seen in figure 5.1. The fibers orientation of the layers in both of PP and LPET NCFs are +45° and -45° as well as straight-paralleled stitch fibers. The stitch fibers are made of polyester and are connecting both of the two layers together. Figure 5.2 shows the commingled fibers and stitch fibers orientation in the NCF. Both of the PP and LPET NCFs were obtained from Metyx Composites Corporation, Istanbul/Turkey. The specifications and properties of PP NCF and LPET NCF can be seen in Tables 5.1 and 5.2 respectively.

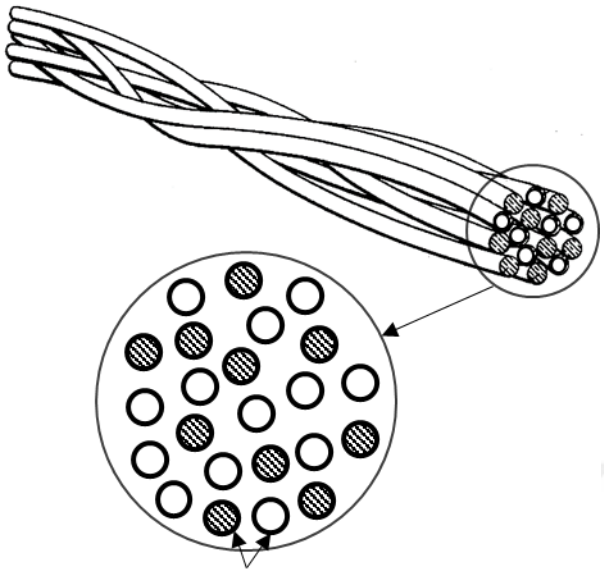

Figure 5.1. Structure of a single strand of commingled fibers showing the fibers constituents (PP/ GF) or (LPET/ GF)

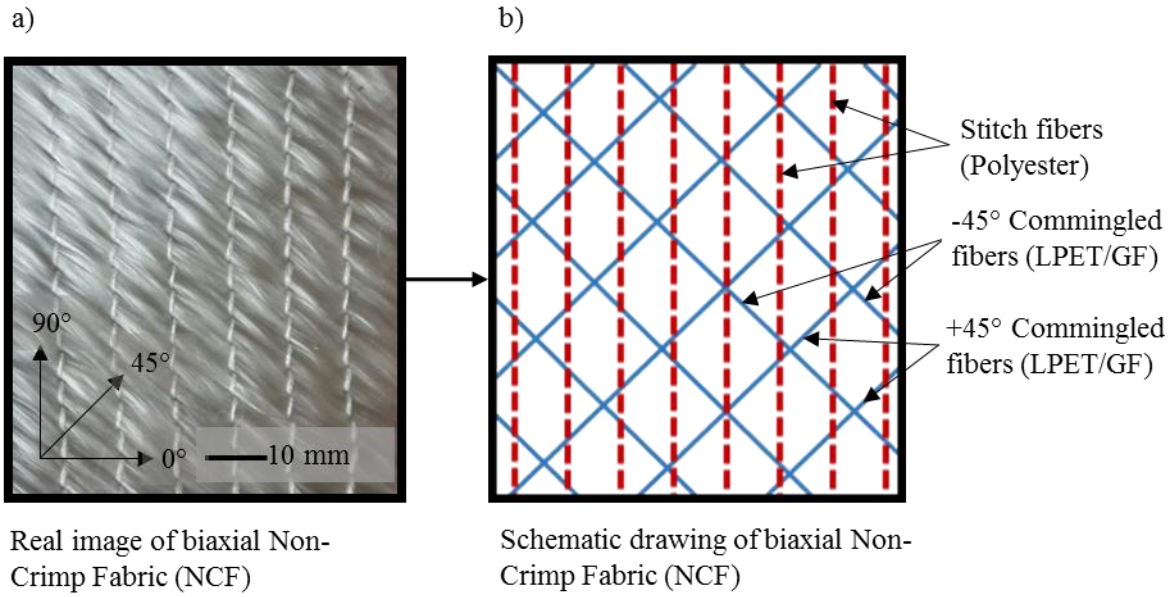

Figure 5.2. Commingled fibers and stitch fibers orientation in the NCF (a) Real image of biaxial Non-Crimp Fabric (NCF), (b) Schematic drawing of biaxial Non-Crimp Fabric (NCF)

Table 5.1. PP Non-crimp fabric (NCF) specifications

	+45 Fibers direction	**-45 Fibers direction**	**Stitch fibers**
Composition	60% Glass 40% PP	60% Glass 40% PP	100% Polyester
Color	Natural white	Natural white	Natural white
Weight (gr/m^2)	362	362	25
Fiber yarn count (TEX)	500	500	7.6

Table 5.2. LPET Non-crimp fabric (NCF) specifications

	+45 Fibers direction	**-45 Fibers direction**	**Stitch fibers**
Composition	60% Glass 40% LPET	60% Glass 40% LPET	100% Polyester
Color	Natural white	Natural white	Natural white
Weight (gr/m^2)	379	379	5
Fiber yarn count (TEX)	524	524	7.6

5.2 Hot-press fabrication process

In the hot-press process, the NCF were positioned in a mold made of copper, and then placed between two heaters. The lower heater is stationary, while the upper one is movable and capable of supplying pressure on the mold. The NCF specimens pressed up to 17 bars and heated to a temperature of 165 °C. Then, the specimens cooled down to room temperature using internal water cooling system while keeping the same pressure on the composite. These temperature and pressure were used for all of the fabricated

specimens. Figure 5.3 shows a schematic drawing of the main parts of the hot-press machine used in this experiment.

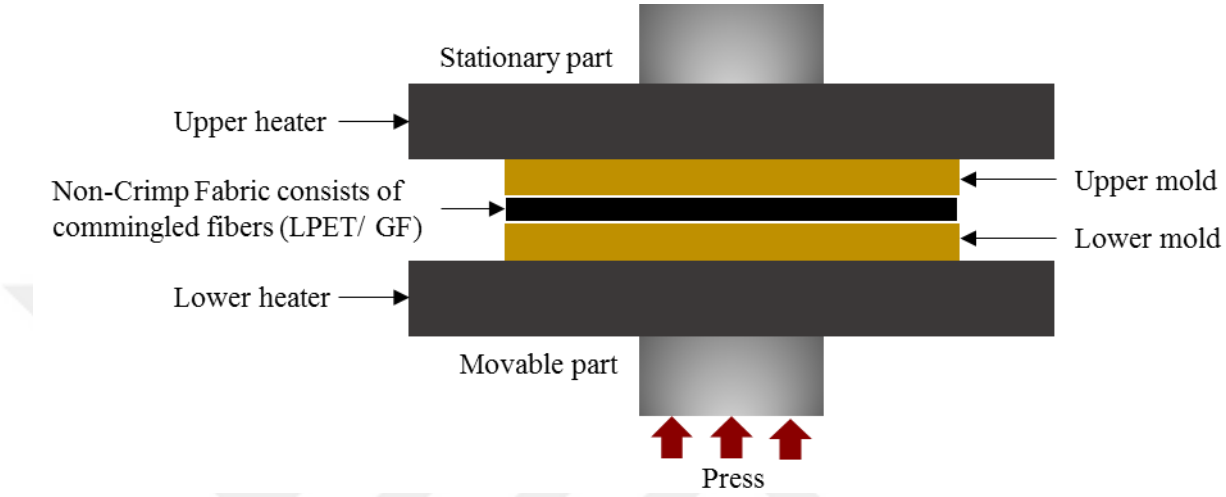

Figure 5.3. Hot-press main parts

5.3 Sampling method

The orientation of reinforcement [46, 47] has a big influence on the mechanical properties of composites such as tensile [48] and flexural properties [49, 50]. The composite plate fabricated in the hot-press machine were prepared for sampling by assigning three different orientations of fibers based on the stitch fibers direction. As can be seen in Figure 5.4, the format of the stitch fibers are longitudinal, thus they considered to form an angle of 90° with the horizontal line. For further clarification, three samples can be identified:

- Samples parallel to the stitch fibers direction. We called them 90° samples.
- Samples perpendicular to the stitch fibers direction. We called them 0° samples.
- Samples with 45° direction of stitch fibers. We called them 45° samples.

In this sampling method, the effect of the direction of the stitch and reinforcement fibers on the mechanical properties of the thermoplastic composites can be studied. [46-50].

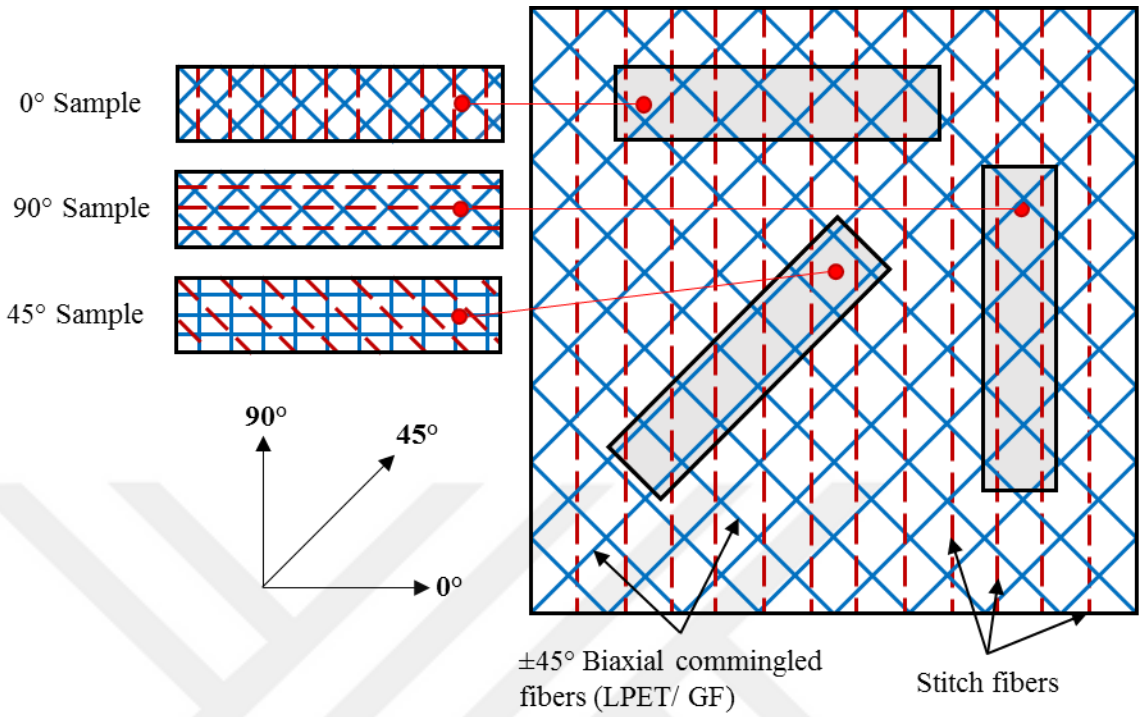

Figure 5.4. Sampling method

5.4 Mechanical characterization

Two mechanical characterization tests were conducted to the specimens, tensile test and 3-point flexural test. For tensile test two layers of NCF were used for fabricating the specimens. The samples dimensions were set according to ASTM-D3039/D3039M standards. The machine used for performing the test is universal testing machine type INSTRON 5982 100KN with tensile test apparatus. The linear displacement speed was 1 mm/min. Figure 5.5 (a) shows side and top view of the samples used for tensile test, in which T_{sp} and T_{Al} represent the thickness of the specimen and the thickness of the Aluminum tab respectively. In values, T_{sp}= 0.7 mm and T_{Al}= 0.2 mm. The width and the length of the specimens were 20 mm and 160 mm respectively. For 3-point flexural test, 8 layers of NCF were used and ASTM-D790–03 standards followed for preparing the specimens. The dimensions of the specimens (Figure 5.5 (b)) were: 80 mm in length, 15 mm in width and 3 mm in thickness. The span length was changeable according to the value of the thickness but it ranged between 48 mm and 52 mm.

