ANKARA YILDIRIM BEYAZIT UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

COMPARISON OF FLEXURAL AND PHYSICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBES ADDED GLASS FIBER REINFORCED POLYMER COMPOSITES PRODUCED BY CONVENTIONAL DIRECT MIXING AND INNOVATIVE SPRAY METHOD

M.Sc. Thesis by

Bahadır TÜRKYAMAN

Department of Material Engineering

January, 2021

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Bahadır TÜRKYAMAN

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"COMPARISON OF FLEXURAL AND PHYSICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBES ADDED GLASS FIBER REINFORCED POLYMER COMPOSITES PRODUCED BY CONVENTIONAL DIRECT MIXING AND INNOVATIVE SPRAY METHOD"** completed by **BAHADIR TÜRKYAMAN** under the supervision of **Asst. Prof. Dr. MEHMET FATİH ÖKTEM** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Asst. Prof. Dr. MEHMET FATİH ÖKTEM

Supervisor

Prof. Dr. CİHANGİR DURAN

Jury Member

Assoc. Prof. Dr. AHMET SINAN ÖKTEM

Jury Member

Prof. Dr. ERGÜN ERASLAN

Director

Graduate School of Natural and Applied Sciences

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COMPARISON OF FLEXURAL AND PHYSICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBES ADDED GLASS FIBER REINFORCED POLYMER COMPOSITES PRODUCED BY CONVENTIONAL DIRECT MIXING AND INNOVATIVE SPRAY METHOD

ABSTRACT

Glass fibers show significantly low out of plane/through thickness/z-axis properties because of weak fiber/matrix interphase. This weak interphase directly affects z-axis properties such as interlaminar shear strength, flexural strength, delamination resistance etc. In this study, it has been aimed to enhance the through thickness properties of MWCNTs grafted GFPCs produced by using different production methods which are Direct Mixing Method and Spray Method. Also, Triton X-100 has been used in some composite productions to distribute MWCNTs more homogeneously. To see the effects of these methods on the composite materials Three-Point bending test, Shore D and Vickers hardness tests and, SEM analysis have been conducted.

As a result of conducted studies, the best flexural strength and flexural modulus are obtained as 411.309 MPa and 20.186 GPa in composite materials produced by Spray Method with the aid of Triton X-100. Also, increases in flexural strength and flexural modulus are about 5.33 percent and 19.79 percent as compared to control sample. In the other hand, when composite materials compared with control sample, decreases in flexural strength and increases in flexural modulus are observed. Also, Shore D and Vickers hardness test results revealed that hardness of composite materials produced by Direct Mixing Method and Spray Method increase with the addition of MWCNTs to the composite structure. The SEM images revealed that best dispersion of MWCNTs are obtained from composite materials produced by Spray Method with Triton X-100. Also, the images clearly demonstrated that the effect of Triton X-100 on the dispersion of MWCNTs in parallel with flexural properties of composite materials produced by using Triton X-100.

Keywords: Multi-walled Carbon Nanotubes, glass fibers, epoxy, spray method, direct mixing method, through thickness/out of plane/z-axis properties

KONVANSIYONEL DİREK KARIŞTIRMA VE YENİLİKÇİ SPREY METOTLARI İLE ÜRETİLEN KARBON NANOTÜPLER İLE KUVVETLENDİRİLMİŞ CAM FİBER KOMPOZİTLERİN EĞİLME VE FİZİKSEL ÖZELLİKLERİNİN KIYASLANMASI

ÖZ

Cam elyaflar kullanılarak üretilen kompozit malzemeler zayıf elyaf / matris ara yüzü nedeniyle önemli ölçüde düşük düzlem dışı / kalınlık yönü / z ekseni özellikleri göstermektedir. Bu zayıf ara faz, levhalar arası kayma mukavemeti, eğilme mukavemeti, katman ayrılma direnci vb. gibi z-ekseni özelliklerini doğrudan etkilemektedir. Bu çalışmada, Doğrudan Karıştırma ve Püskürtme üretim yöntemleri kullanılarak Çok Duvarlı Karbon Nanotüpler (ÇDKNler) ile takviye edilmiş Cam Elyaf ile kuvvetlendirilmiş Epoksi Matris Kompozitlerin (CKEK) kalınlık yönündeki özelliklerinin iyileştirilmesi amaçlanmıştır. Ayrıca, bazı kompozit üretim adımlarında karbon nanotüplerin daha homojen bir şekilde dağılması için yüzey aktif madde olarak Triton X-100 kullanılmıştır. Bu yöntemlerin kompozit malzemeler üzerindeki etkilerini görmek için Üç Nokta Eğme Testi, Shore D ve Vickers Sertlik testleri ve Taramalı Elektron Mikroskobu (SEM) Analizi yapılmıştır.

Yapılan çalışmalar neticesinde Triton X-100 yardımı ile Püskürtme Metodu ile üretilen kompozit malzemelerde en iyi eğilme mukavemeti ve eğilme modülü 411,309 MPa ve 20,186 GPa olarak elde edilmiştir. Ayrıca, eğilme mukavemeti ve eğilme modülündeki artışlar, kontrol numunesine kıyasla yaklaşık yüzde 5,33 ve yüzde 19,79'dur. Öte yandan, diğer yöntemlerle üretilen kompozit malzemelerin sonuçları, kontrol numunesine göre bükülme mukavemetinde azalma ve bükülme modülünde artış olduğunu göstermektedir. Shore D ve Vickers sertlik testi sonuçları, Doğrudan Karıştırma Metodu ve Püskürtme Metodu ile üretilen kompozit malzemelerin sertliğinin, kompozit yapıya ÇDKNler eklenmesiyle arttığını ortaya koymuştur. SEM analizi ile alınan görüntülerde, en iyi ÇDKN dağılımının Triton X-100 kullanılarak Sprey Metodu ile üretilen kompozit malzemelerden elde edildiğini ortaya koymuştur.

Anahtar Kelimeler: Çok Duvarlı Karbon Nanotüpler, cam fiberler, epoksi, sprey metot, doğrudan karıştırma metottu, kalınlık yönü/düzlem dışı/z-eksini özellikleri

CONTENTS

NOMENCLATURE

Symbols

n,m	Chiral Indexes
S/m	Siemens per meter
W/mK	Watts per meter-Kelvin
Ω.m	Ohm meter
in.	inch
E_H	Flexural Modulus
S_M	Flexural Strength
r_{max}	Deformation
L	Span
h	Thickness
Kgf	Kilogram-Force

Abbreviations

GPa	Gigapascal
MPa	Megapascal
mm	Millimeter
min.	Minutes
Rpm	Revolutions Per Minute

Acronyms

CNTs	Carbon Nanotubes
CKEK	Cam Elyaf Takviyeli Epoksi Matris Kompozit
ÇDKNler	Çok Duvarlı Karbon Nanotüpler
GFECs	Glass Fiber Reinforced Epoxy Matrix Composites
MWCNTs	Multi-walled Carbon Nanotubes
SEM	Scanning Electron Mixroscopy
TÜBİTAK SAGE	Türkiye Bilimsel ve Teknolojik Araştırma Kurumu Savunma Sanayii Araştırma ve Geliştirme Enstitüsü

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CHAPTER 1

INTRODUCTION

Composite materials have constituted a new scientific field for researchers, scientists and engineering industry with their high specific strength, high resistance to corrosion, low density compared to metallic materials and other important features in today's technology. Among the composite materials, fiber reinforced polymer matrix composite materials come to the forefront because of their high strength to weight ratio. Composite materials are composed of two distinct phases (see **Figure 1.1**). First phase is called as the matrix phase that holds the structure together and transfers the loads whereas the second phase is called as the reinforcement phase that is the load bearing structure of the composite materials [1-2].

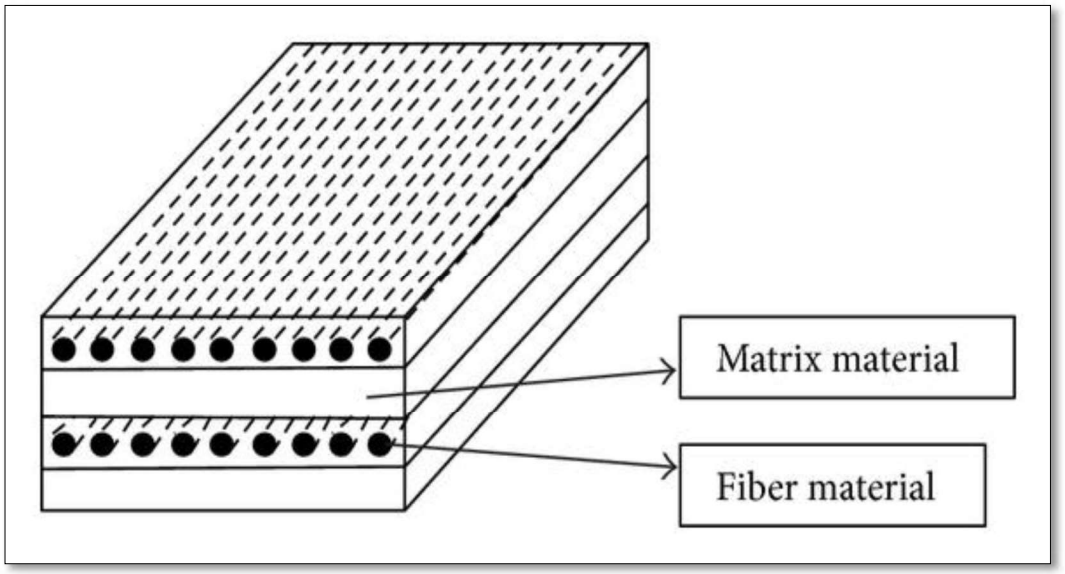

Figure 1.1 Schematic illustration of composite materials' phases [3].