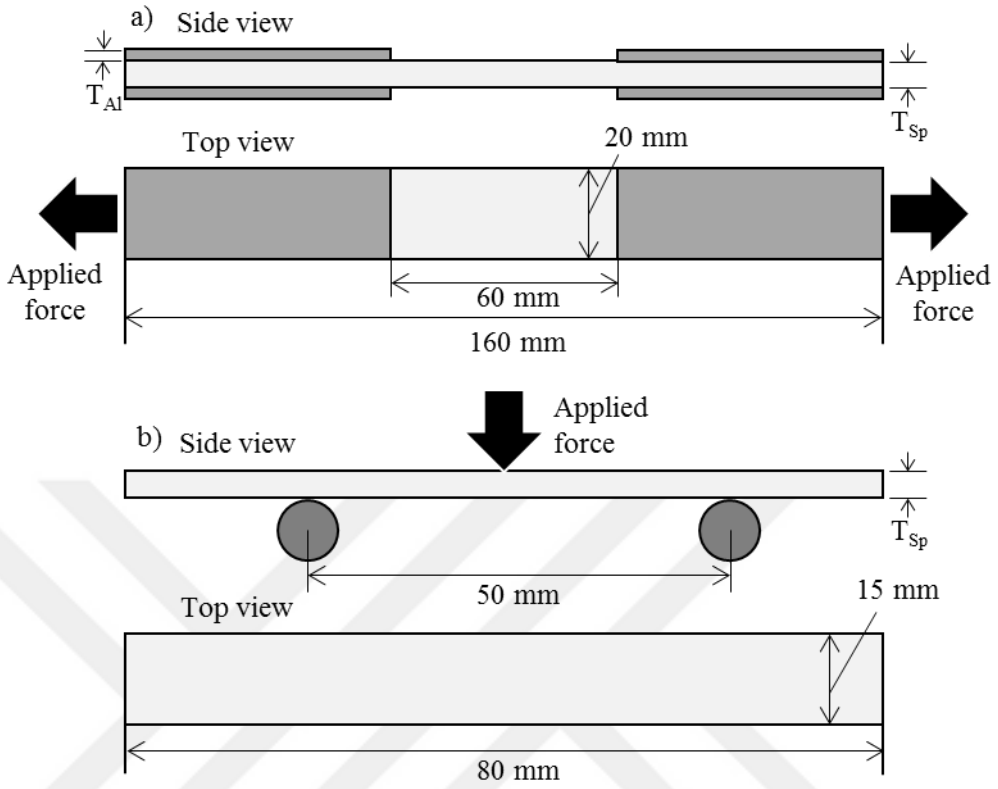

Figure 5.5. Specimens dimensions of (a) tensile test. (b) 3-point flexural test.

5.5 Tensile test results

The stress-strain curves resulted from tensile test can be seen in figure 5.6. Each graph represents a certain orientation of the reinforcement in the composite. It is clear that the tensile stress value of LPET in all of the three graphs shows better results than the tensile stress value of PP. Figure 5.6 (a), (b) and (c) represent the samples with 0°, 45° and 90° stitch fibers orientation respectively. Tensile stress of LPET is 9% better than tensile stress of PP for the 0° stitch fibers orientation. For 45° samples, LPET shows tensile stress 21% better than PP. For 90° samples, LPET tensile stress shows the highest value with 73% better than PP.

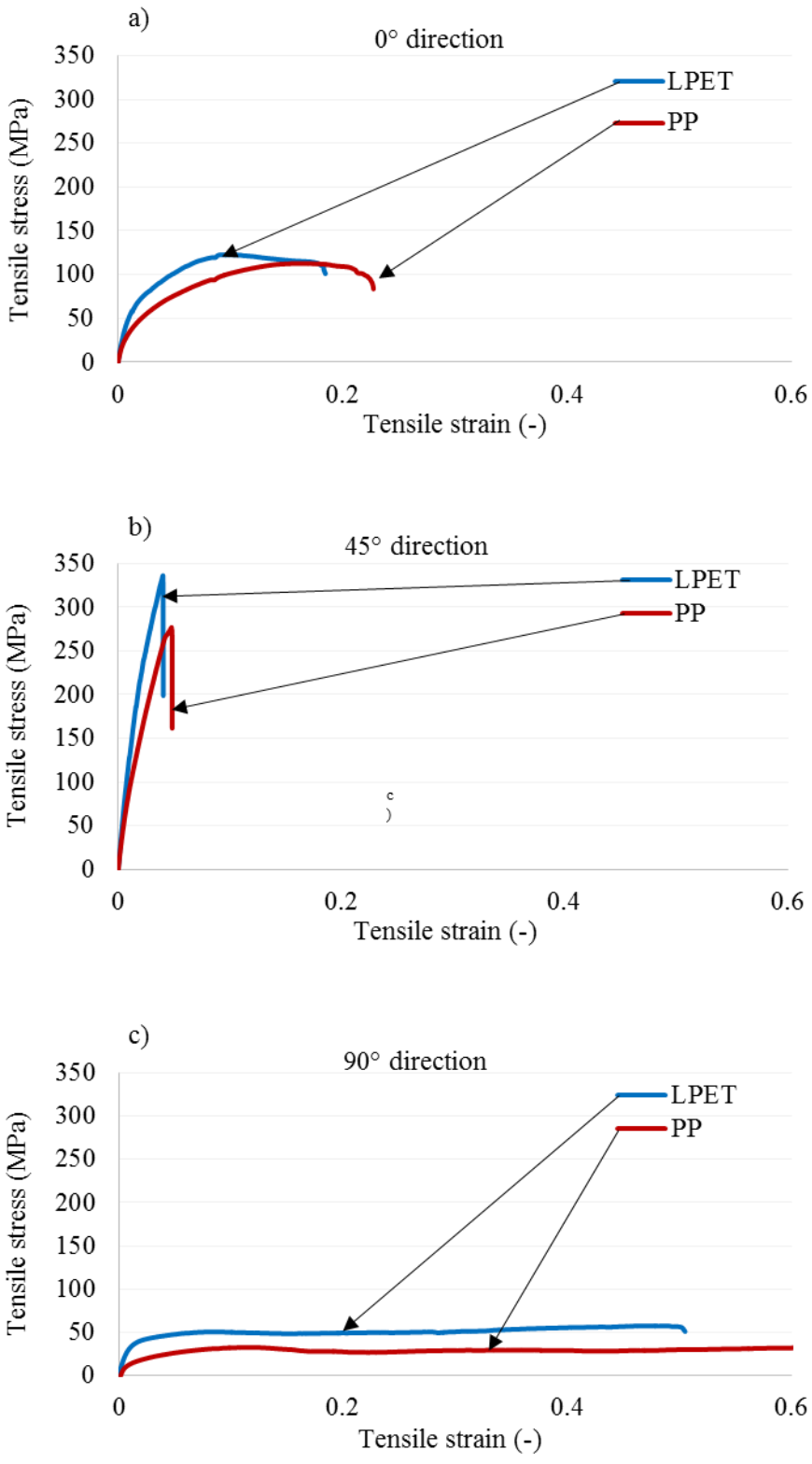

Figure 5.6. PP and LPET tensile stress-strain curves of; (a) 0° stitch fibers direction, (b) 45° stitch fibers direction and (c) 90° stitch fibers direction

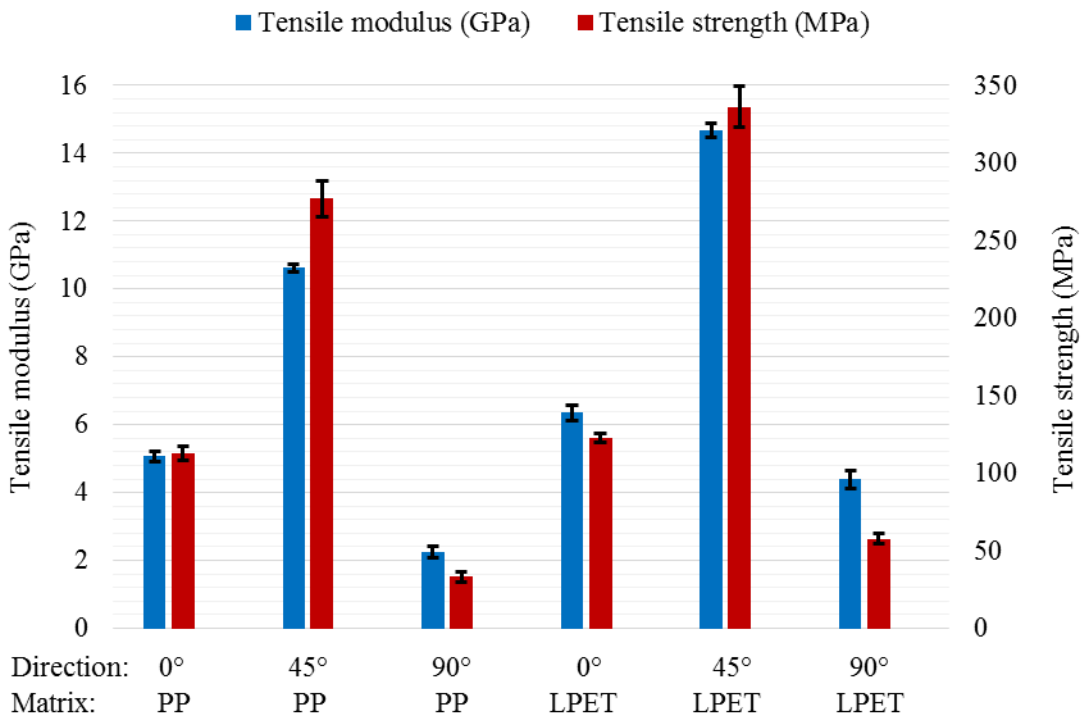

Figure 5.7. Tensile modulus and strength of PP and LPET

Figure 5.7 shows results of tensile modulus and strength for different stitch fibers orientation. The tensile modulus of LPET show better values than tensile modulus of PP as following: 26 % for the 0° samples, 39% for the 45° samples and 95% for the 90° samples. The effect of reinforcement orientation on the mechanical properties would be discussed in the next chapter.

5.6 3-point flexural test

Figure 5.8 shows the results of 3-point flexural stress-strain curves. It is obvious that the flexural stress of LPET in the three graphs shows better results than flexural strength of PP. figure 5.9 represents results of flexural modulus and flexural strength of all of the samples. LPET tensile strength show better properties by 39%, 8% and 29% than 0° samples, 45° samples and 90° samples respectively. The flexural modulus of LPET also show better results than flexural modulus of PP according to the following percentages: 79%, 16% and 73% for 0° samples, 45° samples and 90° samples respectively.

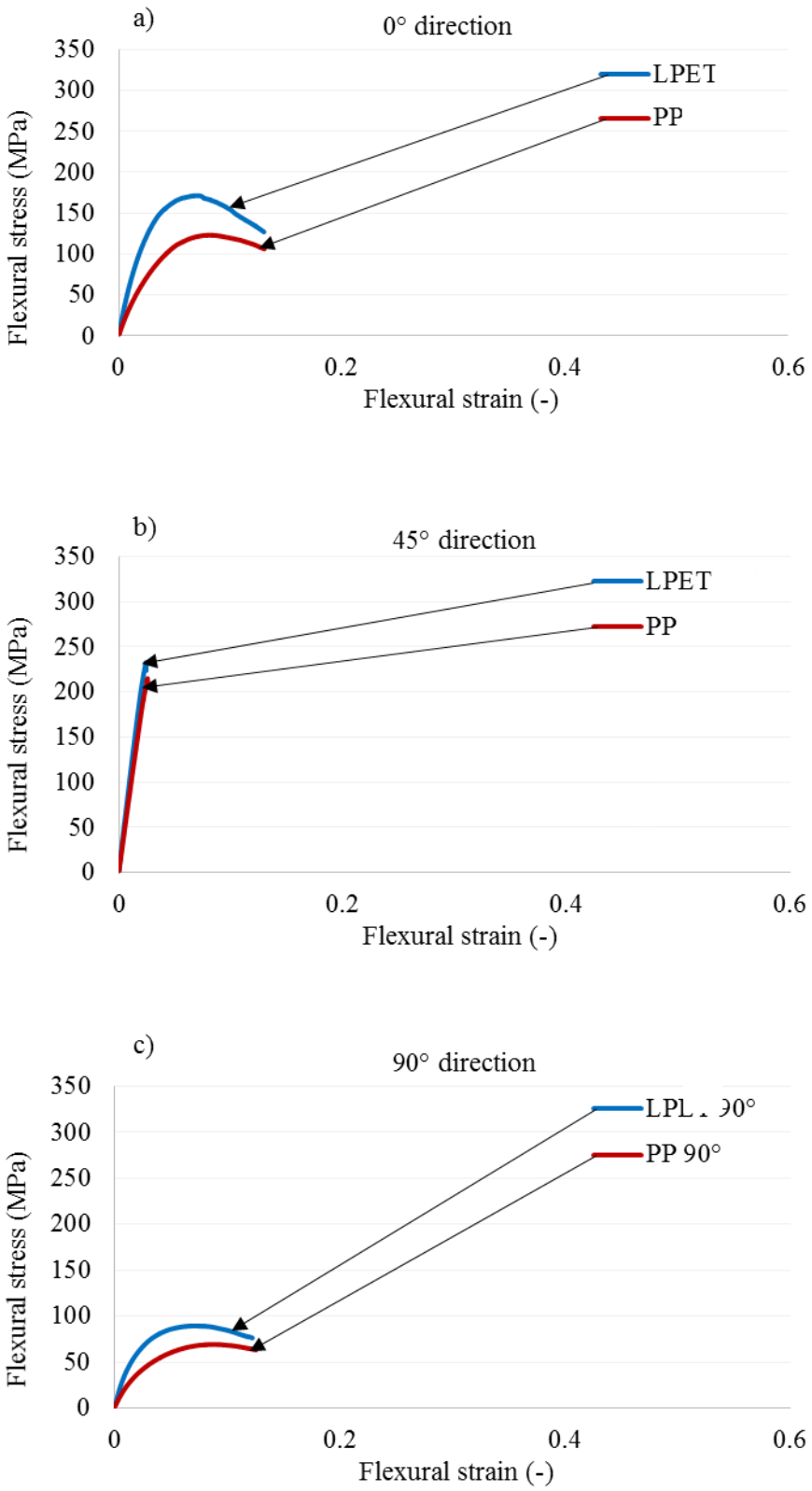

Figure 5.8. PP and LPET 3-point flexural stress-strain curves of; (a) 0° stitch fibers direction, (b) 45° stitch fibers direction and (c) 90° stitch fibers direction

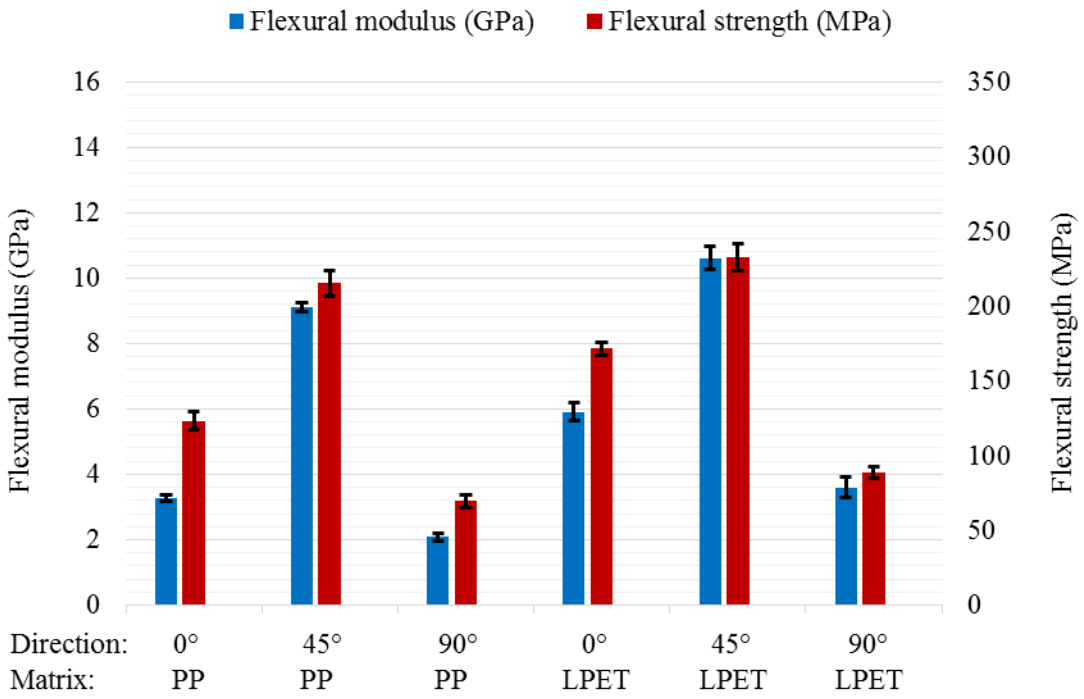

Figure 5.9. Flexural modulus and strength of PP and LPET

From the results obtained from tensile test and 3-point flexural test, we can decide that LPET has better mechanical properties and hence it can be considered for the MWCNTs integration studies.

Chapter 6

Experimental study of the integration of MWCNTs with LPET thermoplastic matrix

According to results regarding PP and LPET obtained previously in chapter 5, the mechanical tests showed better properties for the LPET over the PP. hence, LPET were chosen for MWCNTs integration study.

6.1 Composite constituents

Basically, the composites constituents for this study has the same specifications and properties of the LPET composite plates mentioned previously in chapter 5 with only one difference. The commingled fibers in the NCF in this type were incorporated with MWCNTs as a second phase reinforcement. The specifications and properties of MWCNTs used in this study are illustrated in Table 6.1. The supplier of MWCNTs is Ege Nanotek Kimya Sanayi Izmir/Turkey. Figure 7.1 shows MWCNTs before fabricating the composite, characterized by using SEM technique. In this image, individual MWCNTs were clearly observed.

6.2 MWCNTs solution and NCFs preparation

Ethanol were used for preparing the solution due to its compatibility with MWCNTs and Polyethylene Terephthalate. The preparation of the solution starts with measuring the weight of MWCNTs using sensitive digital scale with an accuracy of 0.0001 gm. Then, 100 grams of ethanol added to the previously weighted MWCNTs. The first stage of dispersing MWCNTs in the ethanol starts with magnetic stirrer in which the MWCNTs distributed all over around the ethanol by the use of a magnet bar, stirred by a magnetic field. The speed of stirring is set to 1000 rpm for 15 minutes. This method minimize the risks of contamination since only an inert magnet bar, which can easily be cleaned, is put inside the solution. In addition, it can ensure a consistent and steady mixing rate comparing to the conventional mixing method. The second stage of dispersing MWCNTs

in the ethanol implemented using ultrasonic technique. In this process, agglomerated MWCNTs would come apart and dispersed homogenously in the ethanol [44, 45]. The working mechanism of this technique were already explained in chapter 4. Figure 6.1 a-c illustrate briefly MWCNTs solution preparation steps.

Different weights of MWCNTs were used in preparing the solution during this study. The aim of using different weights is to investigate the effect of different amounts of MWCNTs on the mechanical properties of the fabricated thermoplastic composites and hence, the optimal percentage of MWCNTs in the composites could be found. Following are the weights of MWCNTs used and their final percentages in the fabricated composite:

- 0.4 grams of MWCNTs give 0.7 weight percentage of MWCNTs in the composite (0.7 wt% MWCNTs).
- 0.5 grams of MWCNTs give 0.9 weight percentage of MWCNTs in the composite (0.9 wt% MWCNTs).
- 0.6 grams of MWCNTs give 1.1 weight percentage of MWCNTs in the composite (1.1 wt% MWCNTs).

Table 6.1. MWCNTs properties

Parameter	**Value**
Outer diameter (nm)	10-30
Interior diameter (nm)	5-10
Length (µm)	10-30
Surface area (m^2/g)	>110
Color	black
Electrical conductivity (S/cm)	>100
Density (tap) (g/ cm^3)	0.28
Density (true) (g/ cm^3)	2.1

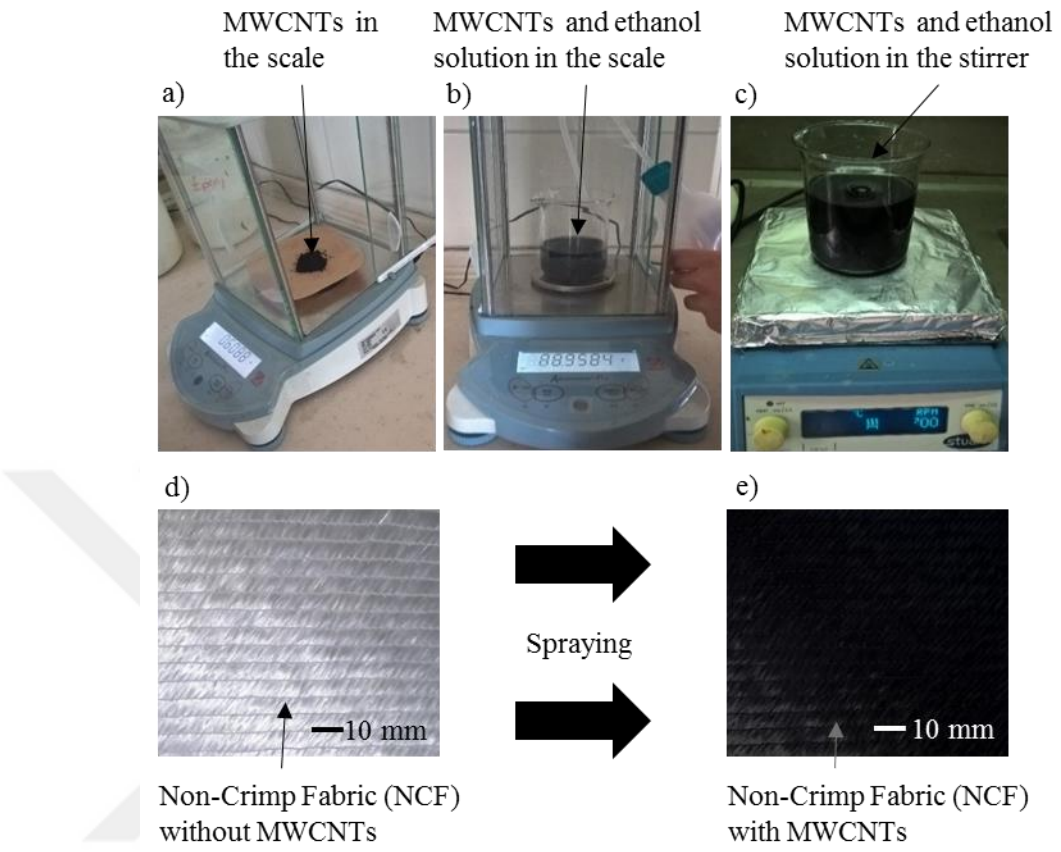

Figure 6.1. MWCNTs solution and NCFs preparation (a) Measuring the weight of the MWCNT used, (b) Prepare the solution by adding Ethanol to the MWCNT, (c) Mixing, using magnetic stirrer, (d) NCF without MWCNT and (e) NCF with MWCNT.

NCF specimens' dimensions that set for coating are (20 X 20) cm. The prepared solution of a certain amount of MWCNTs were coated over two layers of the NCF on both faces (i.e. 4 faces of NCF were coated with each prepared solution). The coating process took place using spraying method. Figure 6.1 d and e show NCF specimen before and after coating respectively.