Fiber glasses are one of the mostly used fiber reinforcement materials, because they show higher mechanical properties with lower density. Also, fiber glasses have low thermal conductivity with low coefficient of linear expansion compared to commonly used steels. The important characteristic of fiber glasses is their dramatically lower tensile modulus that lead to take more strain without breaking [4-5]. They can be used

in the applications where high strength, but lower stiffness i.e. lower Young's Modulus is required.

Thermosetting polymers are generally chosen for composite materials due to their relatively better mechanical characteristics. Epoxy is amongst one of the commonly used matrix materials. Although, epoxy is pricier than other thermosetting polymers, its performance to cost ratio makes epoxy the best candidate. Also, epoxy systems are compatible with most of the reinforcing fibers [1].

The phase between matrix and reinforcement is called as interphase. Interphase between matrix and reinforcement phases is significant to get desired properties with fiber reinforced polymer matrix composite materials, because this phase allows transferring incoming load to the reinforcement phase. When the better interfacial bonding between phases is achieved, better properties obtained from the composite materials [6].

Glass fiber reinforced epoxy composite materials show excellent in-plane mechanical properties, but out of plane/through thickness properties of these composites are significantly low due to weak fiber/matrix interphase. This weak interphase directly affects z-axis properties such as interlaminar shear strength, flexural strength, delamination resistance etc. To enhance interfacial bonding between two phases is common challenge in material science [7]. With the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [8], superior mechanical, electrical and thermal properties with high surface area make the CNTs one of the best candidates to enhance interphase properties of glass fiber/epoxy composite systems. CNTs offer better performance to composites than other methods such as z-pinning, stitching, braiding, coating, etc. because other methods can disrupt and damage the primary fibers and can reduce through thickness properties of composites [7,9-10].

Two main ways of grafting the CNTs onto glass fiber reinforced epoxy composite can be found in the literature: (a) attaching the CNTs onto fibers and, (b) direct mixing of CNTs with epoxy. In direct mixing of CNTs, ultrasonic mixer, high speed mixer or three ball milling are used to disperse CNTs into epoxy system. In attaching the CNTs onto fibers, direct growth of CNTs on fibers and, deposition or coating of CNTs on the

fibers are commonly used methods in the literature. In this study, I have used another method that is mentioned less in the literature as one of the methods of attaching the CNTs onto fibers. This method is called as spraying method.

In these two main ways to grafting CNTs to glass fiber reinforced epoxy matrix composite, main problem is the dispersion of CNTs into matrix or onto fibers. With well dispersed CNTs, desired characteristics can be obtained [7]. Dispersion of CNTs is another important challenge to produce composite materials. Because of high aspect ratio and Van der Walls bonds between CNTs, bundle like structure of CNTs is created that it can cause decrease in the desired properties. To disperse CNTs homogenously, two approaches can be mentioned: (a) chemical approach and, (b) mechanical (physical) approach. In mechanical approach, high shear force is applied to disperse CNTs into a matrix or solvent. In chemical approach, there are two pathways: (a) covalent modification and, (b) non-covalent modification [11-13]. In covalent modification, strong acids are used to get a homogenous dispersion with CNTs, but they can damage the structure of CNTs that directly affect mechanical, electrical and thermal properties, so, scientists turned to an alternative method which is non-covalent modifications. In this method, surfactants are commonly used to disperse CNTs into medium, because surfactants don't damage the structure of CNTs and don't reduce the desired properties. In recent years, researchers have started to combine both mechanical approach and chemical approach to take advantages of these two [12, 14-16].

1.1. Objectives of This Study

The current study aims several purposes. Main purpose of this work is to strengthen interphase bonding between glass fiber and epoxy to enhance through thickness properties of glass fiber reinforced epoxy matrix composites (GFECs) by grafting Multi-Walled Carbon Nanotubes (MWCNTs). Also, in the current work, two different methods to graft CNTs have been used to produce GFECs. In the first method, MWCNTs have been directly mixed with epoxy system by using ultrasonic mixer. In the other method, a novel approach has been proposed and realized in which MWCNTs have attached onto glass fibers by using spray method. Another aim is to see effects of

production methods into through thickness properties of GFECs. In addition, MWCNTs have been functionalized with non-ionic surfactant and, it is also targeted with this process to see the effects of surfactants on the dispersion of MWCNTs and the through thickness properties of GFECs.

1.2. Outline of the Thesis

This thesis has been organized as follows. Chapter 2 gives general information of literature review that about fiber reinforced polymer composites, dispersion and functionalization of carbon nanoparticles, production ways of CNTs added fiber reinforced polymer composites. Methodology has been followed in this study given in Chapter 3. Experimental procedure, results and discussions are given in Chapter 4 and Chapter 5. Also, conclusions of this study and future works are given in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1. Fiber Reinforced Polymer Matrix Composites

The demand for high strength to weight ratio has been gaining attention in several areas especially in weight critical sectors such as aerospace. Due to the superior properties in terms of light weightiness, high strength, easy manufacturability and formability, corrosion resistance, etc., fiber-reinforced polymer matrix composite materials have gained great importance in terms of material science, and the interest in this new field has continued to grow gradually over the last forty years in the entire engineering industry [17-18].

Polymer matrix composite materials consist of three different phases: (a) reinforcement phase, (b) matrix phase and (c) phase between matrix and reinforcement called as interphase. All these phases show their unique properties in composite structure. Fibers act as reinforcement phase due to their high mechanical properties. Also, the task of the reinforcing phase is to protect the composite material against deformations by resisting external loads. Polymeric materials are used as matrix phase in composite materials and they transfer the load coming from outside to reinforcement phase and distribute the stresses over the entire area. Also, this phase covers the fibers to hold them together and to protect fibers from environmental effects. The interphase between matrix and reinforcement controls the load transfer between these two and directly affect mechanical properties of composite materials [6].

Glass fibers are one of the most important fibers used as reinforcement for all polymer matrix composites, and they are commonly used as reinforcement phase in the industry. Their outstanding properties in terms of excellent impact resistance, high strength to weight ratios and high corrosion resistance make the glass fibers one of the most significant candidates. There are six types of glass fibers that are E (electrical), S (strength), C (chemical), M (modulus), A (alkali) and D (dielectric). These fibers are classified under two main groups: (a) general purpose glass fiber (E) and (b) special-

purpose glass fibers (S, C, M, A and D) [19-21]. Properties of most commonly used classes are given in **Table 2.1** [21].

Table 2.1 Properties of Different Glass Fibers [19], [21]

Properties	**E-Glass**	**S-Glass**
Tensile Strength (GPa)	3.5	4.6
Elastic Modulus (GPa)	73.5	86.8
Elongation (%)	4.8	5.4
Density (g/cc)	2.57	2.46

Thermosetting resins are commonly used matrix materials in fiber reinforced composite materials because their mechanical properties and thermal resistivity are better than that of thermoplastic resins. Epoxy resins are one of the best candidates among thermosetting polymers because although they are more expensive than other thermosetting polymers, they show better mechanical strength and higher resistance to moisture and corrosion. Also, they interact very well with other substrate and additives (e.g. metal or plastic or fibers or nanoparticles). In addition to these properties, epoxy resins are consonant with the manufacturing techniques of composites (e.g. vacuum bagging, hand lay-up, etc.). Mechanical properties of epoxy resin are given in **Table 2.2** [22].

Table 2.2 Mechanical Properties of Epoxy Resin [22].

Properties	**Values**
Tensile strength (MPa)	28–91
Young modulus (GPa)	2.4–4.5
Elongation at break (%)	2–6
Poisson's ratio	0.29–0.34
Izod impact strength (J/m^2)	10–50
Hardness Rockwell M	100–112

Load transfer capability of composite materials from matrix phase to reinforcement phase is the key factor to reach desired properties and, based on interphase between these two phases [6]. The results of conducted study on modification of fiber/matrix systems demonstrated that fiber and matrix phases are not only important parameters to determine properties of composite materials, but also interphase between them plays a significant role to get desired properties [23]. Interphase is defined by Reifsnider [23] as " *the region that is formed as a results of the bonding between fiber and matrix which has significantly distinct morphology or chemical composition compared with fiber or matrix material."* Also, the mechanical interlocking, chemical bonds and physical adhesion between matrix and reinforcement phases are significant factors that affect interfacial bonding [17, 24].