6.3 Hot-press fabrication process

After coating the NCF with the MWCNTs solution, specimens were left for two days to ensure full evaporation of the ethanol and obtaining dry specimens to use them in the hot-

press machine. Basically, the same procedure from chapter 5 were applied to fabricate the thermoplastic composite (Figure 5.3)

6.4 Sampling method

The sampling method were already illustrated in chapter 5. See figure 5.4 for more details.

6.5 Volume & Weight fraction

In order to determine the percentages of each of the constituent in the thermoplastic composites, burn off method in a muffle furnace were followed. The operation were done in accordance with ASTM D3171–99 standards. The process can be summarized into three basic steps (figure 6.2):

1. Calculate the density (ρ_c) and the mass (M_i) of the specimens and the weights of the crucibles used.
2. Burn off the matrix using muffle furnace with a temperature of 620 °C for 5 hours.
3. Measure the mass of the reinforcements fibers (M_f) left in the crucibles. Apply the following the equations to determine the volume fraction V_r and the weight fraction W_r of the reinforcement constituent:

$$W_r = M_f/M_i \times 100$$

$$Vr = M_f/M_i \times 100 \times \rho_c /\rho_r$$

The values of the volume and weight fraction of all the specimens of tensile test and 3-point flexural test can be seen in Table 6.2

The crucibles are positioned in furnace

Temperature of the furnace set to 620 °C

Pure reinforcement fibers resulted

Figure 6.2. Burn off in a muffle furnace method for the calculation of reinforcement volume and weight fraction of the thermoplastic composite

Table 6.2. Weight and volume fraction of reinforcement for the tested specimens

Fabric layers number	**Specimen's weight percentage of MWCNTs (wt. %MWCNTs)**	**Glass fibers weight percentage (wt. %GF)**	**Glass fibers volume percentage (vol. %GF)**	**Density (gm/ cm^3)**	**Thickness (mm)**
2	0.0	62.8	45.1	1.8673	0.71
2	0.7	57.4	40.7	1.8492	0.78
2	0.9	61.9	44.1	1.8423	0.75
2	1.1	60.5	43.9	1.8331	0.76
8	0.0	59.3	42.7	1.8703	3.09
8	0.7	57.3	40.3	1.8571	3.03
8	0.9	57.7	41.1	1.8485	2.98
8	1.1	57.1	40.4	1.8383	3.11

6.6 Mechanical characterization

Scanning Electron Microscope (SEM) images of MWCNTs were obtained in a JSM-7001 F analytical field-emission SEM apparatus.

The samples dimensions already discussed in chapter 5. See Figure 5.5 for more details.

Chapter 7

Results and discussion

After tensile and 3-point flexural tests, specimens' densities were measured (Table 6.2). The results showed that the increasing of the weight percentages of MWCNTs lead to decreasing the density of the composite. Composites with nanoparticles of 0.7, 0.9 and 1.1 wt% MWCNTs had around 0.9, 1.25 and 1.75% lower density compared to the composites without nanoparticles of CNTs in both two and eight layers.

MWCNTs were characterized by using the Scanning Electron Microscope (SEM) technique. The SEM image of nanotubes is shown in Figure 7.1. Individual MWCNTs were clearly observed in this image.

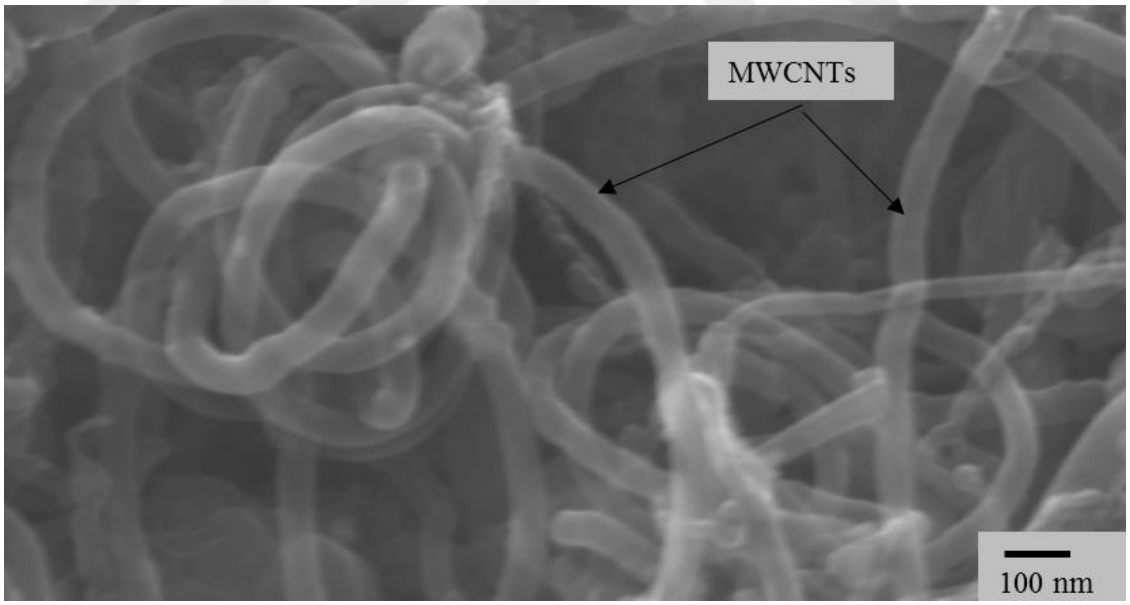

Figure 7.1. Scanning Electron Microscope (SEM) images of MWCNTs

Before fabricating the prepared NCFs, SEM image were obtained to see the distribution of the MWCNTs over the fabric. Figure 7.2 shows SEM image for a sample with 1.1 wt% MWCNTs. Another SEM image were obtained after fabricating the NCF into composite.

Figures 7.3, 7.4 and 7.5 show a cross section SEM image of a 1.1 wt% MWCNTs sample. MWCNTs can be seen partially embedded into the matrix

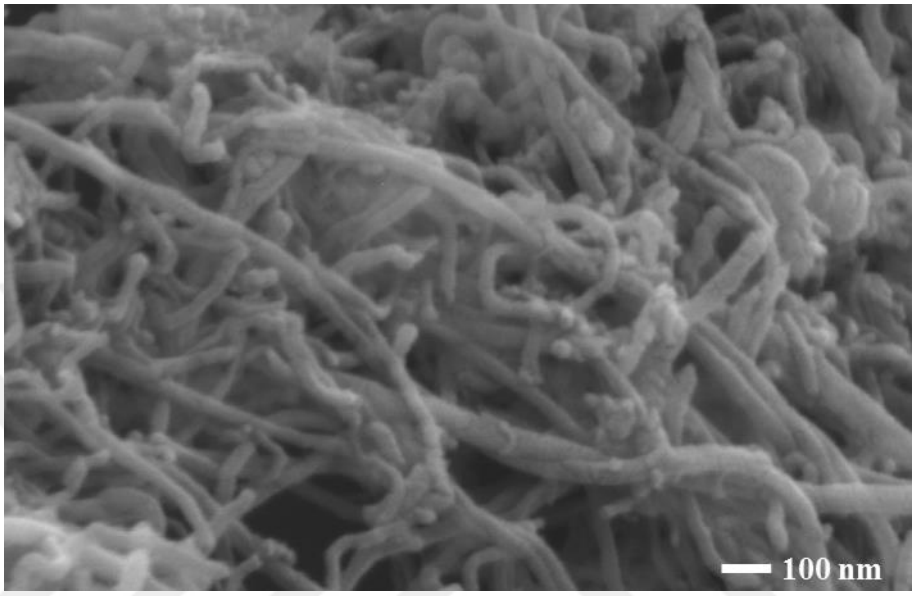

Figure 7.2. SEM image of the NCF coated with 1.1 wt% MWCNTs before fabrication

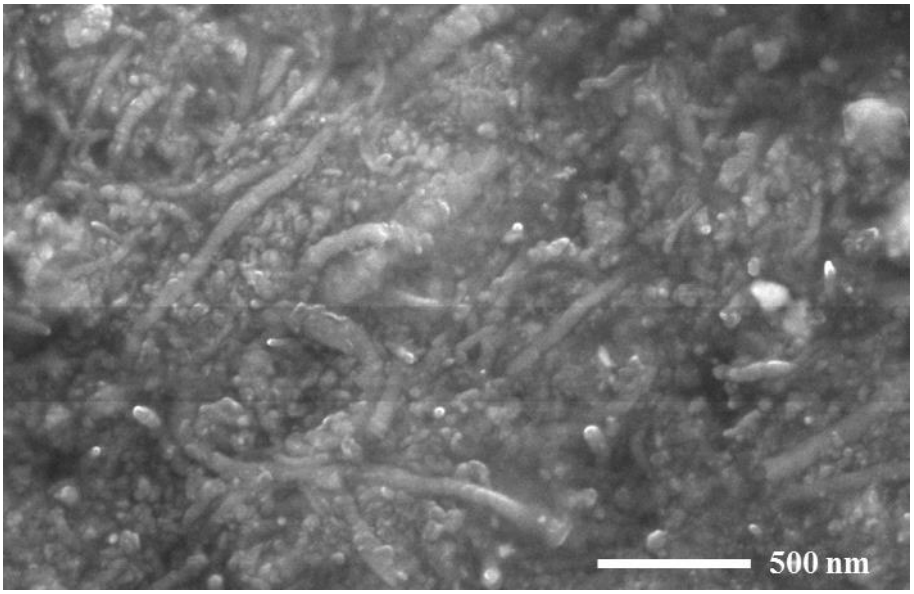

Figure 7.3. SEM image of the fabricated composite with 1.1 wt% MWCNTs

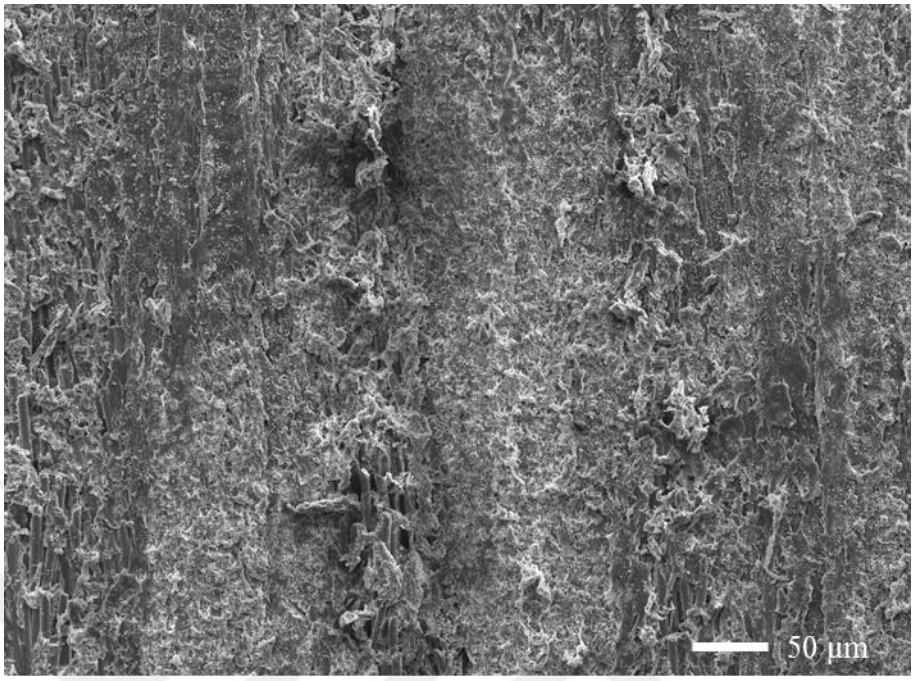

Figure 7.4. SEM image of the fabricated composite with 1.1 wt% MWCNTs with different magnification

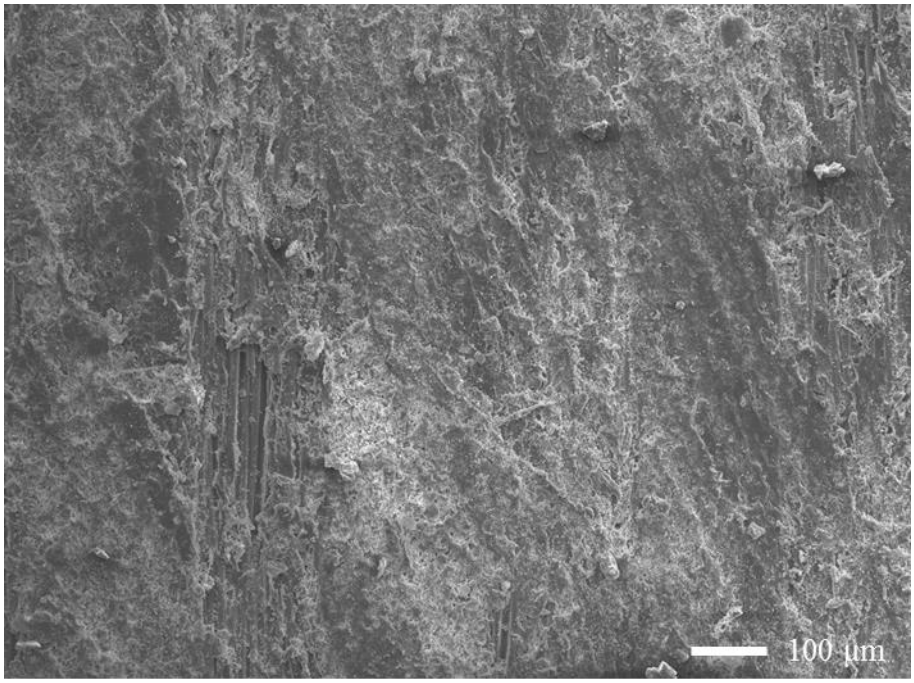

Figure 7.5. SEM image of the fabricated composite with 1.1 wt% MWCNTs with smaller magnification

7.1 Tensile test

Figure 7.6 a-c shows graphs of the stress-strain curves from the tensile test. As can be seen in all of the graphs, the tensile stress starts increasing linearly with the increasing in strain. Then, a sudden decreasing in tensile stress happens. In Figure 7.6 a-c, the specimens with 0.9 wt% MWCNTs had the highest tensile stress among other specimens, while the specimen with 0.0 wt% MWCNTs showed the lowest tensile stress. Figure 7.7 represents an overall diagram for all of the samples. Figure 7.8 shows the results of the tensile modulus and strength of all the specimens. The specimens in 45° directions with 0.9 wt% MWCNTs had the highest values of the tensile modulus (15.1 GPa) and strength (343 MPa) among their groups. The specimens in 90° directions with 0.0 wt% MWCNTs had the lowest value of tensile modulus (2.97 GPa) and strength (45.6 MPa). An increasing of 35% in the tensile strength took place for the specimen incorporated with 0.9 wt% MWCNTs comparing to the specimen with 0.0 wt% MWCNTs in 0° direction. The tensile strength was improved 3% for the specimens with 0.9 wt% MWCNTs comparing to the specimens with 0.0 wt% MWCNTs in 45° direction. An improvement of 34% of the tensile strength was happened for the specimen with 0.9 wt% MWCNT comparing to the specimens without MWCNTs in 90° direction. The possible reason for the obtaining of the improved tensile properties for the specimens incorporated with the MWCNTs was the synergy created by the MWCNTs between the various constituents of the composite material. The fracture aspects after the tensile test of the specimens without MWCNTs in 0°, 45° and 90° directions were shown in Figure 7.9 a-c. The fracture aspects of the specimens had good agreement with the tensile test results. The photo of the fractured specimen in 45° direction was shown that the path of the fracture was perpendicular to the pulling direction of the specimen (Figure 7.9 a). This was proved that the specimens in 45° direction showed higher resistance against to the tensile loading. And it was resulted with the highest tensile properties of the specimens in 45° direction compared to the others. The path of the fracture was the same as the direction of the ±45° reinforcement fibers in 0° and 90° directions. Both of the specimens in 0° and 90° directions showed the similar fracture aspects after the tensile tests (Figure 7.9 (b) and (c)). The longer ends of the fractured fibers in Figure 7.9 (b) and (c) were proved that the specimens in 0° and 90°directions showed the lower resistance against to the tensile loading.

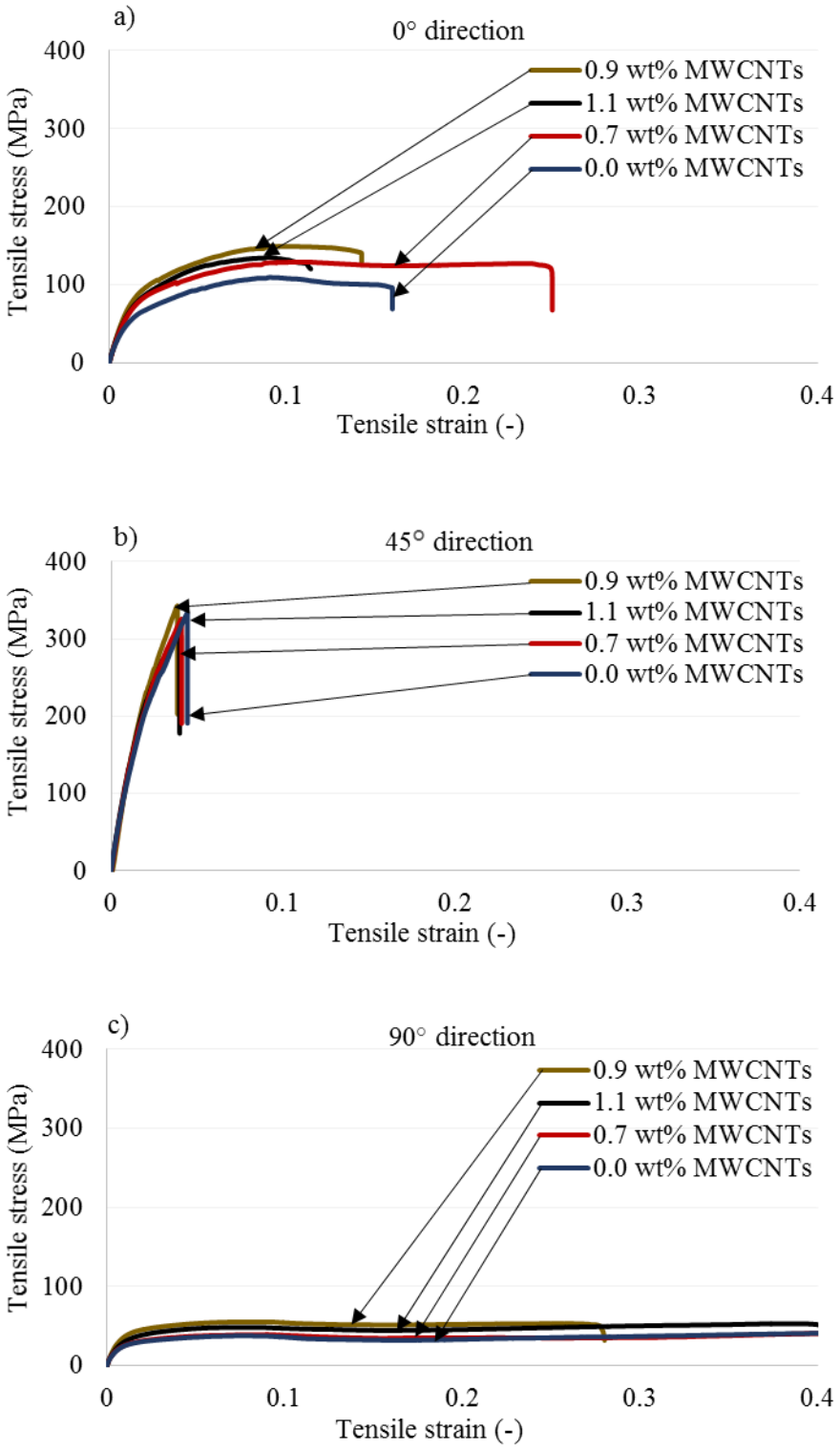

Figure 7.6. Stress-Strain curves of tensile test for (a) 0° specimens, (b) 45° specimens, and (c) 90° specimens

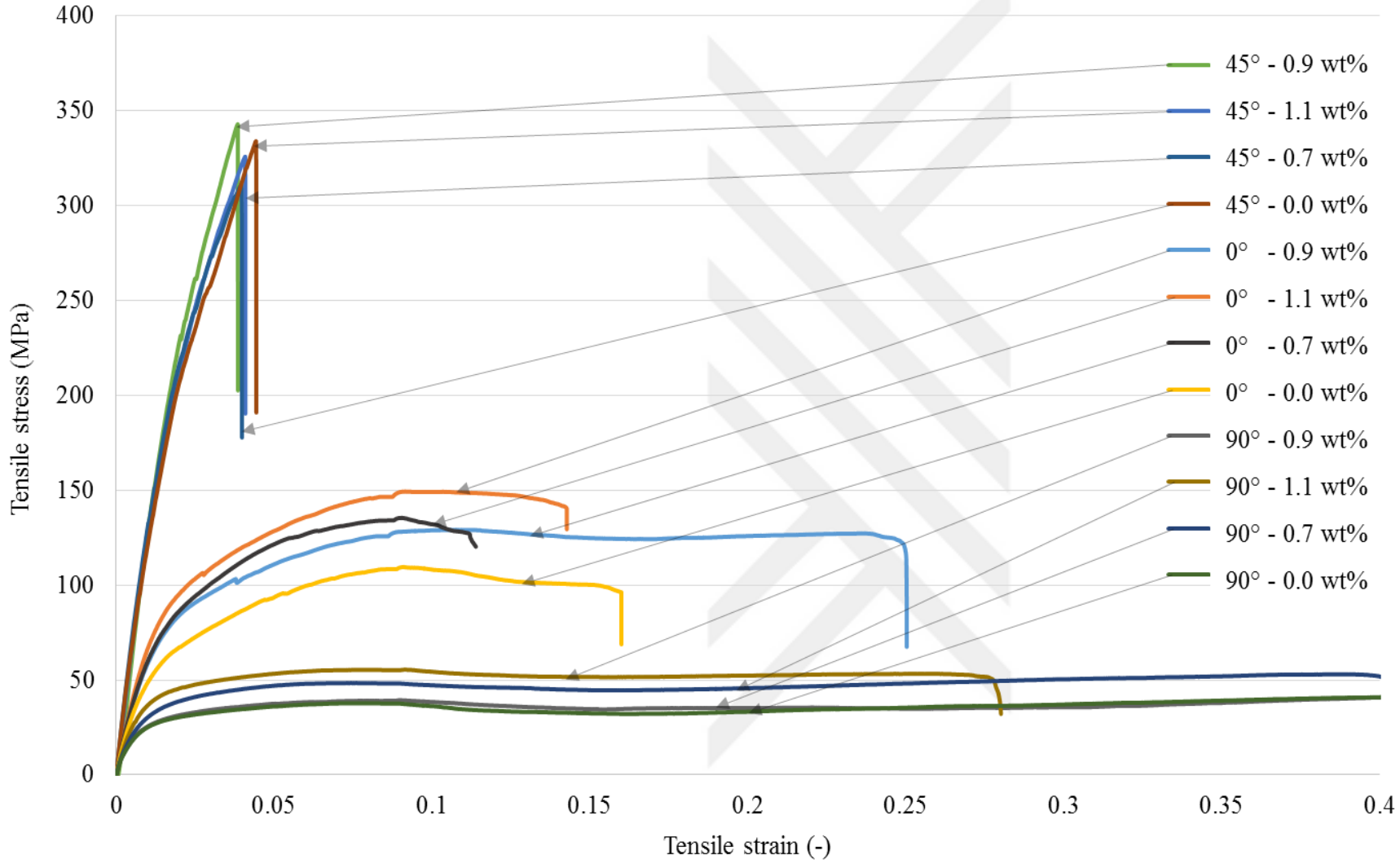

Figure 7.7. Stress-strain curves of all of the specimens obtained from the tensile test