Fiber reinforced laminated composites demonstrate high in-plane properties along the fiber direction. But there is an important challenge with fiber reinforced polymer matrix composites, this is fiber/matrix interface that is the weakest part of these composites. The fiber/matrix interface directly affects the through thickness/out of plane/z-axis/transverse direction properties of composites. This is because of the manufacturing techniques to produce fibers are not enough to orient reinforcing fibers

in the z-axis. This situation is limiting the properties of fiber composites, such as interlaminar shear strength (ILSS), flexural strength, stiffness, fatigue strength, against loads that applied through thickness direction [25]–[29]. So, it is important to enhance the fiber/matrix interphase to reach maximum mechanical strengths. In the past years, researchers have studied on many various techniques to improve interfacial adhesion between glass fiber and polymer matrix. These techniques are coating/sizing, electrodeposition, plasma treatment, acid-base etching, coupling agent and, z-pinning and stitching fibers. All these techniques have some disadvantages like damaging the fibers, manufacturing complexity and cost [17, 25, 30-34]. In recent years, these drawbacks have drawn the attention of researchers to use carbon nanoparticles in order to enhance interface between glass fiber and polymer matrix. Carbon nanotubes (CNTs) are one of the significant candidates due to their excellent mechanical, electrical and thermal properties. Also, CNTs have high surface area. When CNTs are used as additive into glass fiber reinforced polymer matrix composites, they enhance the surface roughness of fibers that is one of the key factors to improve fiber/ matrix interphase. As a result of surface modification with nanoparticles, interfacial contact between fiber and matrix is improved and also, higher bond strength is achieved with mechanical interlocking [33, 35-36]. In the literature, many studies were conducted by researchers to demonstrate the effect of CNTs on interface between not only glass fiber and polymer matrix but also carbon fiber and polymer matrix phases. In 2019, Panchagnula et al. [37] studied effect of multi-walled CNTs (MWCNTs) on glass fiber reinforced polymers (GFRP). The results of this study showed that nearly 39.41% increases in the flexural strength of MWCNTs grafted GFRP composites observed with addition of 0.3% MWCNT to neat epoxy that improved interfacial adhesion between glass fiber and matrix. Also, another study on the improvement of interfacial strength of glass fiber reinforced polyphenylene sulfide composites with grafting MWCNTs, was conducted by Li et al. [31]. According to the results of this study, it was demonstrated that with the addition of MWCNTs to the composite materials enhance was observed in interface by improving the contact area between the glass fiber and matrix, and bending strength of composite material increased from 67 MPa to 85 MPa. In addition, study conducted by Awan [32] showed the effects of CNTs on the interfacial properties of carbon fiber reinforced polymer matrix composite. As a

result of the study, presence of the MWCNTs enhanced the fiber roughness that improve mechanical bonding between fibers and matrix phase and significant improvements were seen in the interlaminar shear strength (improvement up to rises of 18%) and flexural strength (improvement up to rises of 15%).

In order to enhance properties of glass fiber reinforced polymeric matrix composites with addition of CNTs, there are two critical pathways (see **Figure 2.1**) to produce CNTs grafting fiber reinforced polymeric composites: (a) dispersing CNTs into matrix phase or (b) adding CNTs onto fibers that are reinforcement phase [7, 38].

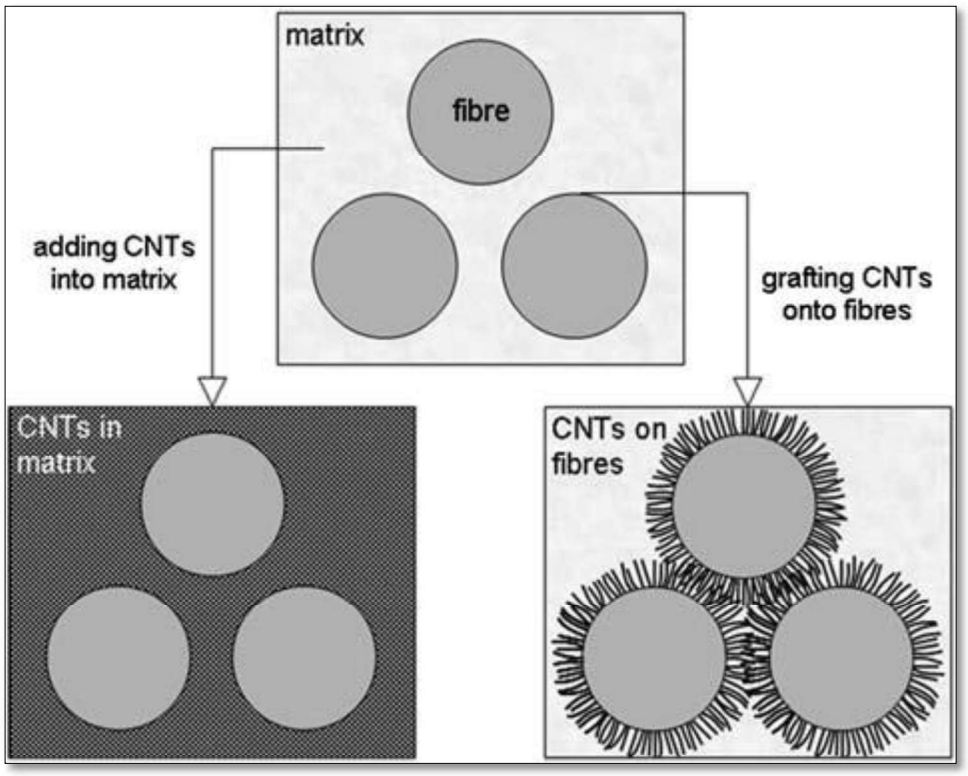

Figure 2.1 Schematic demonstration of two routes for producing CNTs grafting fiber reinforced polymer matrix composites [7].

Directly mixing CNTs into matrix phase is the most ordinary process to modify matrix phase of fiber reinforced composites. This method is commonly used in industry due to primitiveness and conformality with industrial techniques. To disperse CNTs into the matrix phase, different techniques are used such as ultrasonic method, shear mixing and ball milling. The main challenges in these methods are to prevent agglomeration

of CNTs and homogenously distribution of them that can decrease matrix phase performance, so this situation directly affects composite materials performance. When CNTs cannot be dispersed well into the matrix, they can act as pathway for crack propagation. To overcome these problems, CNTs should be functionalized chemically. Surfactants are commonly used chemicals to overcome agglomeration problem between CNT bundles. Also, another limitation in these techniques is their relatively low loading fraction, because after specific volume content addition of CNTs, properties of matrix phase starts to decrease, and the viscosity of matrix increases that affects the workability. So, loading fraction should be kept optimum. To impregnate CNTs grafting matrix phase to fibers, there are several methods: (a) resin transfer molding (RTM), (b) vacuum-assisted resin transfer molding and (c) hand-layup method. Among these methods, the hand-layup method is the most preferred technique because it is easily applicable [7].

Other manufacturing process is grating CNTs onto fibers. There are some important differences between two important routes. Impregnation of epoxy system with CNTs by mixing can lead CNTs align parallel to fibers which makes this orientation less effective to enhance z-axis properties of composite materials. On the other hand, grafting CNTs onto fiber surfaces provides higher loading of CNTs and radial orientation that is the desired orientation to enhance through thickness properties. To graft CNTs onto fibers, different techniques are used: (a) direct growth of CNTs on fibers, and, (b) deposition or coating that involves electrophoretic deposition (EPD), coating of fibers [7, 32, 38-42]. In the recent years, an alternative technique to attach CNTs to fiber surface was reported by Davis and Whelan in 2011 [43]. The technique was spraying of CNTs on fiber surfaces via suitable solvent. Davis and Whelan used this technique to attach CNTs onto carbon fabric in order to enhance through thickness properties of composite materials. After this publication, in 2012, Mujika et al. [44] used spraying method to disperse CNTs onto fiber surface. The results of the study showed an increase of 22 % in the initiation fracture toughness according to the value observed in the neat sample. Also, Shan et al. [45] used spraying technique in their studies to improve interlaminar properties of carbon fiber-reinforced epoxy composites with grafting of CNTs. In the conducted study, it is concluded that the spraying technique is effective, simple and inexpensive method to attach CNTs onto

fiber surface and, this method can easily applicable to the industry [43-45]. Also, spraying method eliminates viscosity problem of matrix with addition of CNTs. But, controlling dispersion of CNTs onto fiber surface is the main challenge in this method. So, CNTs should be functionalized to prevent agglomeration problem [45].

2.2. Carbon Nanotubes (CNTs)

Nowadays, as the dependence on technology increases, the importance of material science is getting stronger. In addition, materials science has begun to play an important role in the development of technology. To meet the demands of technology, the relationship between structures and properties of materials should be well understood. The greatest demand in the technology is high strength to weight ratio. In that point, nanotechnology has become the most important part of composite science, because addition of nanofillers can dramatically improve mechanical, thermal and electrical properties of composite materials. Carbon nanotubes (CNTs) that have excited the attention of many scientists are regarded one of the important nanofillers due to their excellent mechanical, thermal and electronical properties [46-48].

2.2.1. History of Carbon Nanotubes

Before the transmission electron microscope (TEM) was discovered by Knoll and Ruska in 1931, it was not possible to see nano size particles. With the discovery of TEM, this obstacle was removed, and important steps were taken in the field of nanotechnology and nano scale carbon structure has been detected by different group of scientists [49]. With Sumio Iijima's [8] discovery of carbon nanotubes in 1991, a new branch of knowledge has emerged for nanoscience and this discovery was made with the help of TEM [50]. SWCNTs were firstly mentioned in two different papers published by journal Nature, a work by Iijima [51] and by Bethune et al [52].