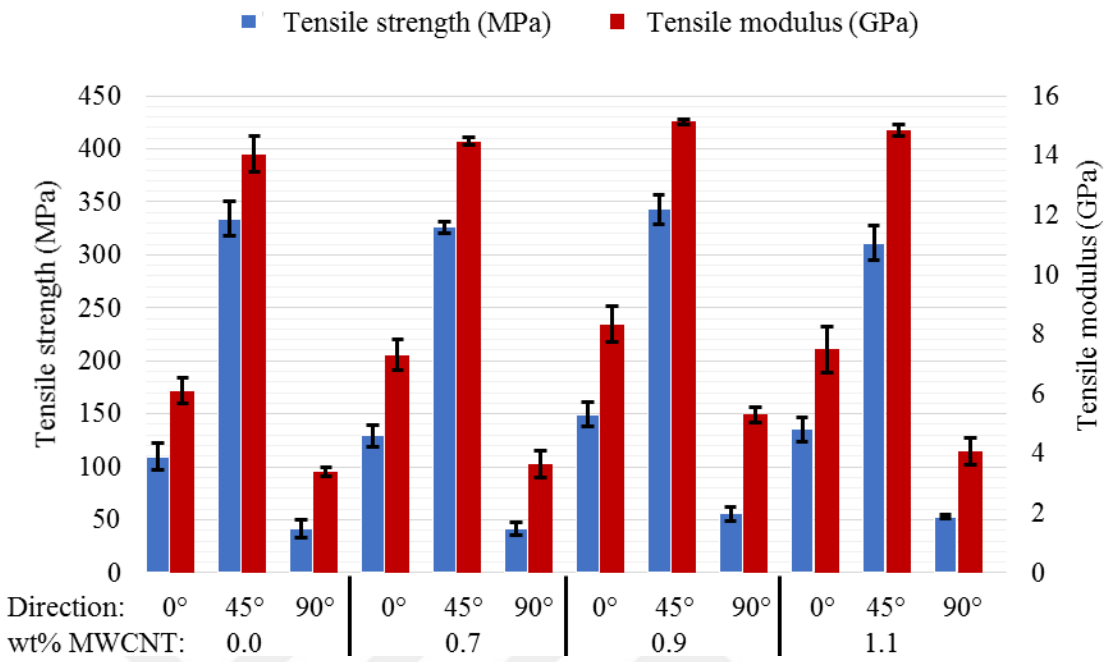

Figure 7.8. Results of tensile strength and tensile modulus of different MWCNTs wt% obtained from tensile test

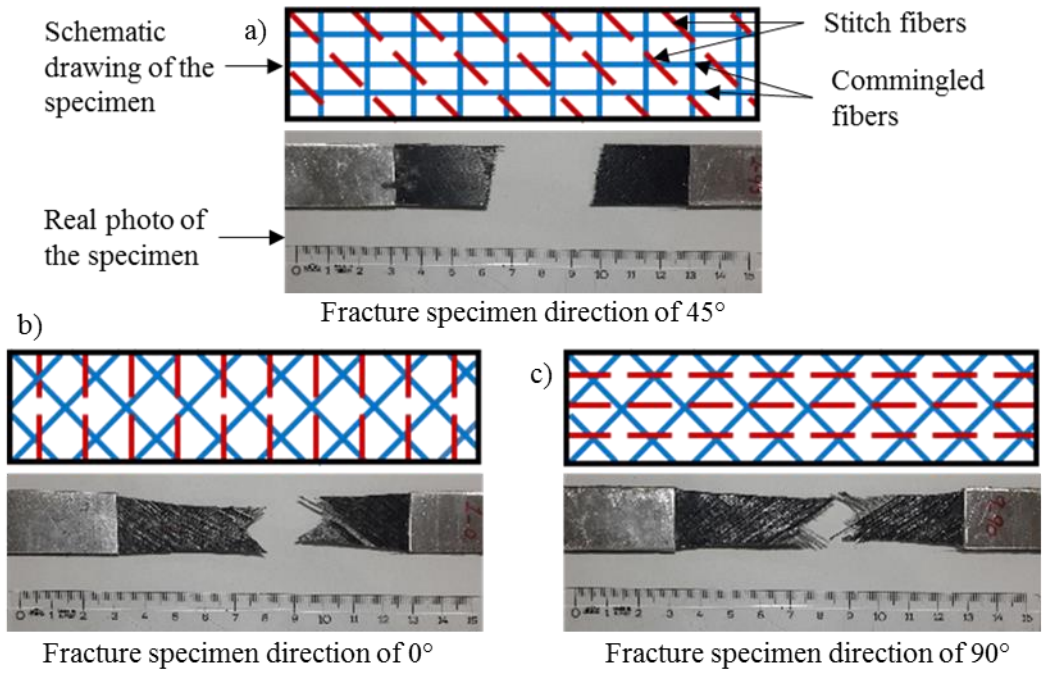

Figure 7.9. Fracture aspect after tensile test of (a) 45° stitch fibers direction, (b) 0° stitch fibers direction, and (c) 90° stitch fibers direction.

Due to have the orientation of the ±45° reinforcement fibers in the direction of pulling (Figure 5.4, 45° direction), the specimens in 45° direction can resist against the more tensile stress than the others. Therefore, the specimens in 45° direction had the highest tensile modulus and strength compared to the others. Despite of the fact that the specimens in 0° and 90° directions had the same reinforcement orientation (i.e. both had ±45° fibers orientation) (Figure 5.4), they showed the different results of the tensile tests. And the tensile properties of the specimens in 0° directions were higher than 90° directions. This was primarily because of the orientations of the stitch fibers.

The stitch fibers are made of polyester and has a modulus of 6 GPa and strength of 650 MPa. They acted as a holder for the fiber bundles in 0° direction of the samples by preventing them from dissipation, when a force applied. Therefore, the results of the tensile tests in 0° direction was higher compared to the 90° direction. Stitch fibers are essential element in any NCF because they connect the layers with each other. However, their existence have a great effect on the mechanical properties. Figure 7.10 represents tensile stress-strain diagram for samples with 0° stitch fibers, 90° stitch fibers and without stitch fibers. Samples without stitch fibers show lower tensile stress comparing to the other samples.

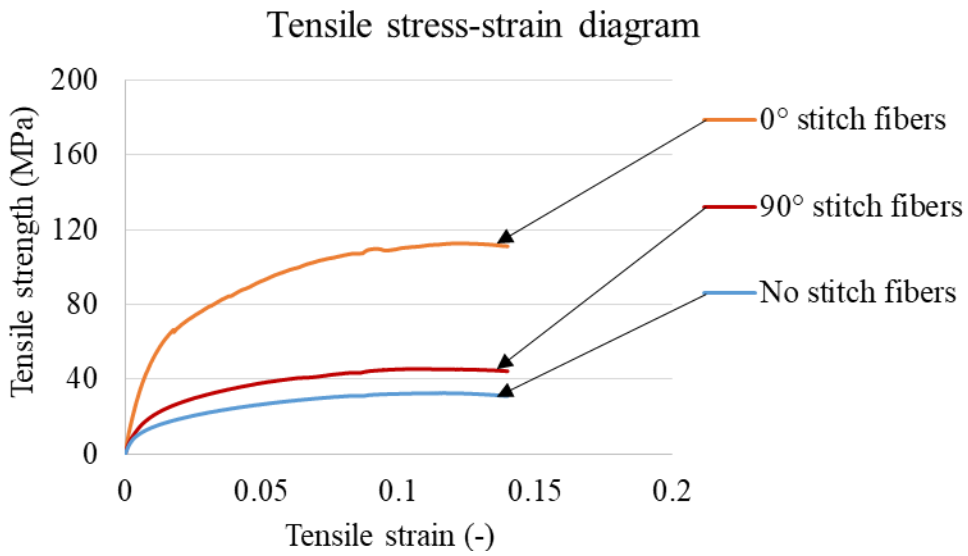

Figure 7.10. Tensile stress-strain diagram of 0°, 90° and without stitch fibers samples

Figure 7.11 shows the tensile modulus and strength of the samples with 0° stitch fibers, 90° stitch fibers and without stitch fibers. The samples without stitch fibers show lower tensile modulus and strength comparing to the 90° and 0° respectively. Table 7.1 Shows the actual results obtained from tensile test and the improvement percentages of the 0° and 90° samples with respect to samples without stitch fibers.

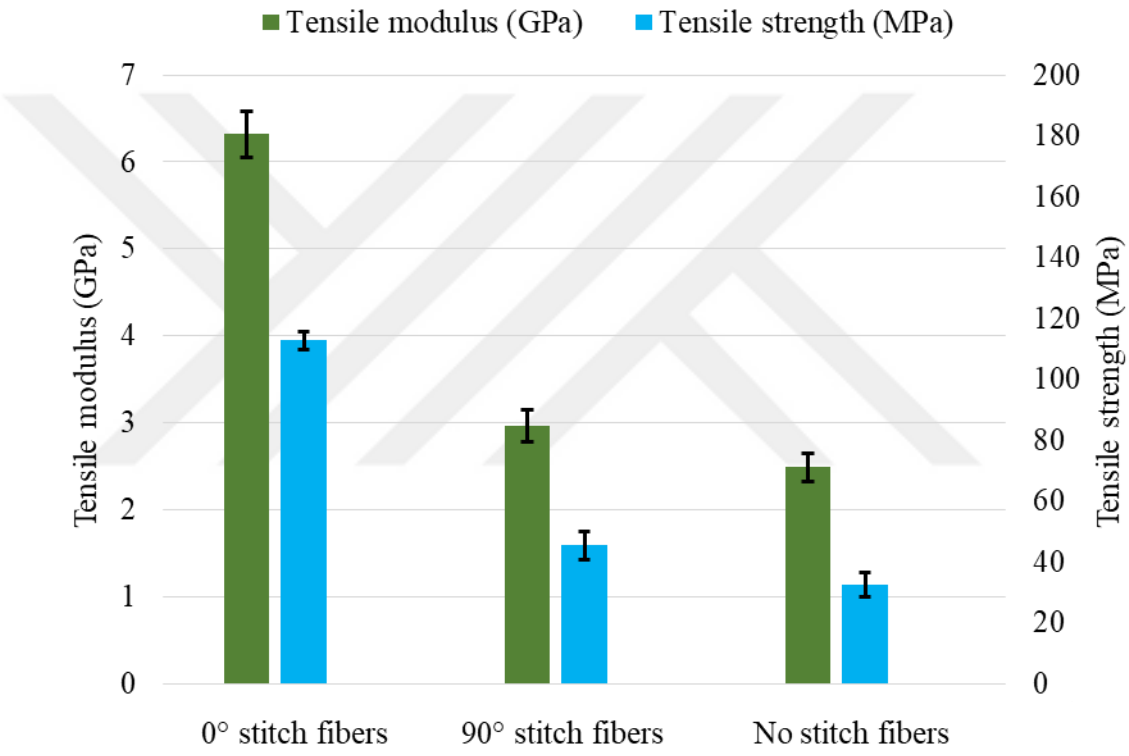

Figure 7.11. Results of tensile strength and modulus for the 0°, 90° and without stitch fibers samples

Table 7.1. Tensile modulus and strength results and the improvement percent.

	Tensile modulus (GPa)	**Tensile strength (MPa)**	**Improvement % in tensile modulus comparing to specimens without stitch fibers**
0° stitch fibers	6.32	112.8	154
90° stitch fibers	2.97	45.6	12
No stitch fibers	2.49	32.6	-

7.2 3-point flexural test

The flexural stress of the composites was defined as its ability to resist the deformation under the bending load. Figure 7.12 a-c shows the stress-strain curves from the three-point flexural test. In Figure 7.12 a-c, the specimens with 0.9 wt% MWCNTs had the highest flexural stress among other specimens, while the specimen with 0.0 wt% MWCNTs showed the lowest flexural stress. All of the results were summarized in Figure 7.13.