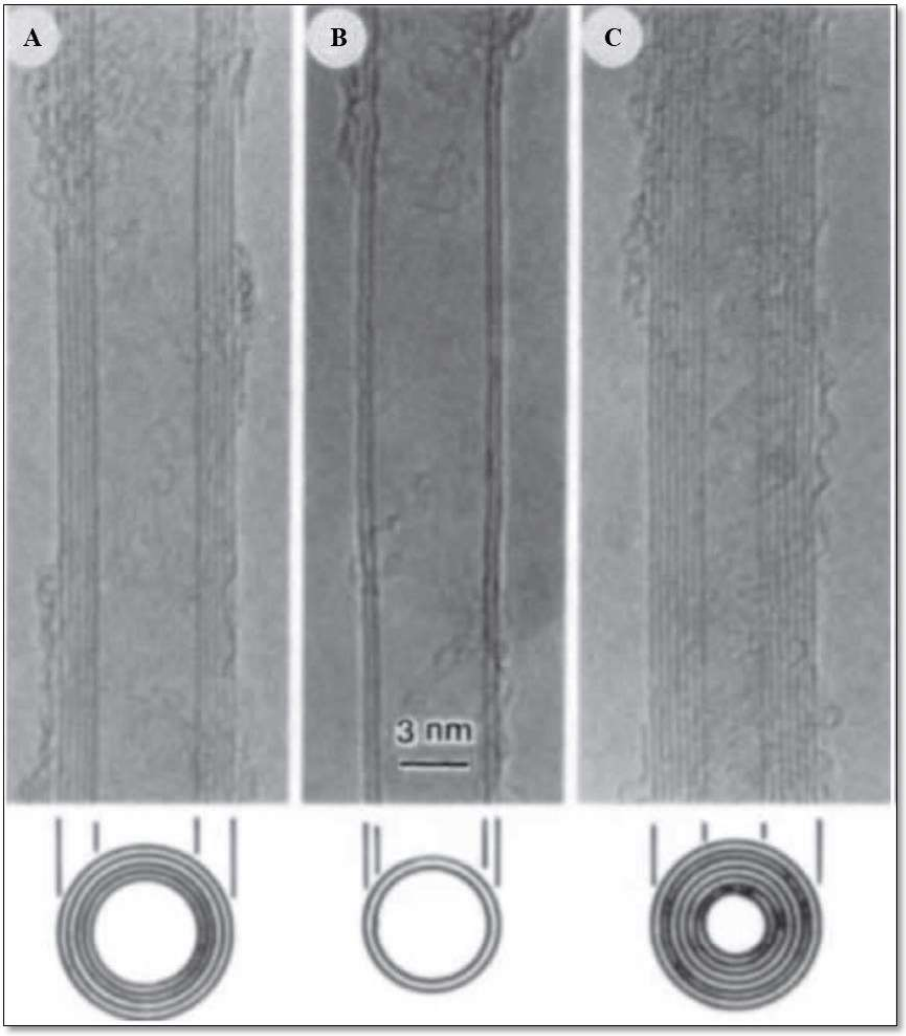

Figure 2.2 Transmission electron microscope image of multi-walled carbon nanotubes with different number of layers: (A) five, (B) two, and (C) seven concentric layers of graphene [53].

Iijima in 1991, used to an electron microscope to see high-resolution images of CNTs that illustrated in **Figure 2.2** [47].

2.2.2. Structure of Carbon Nanotubes

Carbon nanotubes are one dimensional structures and they can be obtained by rolling up of graphene in tubular or cylindrical form. Also, CNTs can be classified into three basic categories (see **Figure 2.3**): (1) Single-Walled Carbon Nanotubes (SWCNTs), (2) Double-Walled Carbon Nanotubes (DWCNTs) and (3) Multi-Walled Carbon Nanotubes (MWCNTs) [54].

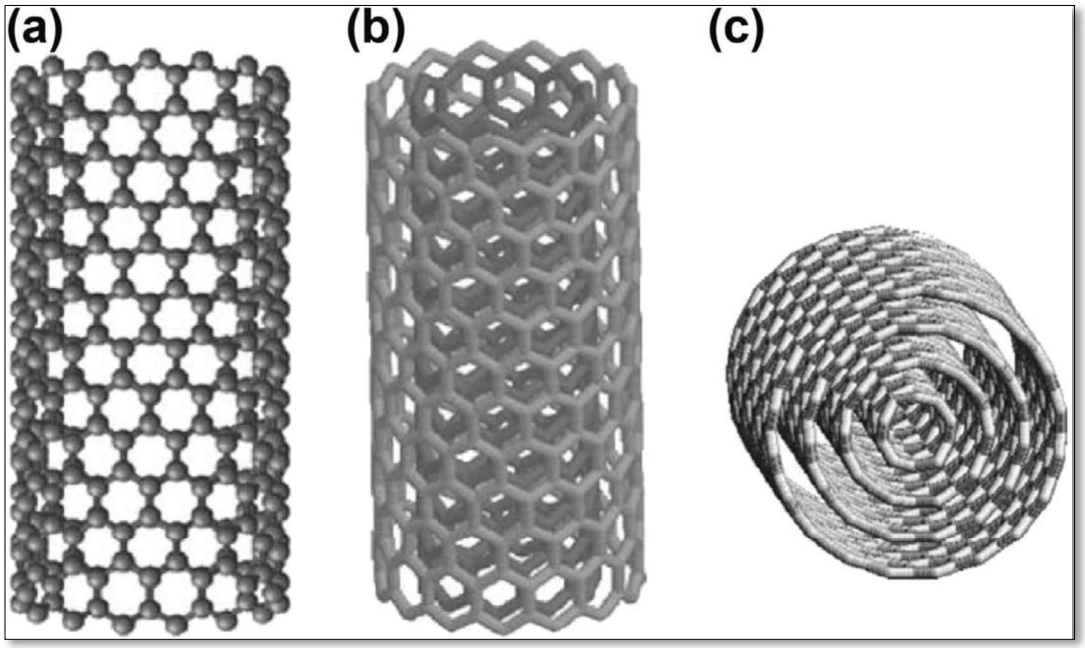

Figure 2.3 Schematic diagram of a (A) single-walled carbon nanotube, (B) double-walled carbon nanotube, and (C) multi-walled carbon nanotube [47].

Carbon nanotubes are structures coming from fullerene family and one allotrope types of a carbon atoms. Sp^2 hybridized bonds are found in chemical bonding of carbon nanotubes that are similar to the chemical bonds of graphene. These bonds show stronger characteristic than the sp^3 bonds that are found in diamond, also supply excellent strength to carbon nanotubes [49, 55-56]. Also, only weak Van der Waals interaction allows to hold all layers of MWCNTs together, this attraction leads to forms agglomeration between form of bundles. The spacing between bundles is similar that given by graphene sheet: 0.34 nm. Also, the spacing in a bundle is related to chirality [47]. The atomic structure of CNTs determines the type of CNTs that can be metallic or semiconducting [46].

To characterize the structure of CNTs, it is necessary to understand their atomic structure. There is correlation between atomic structure of CNTs and atomic structure of graphene, because CNTs are formed by rolling up of two-dimensional (2D) honeycomb lattice structure of graphene sheet given in **Figure 2.4**. Chiral vector, $\mathbf{C}_h$, and chiral angle, $\boldsymbol{\theta}$, are used to define the atomic structure of the CNTs [47, 56]. The relationship is given in Equation 2.1 below [49].

$$C_h = na_1 + ma_2 \quad \textbf{(2.1)}$$

The angle between the vectors $\mathbf{C}_h$ and $\mathbf{a}_1$ define the chiral angle, θ, that determines the degree of "twisting" of the CNTs. The range of chiral angle varies from 0° and 30° [49].

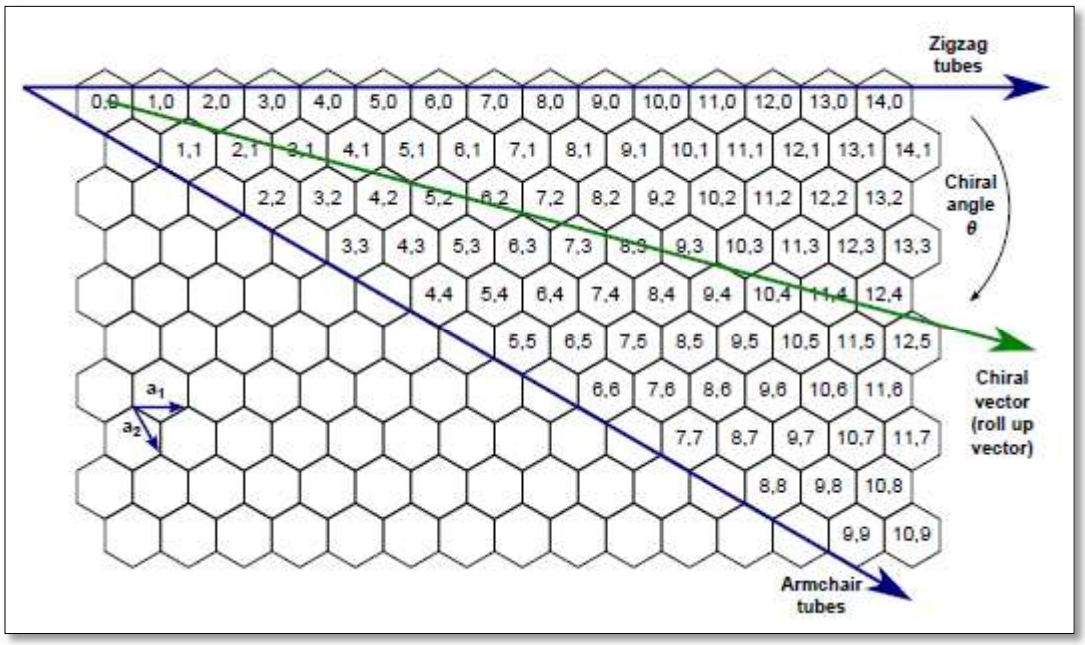

Figure 2.4 Schematic diagram of honeycomb structure of graphene is rolled to form a carbon nanotube [47].

CNTs can be classified by using chiral indices (*n, m*) (see **Figure 2.5**) [47, 49].

- m = 0, zigzag nanotubes, spacing is 0.339 nm,
- n = m, armchair nanotubes, spacing is 0.338-0.341 nm,
- Others called as chiral.

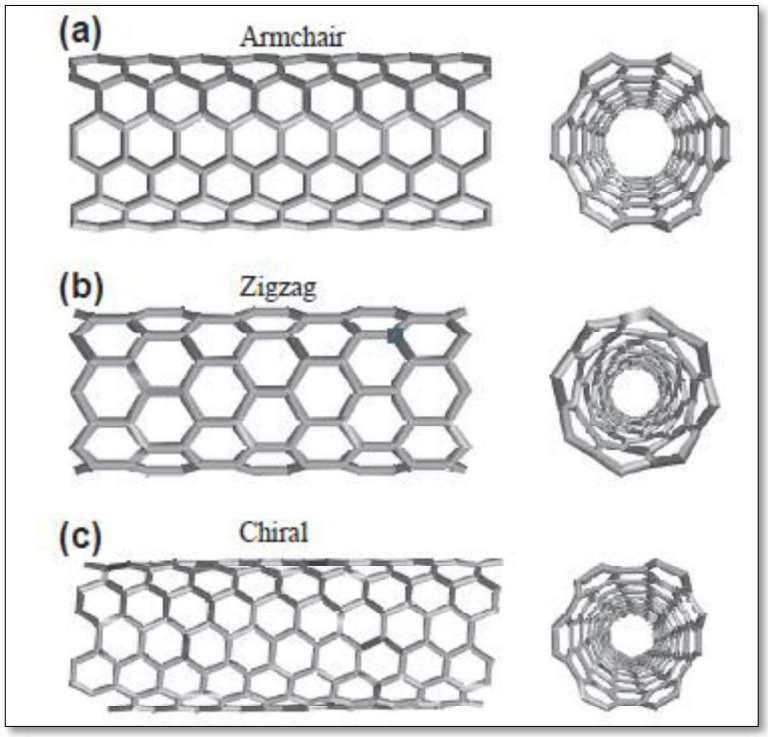

Figure 2.5 Schematic model of types of CNTs: (A) an armchair, (B) zigzag, and (C) chiral nanotubes [47].

2.2.3. Mechanical Properties of Carbon Nanotubes

CNTs are known as one of the strongest and stiffest materials discovered by material scientists up to date. These excellent and unique properties are coming from bonds between carbon atoms, sp^2 bonds are one of the strongest bonds in nature [47, 49]. It is known that the strength of carbon nanotubes is 100 times higher than the steels at the molecular level within the framework of the studies conducted [50]. **Table 2.3** given below shows the comparison of CNTs with other materials in terms of mechanical properties and densities.

Table 2.3 Comparison table of CNTs with other materials in terms of mechanical properties [47].

Material	ρ (g/cm^3)	E (GPa)	σ_m (GPa)	ε (%)
SWCNTs	1.33	1054	150	12
MWCNTs	2.6	1200	150	12
Carbon Fiber	1.93	588	3.82	0.7
S Type Glass Fiber	2.48	86	4.58	5.4
Kevlar 49	1.44	112	3	2.4
Aluminum 2219-T87	2.83	73	0.46	10
Steel 17-7 PH	7.65	204	1.38	6
Epoxy	1.25	3.5	0.005	4
ρ: Density, E: Young's Modulus, σ_m: Maximum Resistance, ε: Elongation at Break				

It can clearly be seen on the table that CNTs are materials with combination of high strength and low density. These properties make the CNTs one of the most crucial materials for applications that need high strength to weight ratio [47].

Amit Kumar et al. [54] worked on carbon nanotube and graphene-reinforced multiphase polymeric composites and they published a review paper in 2019. According to their study on the other papers related to carbon nanotubes, M. M. J. Treacy et al. [57] firstly calculated Young's modulus of CNTs experimentally as 1.8 ± TPa by using the thermal vibration method. Yu et al. [58] worked on Young's modulus and tensile strength of SWCNTs and they obtained tensile strength and Young's modulus values of SWCNTs: ranging from 0.27 to 0.9 TPa and 11 to 63 GPa.

Also, Yu et al. used scanning electron microscope (SEM) to investigate behavior of SWCNTs and MWCNTs under applied tension (see **Figure 2.6**).

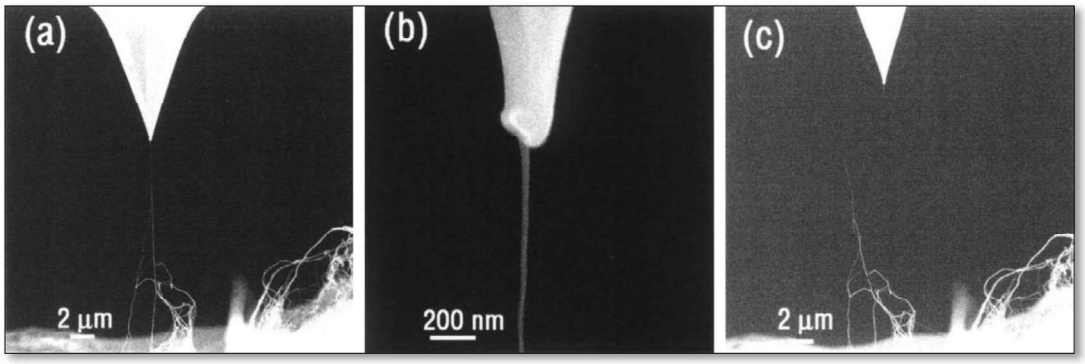

Figure 2.6 Schematic SEM images (A) tension applied to carbon nanotubes (CNTs) by the probe of an atomic force microscope, (B) shows interaction of the tip of probe microscope with the CNTs and (C) before breaking of CNTs bundles [58].

To get mechanical properties given above by using CNTs is a challenging issue. It is known that CNTs are used to improve mechanical, electrical and thermal properties of composite materials. However, these improvements are based on the distribution of CNTs, because their weak Van der Waals interaction between layers can cause aggregation in medium that affects the load transfer from outer layers to internal layers [47].

2.2.4. Electrical and Thermal Properties of Carbon Nanotubes

The electrical properties of CNTs depend on their unique one-dimensional (1D) structure and chirality (see **Figure 2.7**). Chiral vector related to chiral indexes (n,m) determine whether CNTs are conductive (metallic) or semi-conductive. When the integers (n,m), are equal (n = m) or when n – m or m – n are multiples of 3, carbon nanotubes are metallic (conductive), also, all armchair nanotubes show conductive electrical property, because | n – m | = 0. For all other situations, carbon nanotubes are semiconductor [47].

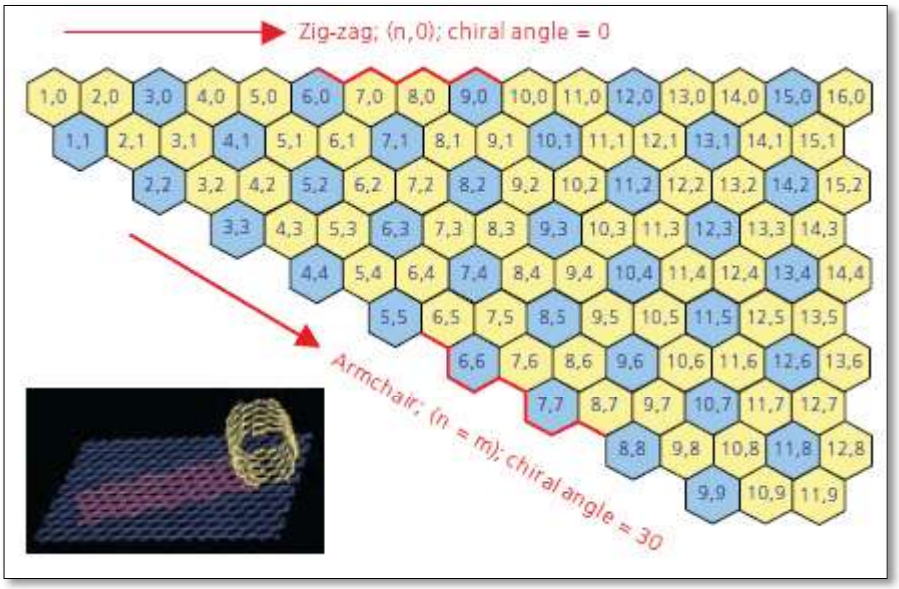

Figure 2.7 Schematic illustration of chirality cases for electrical properties [59].

One dimensional (1D) structure of CNTs directly affects electron motion where electrons move only one path, also this situation decreases the electron scattering. Because of all these circumstances, the electrical resistance of CNTs is relatively low and these properties make the CNTs best candidates for high current applications [47]. Also, comparison table of electrical conductivity of CNTs with different materials is given in **Table 2.4**.

Table 2.4 Comparison table of electrical conductivity of CNTs with different materials [47].

Material	**σ (S/m)**
CNT	10^6-10^7
Copper	6 x 10^7
Silver	6.3 x 10^7
Iron	1.00 x 10^7

Material	σ (S/m)
Glass Fiber	10^{-14}
Carbon Fiber - Pitch	2-8.5 x 10^{6}
Carbon Fiber - PAN	6.5-14 x 10^{6}
Epoxy	10^{-8}

In studies, effects of CNTs on electrical properties of composite materials have been investigated by several researchers. Jyoti et al. [48] dispersed different wt.% MWCNTs in acrylonitrile butadiene styrene (ABS) to see the effect of CNTs on electrical properties of composite material. The results given in **Figure 2.8** showed that they obtained improvement of up to ~7 orders of magnitude on electrical properties that increased from 10^{-12} to 10^{-5} S/cm.