Figure 7.14 represents the results of the flexural modulus and strength of the specimens. Regardless of the directions of the specimens, the 0.9 wt% MWCNTs had the highest flexural modulus and strength among their groups. The specimens in 45° directions with 0.9 wt% MWCNTs had the highest values of the flexural modulus and strength (14.1 GPa and 402 MPa respectively). The specimens in 45° directions showed 33% and 65% higher flexural modulus and strength comparing to the specimen with the same direction but without MWCNTs. The specimens with 0.9 wt% MWCNTs had the best results of the flexural strength with an improvement of 15% comparing to the specimens with 0.0 wt% MWCNTs in 0° directions. Similarly, the specimens with 0.9 wt% MWCNTs had the highest values of the flexural strength with an improvement of 38% comparing to the specimens without MWCNTs in 90° directions, respectively. The specimens with the 1.1 wt% MWCNTs came with second best results in terms of the flexural properties, followed by the specimens with the 0.7 wt% MWCNTs. The lowest values were obtained from the specimens without MWCNTs. As mentioned earlier, the possible reason for the improvement in flexural strength and modulus was the synergy created by the MWCNTs between the various constituents of the composite material.

The specimens with 45° directions demonstrated better results compared to the others due to the orientation of the ±45° reinforcement fibers. Some of the reinforcement fibers were parallel and some of the reinforcement fibers were perpendicular against to the applied forces (Figure 5.4, 45° directions). Due to have a perpendicular orientation of the reinforcement fibers against to the applied flexural forces, the specimens with 45° directions demonstrated the more resistance against to the flexural loads. And it was resulted with a higher flexural property of the specimens with 45° directions compared to the 0° and 90° directions.

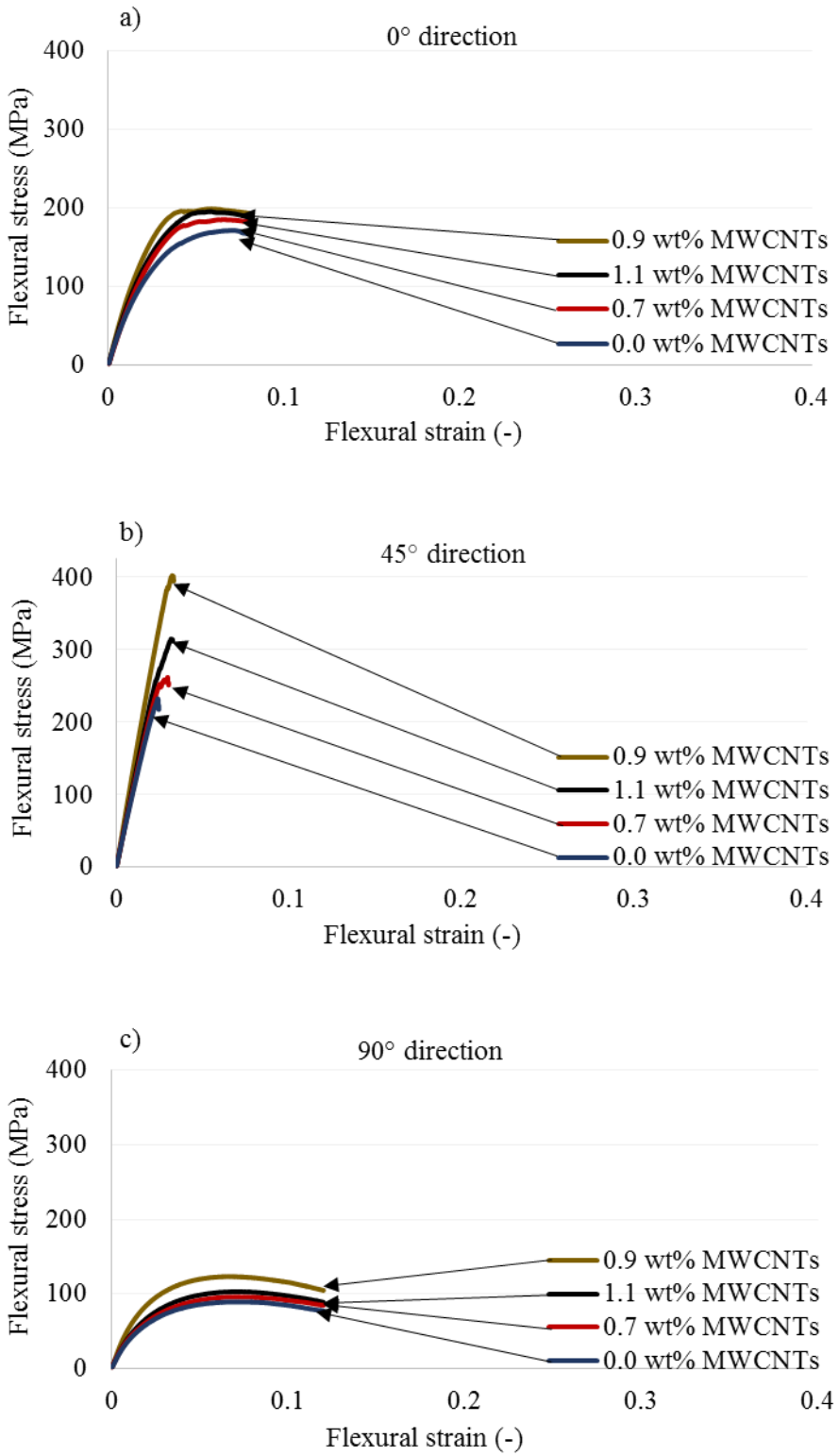

Figure 7.12. Stress-Strain curves of 3-point flexural test for (a) 0° specimens, (b) 45° specimens, and (c) 90° specimens.

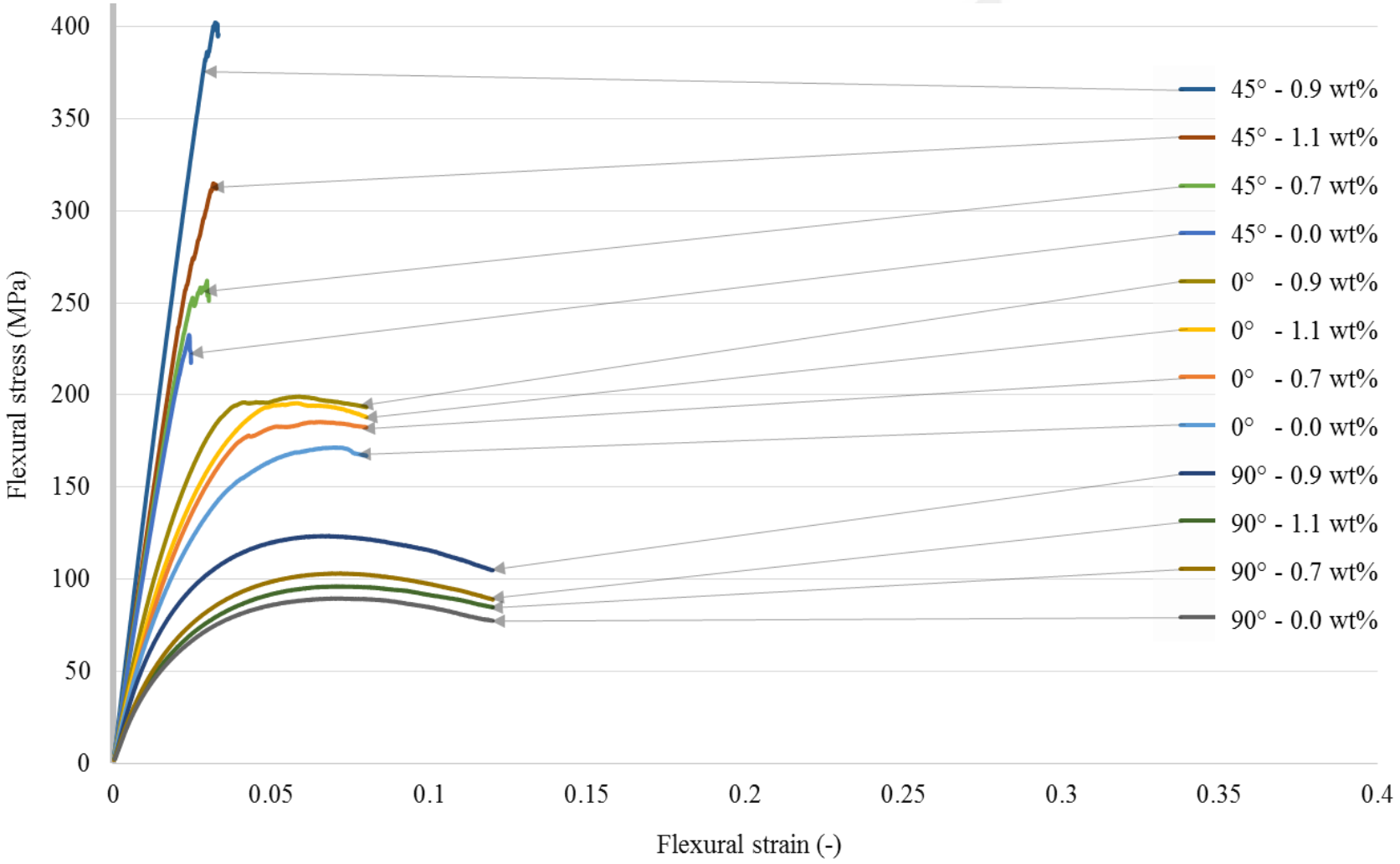

Figure 7.13. Stress-strain curves of all of the specimens obtained from the 3-point flexural test

The specimens in 0° direction were shown better flexural results than the specimens in 90° direction. As mentioned earlier, the stitch fibers hold the reinforcement fibers together in the specimens with 0° direction, while the stitch fibers had lower effect in the specimens of 90° direction.

The fracture aspects after the three-point flexural tests in 0°, 45° and 90° directions can be seen in Figure 7.15 a-c. The photo of the fractured specimen in 45° direction was shown that the path of the fracture was perpendicular to the pulling direction of the specimen (Figure 7.15 a) as the fracture aspect of the specimen from the tensile test. This was proved that the specimens in 45° direction showed the higher resistance against to the flexural loading. Both of the specimens in 0° and 90° directions showed similar fracture aspects after flexural tests (Figure 7.15 (b) and (c)). The path of the fracture was the same as the direction of the ±45° reinforcement fibers in 0° and 90°directions.