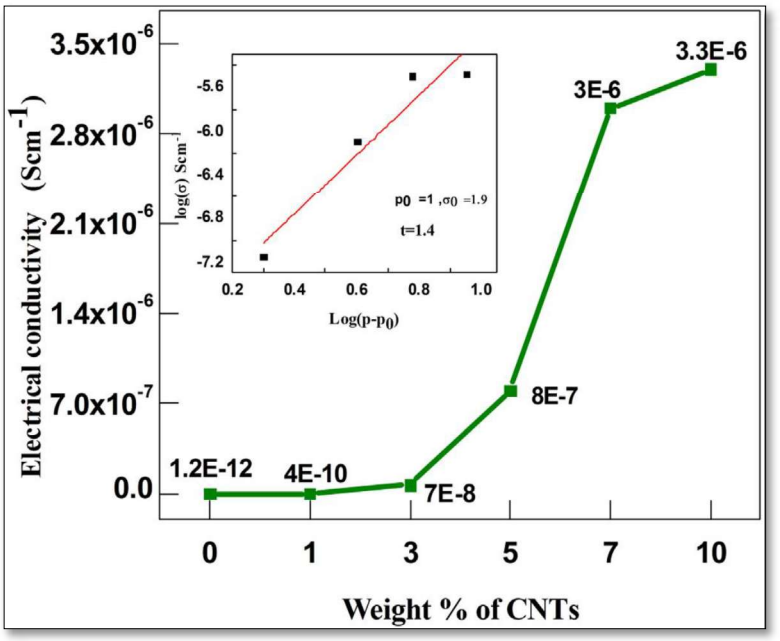

Figure 2.8 Electrical conductivity of CNTs doped composites [48].

Zhou et al. worked on electrical properties of MWCNTs reinforced epoxy composites. They mixed different wt.% CNTs with epoxy and evaluated their electrical properties. According to test results, MWCNTs improved the electrical conductivity of epoxy and decreased the resistivity of epoxy from 10^{14} Ω.m of neat epoxy down to 10 Ω.m with CNT addition [60].

CNTs show superior thermal properties beside the mechanical and electrical properties. After the discovery of carbon nanotubes, diamond was known as the best conductor in material science and CNTs became the one of the significant candidate nanomaterial for thermal applications. The thermal conductivity of diamond is known as half of the thermal conductivity of CNTs. Phonons determine the thermal conductivity and specific heat properties of CNTs as in solids [47]. Also, thermal properties of CNTs depend on their diameter and length. In MWCNTs, interaction of phonons with multi-walled layers determine thermal conductivity, so the thermal conductivity of SWCNTs is expected to be much higher [61]. The study conducted by Fujii et al. [62] shows that the thermal conductivity at room temperature related to diameter of CNTs decreases as the thermal conductivity increases. Park et al. [63] worked on differences between thermal conductivity of long MWCNTs/epoxy composite and short MWCNTs/epoxy composite. Results show that long MWCNTs exhibit better thermal conductivity than that of short MWCNTs. These results show the importance of diameter and length of CNTs on thermal properties. Comparison table of CNTs in terms of thermal conductivity with other materials is given in **Table 2.5**.

Table 2.5 Comparison table of CNTs with other materials [47].

Material	K (W/mK)
SWCNTs	>3000
Graphite	>3000
Aluminum 2219-T87	120

Material	K (W/mK)
Copper	400
Silver	420
Iron	80
Glass Fiber	0.046 – 1.13
Carbon Fiber K1352U	140
Epoxy	0.12

Theoretical thermal conductivity of CNTs has been calculated in the studies. The theoretical conductivity of CNTs is over 3000 W/m K and also obtained thermal conductivity of SWCNTs in axial direction can reach 6000 W/mK [47, 63-65].

In many conducted studies by researchers show the effect of CNTs on thermal properties. Chen et al. [66] conducted their studies to understand the effect of SWCNTs on thermal expansion behavior of polymer nanocomposites doped with SWCNTs. Obtained results in this study show that SWCNTs are one of the best candidates to reduce thermal expansion coefficient of polymer nanocomposites.

2.3. Dispersion of Carbon Nanotubes

It is known that CNTs are candidate nanomaterials for applications in industry because of their excellent mechanical, thermal and electrical properties. But to get these unique properties, uniform and stable dispersion of CNTs are inevitable. These are critical necessity because how to change the surface properties of nano-sized particles is a challenging issue to get desired properties. Aggregation problem of CNTs is the challenging issue in the researches [67].

Agglomeration problem of CNTs comes from their high aspect ratio and Van der Waals bonds (it is reported [68] that interaction energy is 500 eV per micrometer of tube-tube contact). These are the reasons of entanglement and bundling of CNTs. Bundle-like structures of CNTs (see **Figure 2.9**) cause low solubility in water or organic solvents [11], [69].

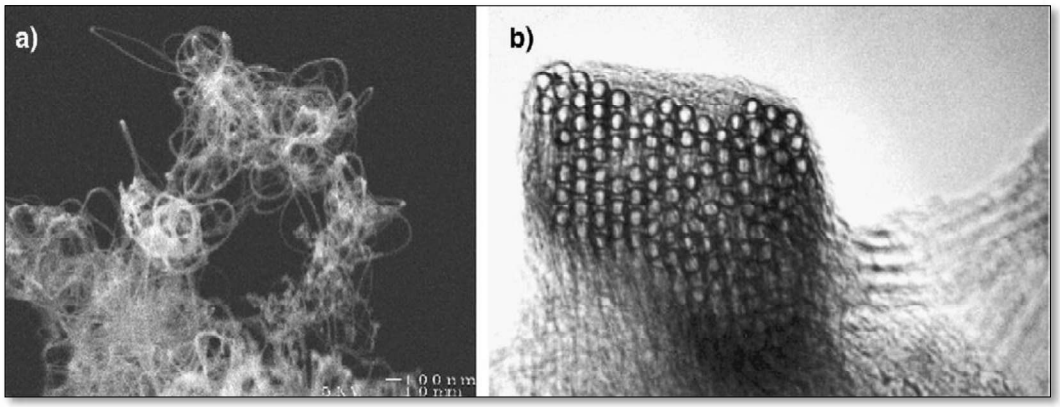

Figure 2.9 (a) a SWNT bundles from SEM image; (b) the cross section of a SWNT bundle from TEM [14].

Aforementioned reasons are obstacles to get excellent mechanical, electrical and thermal properties. Vaisman et al. [14] mentioned that bundle-like structure of CNTs can act as crack initiators and decrease mechanical properties, especially elasticity. To overcome these problems, three significant conditions must be supplied [11, 14, 69]:

- Remove entanglement,
- Destroy agglomerates, and,
- Disperse CNTs stabilized.

The agglomeration problem for CNTs is still up to date and challenging issue for scientists who are trying to find the best solution to distribute CNTs uniformly and prevent agglomeration problem. Rubel et al. [70] published a review paper on carbon nanotubes agglomeration in reinforced composites and they reached the following important conclusions:

- Different dispersion methods were used in literature and these methods can decrease agglomeration problem and contamination can improve re-agglomeration,
- Agglomeration/bundling is caused by Van der Walls force between tubes, directly affects the desired CNTs' properties, because the clusters prevent the transfer of load coming from outside among the grains,
- Also, after addition of maximum weight percentage, the tendency to create cluster is rising.

Jyoti et al. [48] showed that rising CNTs content reaching a threshold value reduces the mechanical properties of composite material due to agglomeration of CNTs. They dispersed MWCNTs into acrylonitrile butadiene styrene (ABS) and applied mechanical characterization to samples. Their results showed that ultimate tensile strength (UTS) is rising up to 70 MPa with an addition of 3 wt.% MWCNTs. But with increasing MWCNTs (5 wt%) content reduces the UTS to 68 MPa and with 10 wt% addition to ABS, UTS dramatically decreases to 57 MPa.

Another research conducted by Li et al. [71] shows decreasing inter-laminar shear strength of CNT reinforced carbon/carbon composites after a threshold value. They prepared composite materials with four different proportions and characterized flexural properties. Results shows that maximum flexural strength value was reached with 1.2 wt.% of CNTs and the flexural strength was obtained as 67.7 MPa. With these results, maximum 23 % increase was observed from flexural strength of neat C/C composite. With increasing CNTs content up to 1.5 wt.%, flexural strength decreased down to in 66.4 MPa.

Two keyways to enhance mechanical, electrical or thermal properties of composite materials doped with CNTs are (a) uniform distribution of CNTs into matrix phase and (b) effective nanotubes and matrix interaction [12]. In studies conducted on CNTs, many different approaches have been developed by scientists to overcome these problems and to get desired properties. These approaches given in **Figure 2.10** can be classified as (a) physical (mechanical) approach and (b) chemical approach [11-13].

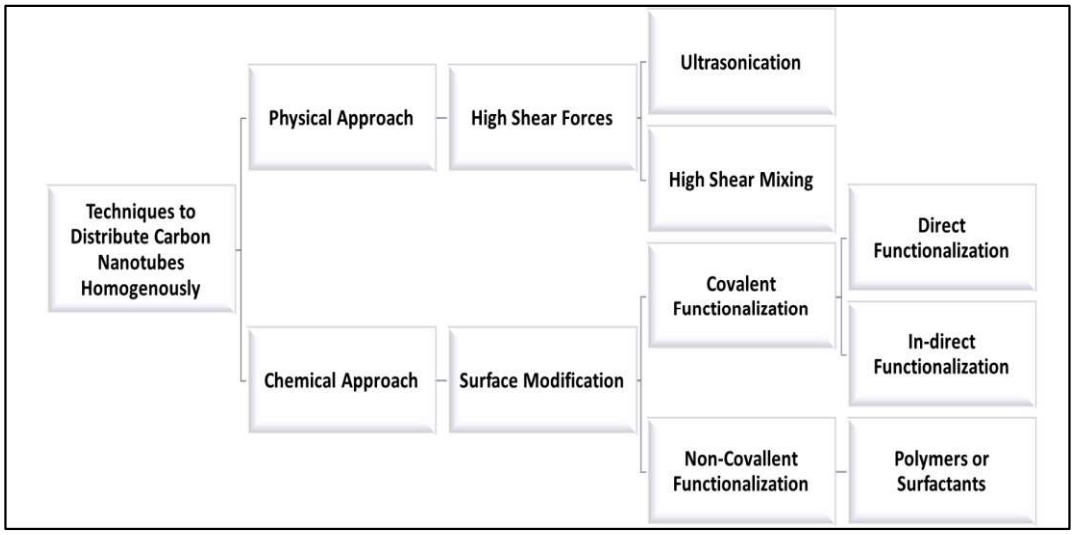

Figure 2.10 Nanofluid Stability Techniques.

2.3.1. Physical (Mechanical) Approach

Physical or mechanical treatments are effective ways to break the binding energy that holds the nanotubes together and to create agglomerates. Ultrasonication and high shear mixing are commonly used methods to obtain desired properties [11-12, 15, 72]. These methods generate local forces on nanotube clusters to deform tube-tube bonds. Critical point in these approaches is such that applied mechanical energy from chosen technique should be higher than the energy of bonds that holds CNTs together [72].

One of the most used mechanical technique is shear mixing method. In this method, high shear forces are generated with dual rotation of the CNTs to disperse CNTs uniformly and to get de-agglomeration of nanotubes clusters in matrix phase [73]. Huang et al. [74] worked on dispersion of MWCNTs in a polymer matrix. They added different weight fractions of MWCNTs to polymer matrix and used a shear mixer to disperse nanotubes. The results of study demonstrated that nanotubes were well dispersed in polymer matrix by using shear mixer.

Ultrasonic dispersion is another important technique used in nanoscience to disperse CNTs. Ultrasonication produces high energy ultrasonic waves in medium to generate shear forces. Once, it is used to disperse and break the CNTs clusters, length of CNTs are shortened and their aspect ratio is decreased. But it is concluded from conducted

studies that ultrasonication is not enough alone to disperse nano particles. To get better homogeneity, it is better the combined this technique with surface modifiers (surfactant etc.) [11, 15, 75]. Sadri et al. [76] worked on the effects of ultrasonication on the thermal conductivity of CNTs added nanofluids. They used ultrasonic waves to prepare nanofluid and in order to break up aggregates in the nanofluid. They concluded that length of carbon nanoparticles has been decreased and CNTs bundles have been broken with sonication. The TEM images (see **Figure 2.11**) demonstrated that aggregate sizes were reduced with short time sonication.

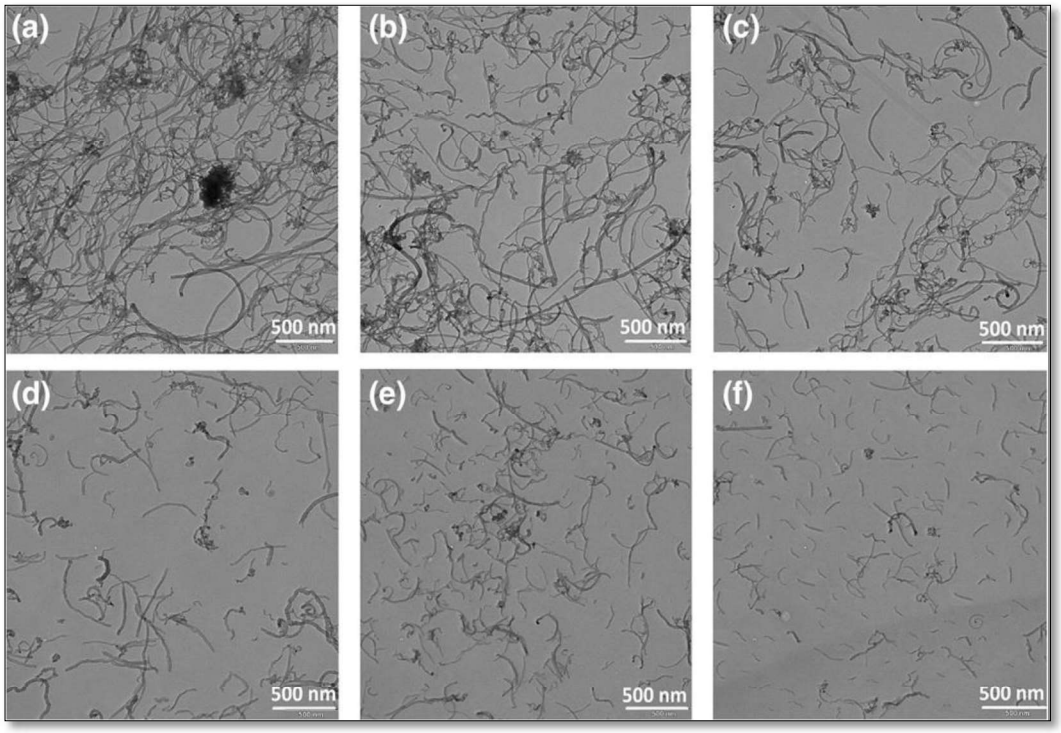

Figure 2.11 TEM images of dispersed MWCNTs in nanofluid via ultrasonication at various times, (A) 2 min. (B) 7 min. (C) 10 min. (D) 20 min. (E) 30 min. and (F) 40 min [76].

Also, Garg et al. [77] studied on the effect of ultrasonication on viscosity and heat transfer performance of MWCNTs. They prepared four aqueous nanofluids samples with 1 wt.% MWCNTs by using ultrasonic waves. They concluded in their studies that better dispersion was observed at the optimum processing time. When ultrasonication reached the optimum processing time, length and aspect ratio of CNTs are reduced, and, viscosity of mixture is increased. Ultrasonication power is as significant as

processing time for dispersion of CNTs. The applied powers have to be enough to break Van der Walls bonds to get stability [15].

2.3.2. Chemical Approach

Although chemical functionalization is one of the important techniques used to ensure homogeneous dispersion of carbon nanotubes. The method is also one of the major challenges in nanotechnology. Also, surface modification of CNTs plays critical role to obtain desired characteristics. This method modifies the surface of CNTs and improve wetting characteristics to decrease tendency to generate CNTs clusters. This approach is applied under two main different ways: covalent and non-covalent functionalization [11, 14, 15, 78].

To eliminate problems coming from heavily entangled bundles of CNTs, surface modification of nanoparticles has begun to be widely used. One of the surface modification method is the covalent functionalization method. In this method, functional groups are covalently bonded carbon atoms of CNTs. Covalent functionalization can be divided into two: (a) direct functionalization and (b) indirect functionalization. Fluorine was used firstly for direct covalent sidewall functionalization where sp^2 bonds of CNTs are converted to sp^3 bonds. These functionalized fluorine atoms can be converted by amino, alkyl, and hydroxyl groups. Indirect functionalization method is indirect covalent treatment. In indirect functionalization, strong acids such as HNO_3, H_2SO_4 or a mixture of them are used to create defects on the side walls or end caps of CNTs with oxidative damage. These methods can improve dispersibility of CNTs in matrix phases and decrease tendency to create bundles. However, there are some important disadvantages of these methods: (a) length of CNTs are shorten, (b) as a result of changing from sp^2 to sp^3, π bonds are disrupted. All these consequences can be observed due to the strong acids that can create structural defects on CNTs and due to this problem thermal, electrical and mechanical properties of CNTs cannot reach desired levels [12, 14, 16, 75, 79].

The major drawbacks encountered in covalent functionalization have forced scientists' attention to non-covalent modification. While this method provides homogeneous dispersion of CNTs, it also does not damage the structure of CNTs and does not affect

mechanical and electrical properties without disrupting π-bonds of CNTs. In non-covalent functionalization, polymers or surfactants are used to create π-π stacking or coulombic attraction on the surface of CNTs. Adsorption of surfactants around the CNTs has been widely used to get homogeneous dispersion in different medium [12, 15-16, 75]. Surfactants are known as wetting agents which are amphiphilic. They consist of hydrophilic or head group and hydrophobic or tail group (see **Figure 2.12**). These groups give the surfactants a unique ability that reduces the surface tension of CNTs with the aid of steric repulsive forces. When the repulsive forces created by surfactants around CNTs reach greater value than the Van der Waals forces between the CNTs, nanotubes begin to disaggregation. Also, surfactants can improve dispersibility of nanotubes in mediums other than water [12, 14-16].

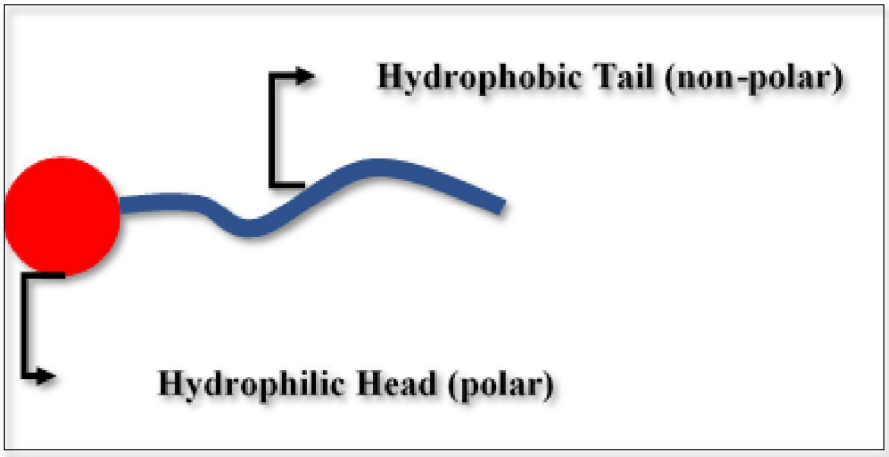

Figure 2.12 Two distinct parts of surfactants.

As a result of studies conducted by Leong et al. [80], it was observed that CNTs dispersed in nanofluids with surfactant demonstrate better stability than CNTs dispersed in nanofluids without surfactant. Also, Fidelus et al. [81] studied on CNTs and epoxy system and their results showed that mechanical properties of CNTs/epoxy composite materials improved by using Sodium dodecyl sulfate (SDS) to disperse CNTs homogeneously into epoxy. Also, effect of surfactants on CNTs are given in **Figure 2.13**.