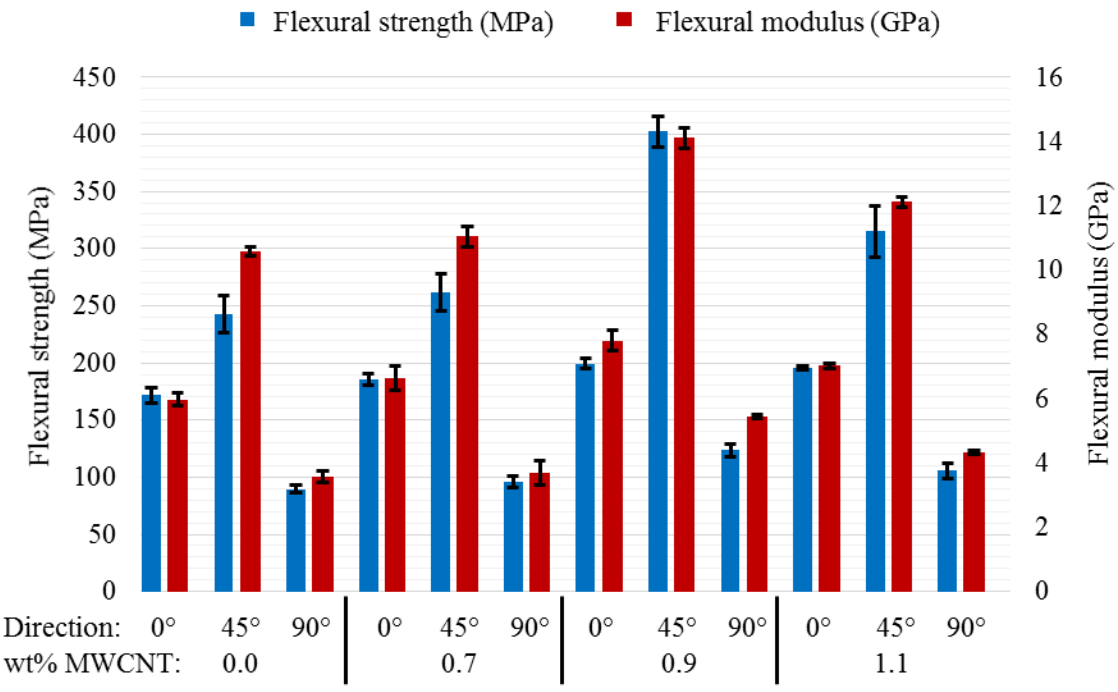

Figure 7.14. Results of Flexural strength and flexural modulus of different MWCNTs wt% obtained from 3-point flexural test

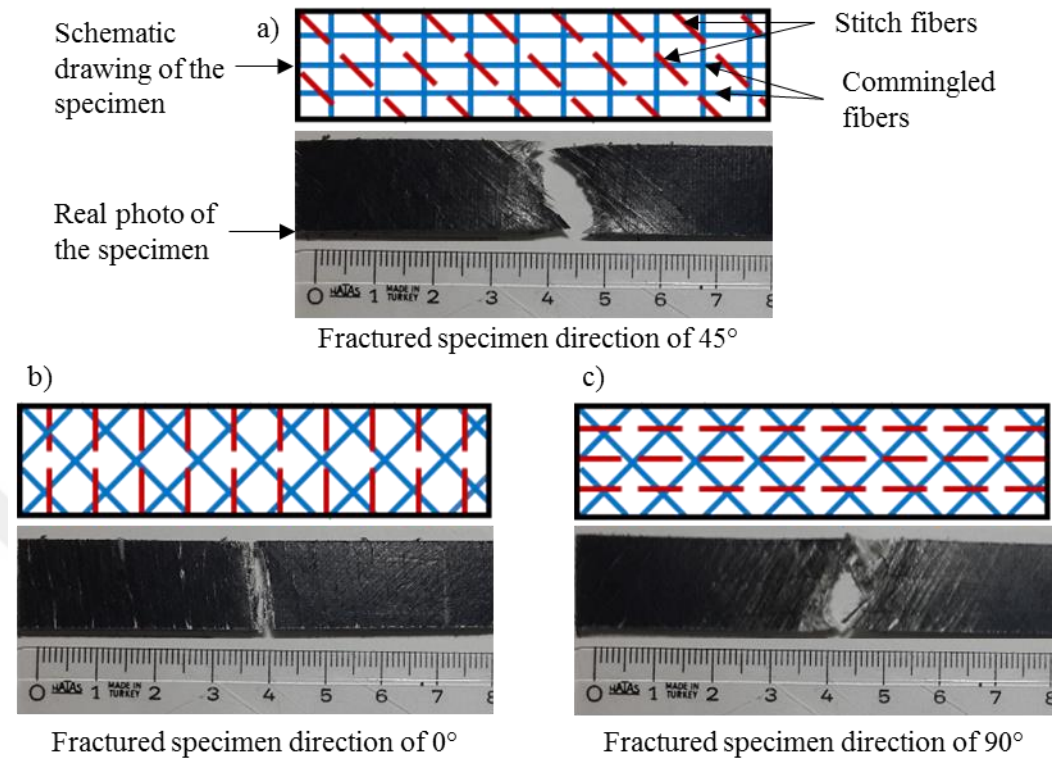

Figure 7.15. Fracture aspect after 3-point flexural test of (a) 45° stitch fibers direction, (b) 0° stitch fibers direction, and (c) 90° stitch fibers direction.

Samples without stitch fibers were prepared and tested in order to investigate the effect of stitch fibers on the flexural properties of the thermoplastic composite. Figure 7.16 represents flexural stress-strain diagram for 0°, 90° and without stitch fibers samples. The 0° stitch fibers direction shows the best flexural strength due to the orientation of the stitch fibers as explained earlier.

Figure 7.17 shows the flexural strength and modulus for the 0°, 90° and without stitch fibers samples. Again, samples without stitch fibers show the lowest values in terms of modulus and strength comparing to the other specimens. The improvement percentages of the 0° and 90° samples with respect to the samples without stitch fibers can be seen in Table 7.2.

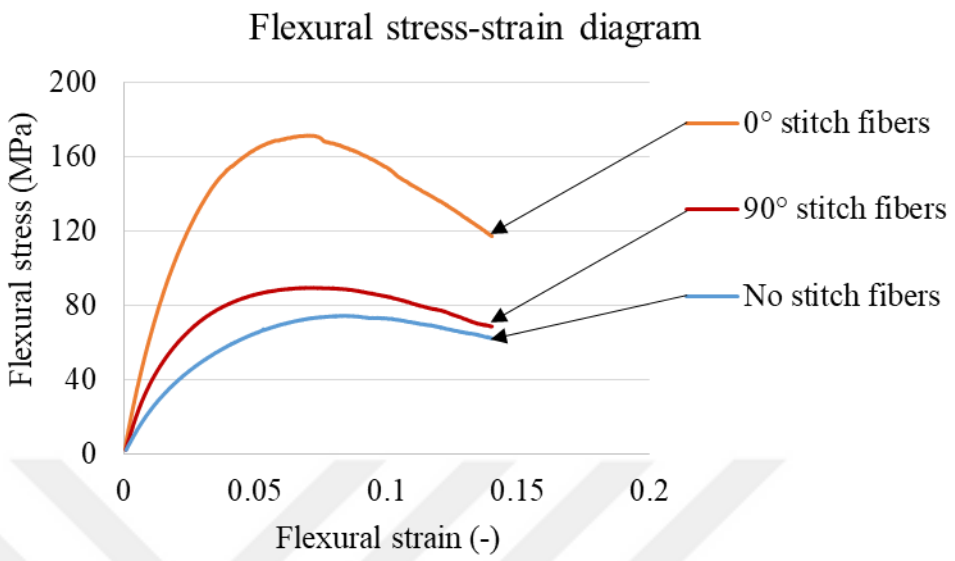

Figure7.16. Flexural stress-strain diagram for the 0°, 90° and without stitch fibers samples

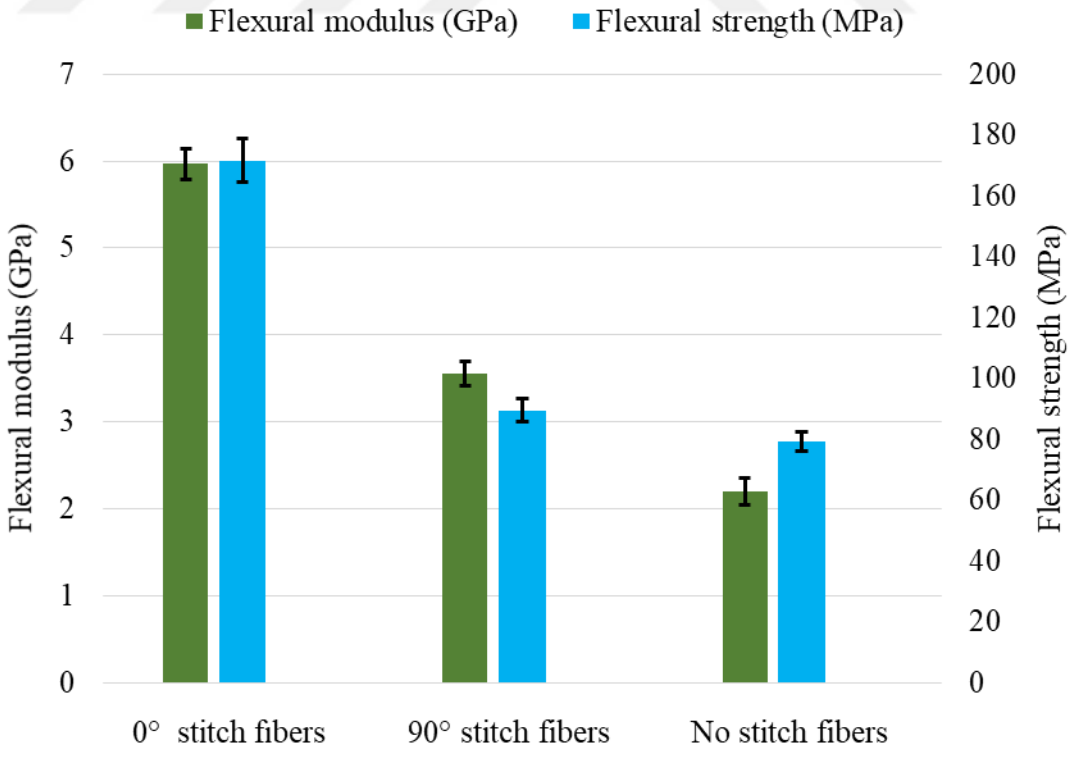

Figure 7.17. Results of flexural strength and modulus for the 0°, 90° and without stitch fibers samples

Table 7.2. Tensile modulus and strength results and the improvement percent.

	Flexural modulus (GPa)	**Flexural strength (MPa)**	**Improvement % in flexural modulus comparing to specimens without stitch fibers**
0° stitch fibers	5.97	171.6	171
90° stitch fibers	3.56	89.6	61
No stitch fibers	2.2	79.3	-

In order to accommodate all of the results obtained from tensile and 3-point flexural test, the modulus and the improvement percentages were summarized in table 7.3

Table 7.3. Tensile and flexural modulus and the improvement percentages comparing to 0.0 wt% specimens with the same fibers orientation

	Tensile modulus (GPa)	**Tensile modulus improvement % comparing to 0.0 wt%**	**Flexural modulus (GPa)**	**Flexural modulus improvement % comparing to 0.0 wt%**
0° - 0.7 wt% MWCNTs	7.31	15.7	6.64	11.2
0° - 0.9 wt% MWCNTs	8.33	31.8	7.81	30.8
0° - 1.1 wt% MWCNTs	7.49	18.5	7.02	17.6
45°- 0.7 wt% MWCNTs	14.4	3.00	11.1	4.84
45°- 0.9 wt% MWCNTs	15.1	7.86	14.1	33.2
45°- 1.1 wt% MWCNTs	14.8	5.71	12.1	14.3
90°- 0.7 wt% MWCNTs	3.65	22.9	3.69	3.65
90°- 0.9 wt% MWCNTs	5.30	78.5	5.45	53.0
90°- 1.1 wt% MWCNTs	4.07	37.4	4.31	21.0

Chapter 8

Conclusion

First of all, the first part of this study showed that composites with LPET matrix has better specifications over composites with PP matrix in terms of tensile and 3-point flexural properties.

In addition, our experiments revealed that the mechanical properties such as tensile and 3-point flexural of LPET thermoplastic composites could be enhanced and improved by incorporating different weight percentages of MWCNTs with the thermoplastic matrix. Specimens with 0.9 wt% MWCNTs specimens showed the best results in terms of tensile modulus, tensile strength, flexural modulus and flexural strength. The specimens with 1.1 wt% MWCNTs came with second best results in terms of the properties mentioned earlier, followed by the specimens with 0.7 wt% MWCNTs. The lowest values were obtained from specimens without MWCNTs incorporated in their matrix.

Our study also showed the effect of reinforcement orientation on the performance of the materials. Regardless the amount of MWCNTs in the composites, the specimens with reinforcement parallel to the direction of the acting force showed the best performance in terms of tensile modulus, tensile strength, flexural modulus and flexural strength among the other. Also, we concluded that stitch fibers direction has an effect on the mechanical properties of thermoplastic composites. The orientation of stitched fibers in 0° specimens acts as a holder for the reinforcement fibers bundle that prevent dissipating them when a force is applied, while they have lower effect in the specimens with 90° direction.

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