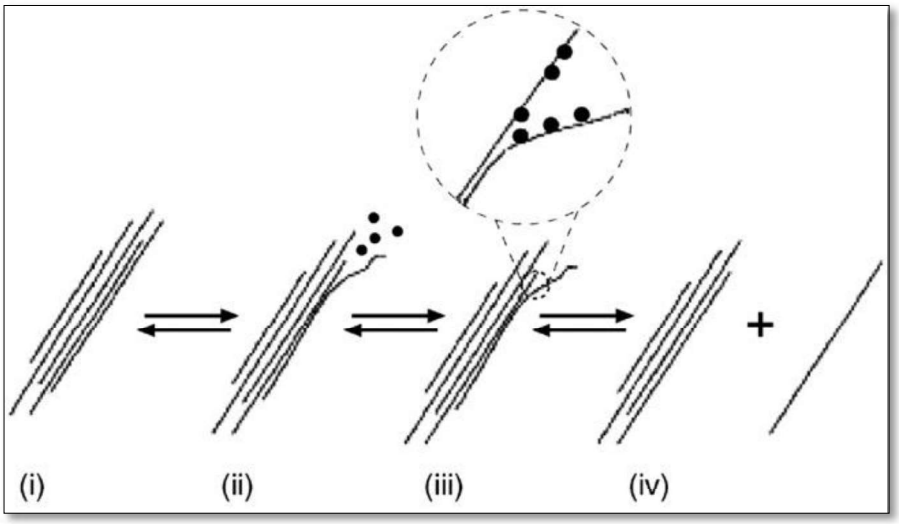

Figure 2.13 Effect of surfactant and high shear forces on CNTs: (A) bundled CNTs, (B) gaps are generated by high shear forces (C) surfactant adsorption to nanotubes, (D) separated CNTs [14].

Surfactants can be classified into three groups (see **Table 2.6**) based on the charge of their head group. They are namely anionic, cationic, and nonionic. Borode et al. [15] used a summary table to classify ionic and nonionic surfactants in their review study, the classification table of surfactants are given below.

Table 2.6 Classification of surfactants [15].

#	Surfactants	Description	Examples
1	Anionic	It has a negatively charged the hydrophilic end	Sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulphonate (SDBS), sodium stearate, etc
2	Cationic	It has a positively charged the hydrophilic end	Cetyl trimethyl ammonium bromide (CTAB), benzalkonium chloride (BAC), dioctadecyl dimethylammonium bromide (DODAB), etc.

#	Surfactants	Description	Examples
3	Nonionic	There is no charge on hydrophilic end	Gum Arabic (GA), Triton X-100, polyvinyl pyrrolidone (PVP), Tween 80, etc.

To understand the interaction mechanisms between surfactants and nanotubes and to get better stability [14] in the conducted studies [82-83], it is observed that MWCNTs are negatively charged in water, so, when the SDS was used as surfactant, insufficient stability was observed due to charge repulsion. So, it is important to know the behavior of nanotubes in different media, because nanotubes can demonstrate different charging characteristic in different media.

Best candidate for CNTs/water solutions is ionic surfactants and, non-ionic surfactants are preferable for CNTs/organic solvents (Acetone, ethanol, dimethyl formamide (DMF), dimethyl acetamide (DMAc), dimethyl pyrrolidone (NMP), etc.) solutions [14].

Adsorption mechanisms of surfactants can vary on CNTs walls: (a) cylindrical, (b) hem-micellar and (c) random (see **Figure 2.14**) [14].

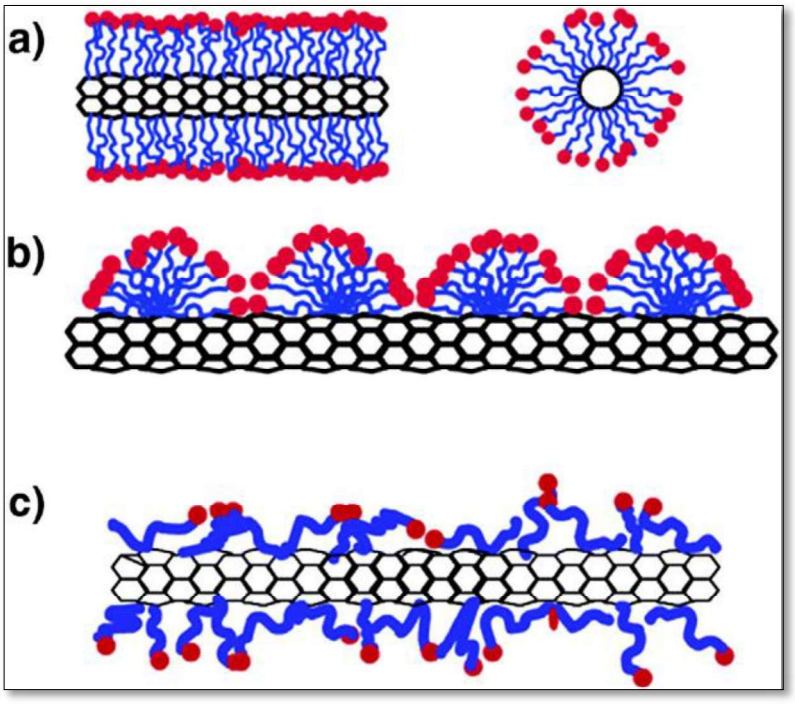

Figure 2.14 Adsorption mechanisms of surfactants on nanotube walls: (A) cylindrical adsorption of surfactants, (B) hemi-micellar adsorption of surfactant and (C) random adsorption of surfactant [14].

Another important point is the concentration of surfactants that must be taken into consideration to get stability in suspension. There is an important threshold value known as critical micelle concentration (CMC) for surfactants (monomers), when concentration of surfactants remains below a threshold value, surfactant can move free inside the solution and also, surface tension of nanoparticles that exposed by surfactants changes robustly. But above CMC, tendency of hydrophobic tails to generate aggregate increases and the surface tension changes slowly or can remain constant [84-85]. CMC characteristic of surfactants are illustrated below.

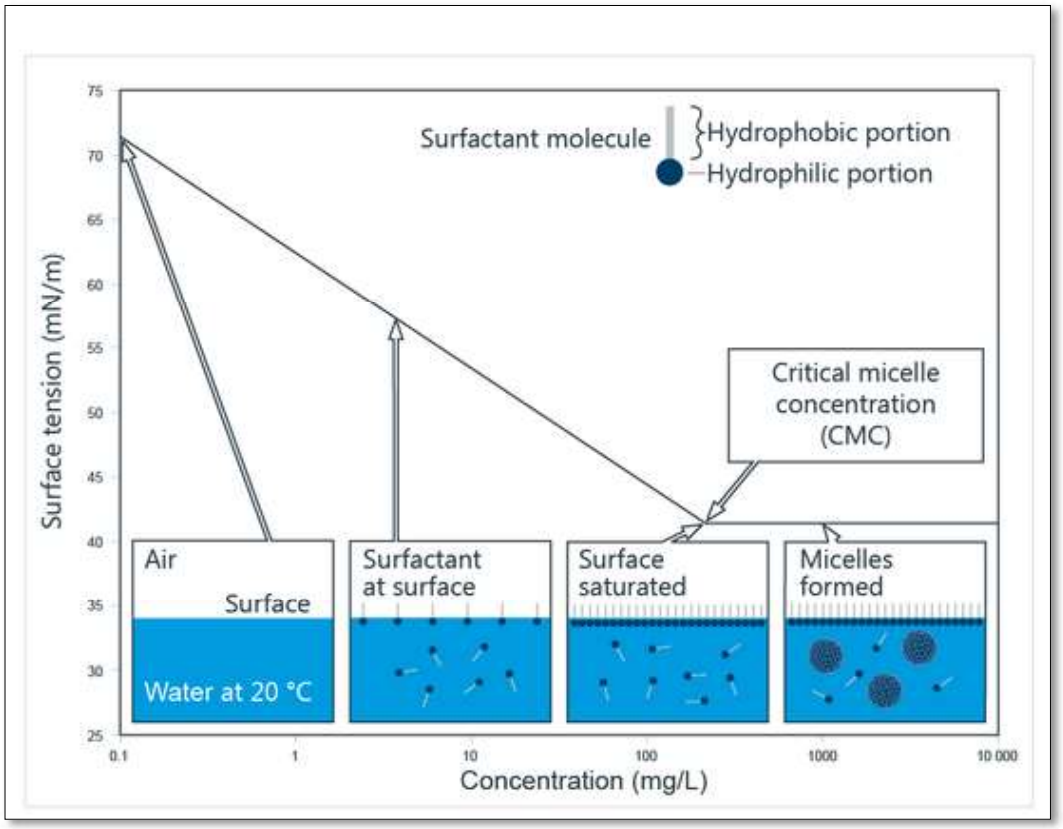

Figure 2.15 Surface tension as a function of the surfactant concentration [86]

In the recent years, researchers have begun to use combined method to prepare composite materials. This method includes both chemical approach and physical approach. Non-covalent functionalization or surfactant is used to get stable solution and to disperse CNTs homogenously by using high shear forces [11]. High shear forces create gaps between CNTs bundles to increase tendency for adsorption of surfactants. Effect of both surfactant and high shear forces are illustrated in **Figure 2.15**. Randhawa et al. [87] dispersed CNTs in water with surfactant (Triton X-100) by using ultrasonication and centrifugation. Also, Madni et al. [13] investigated dispersion stability of CNTs in water and organic solvent (dimethyl formamide(DMF)) with different surfactants (dodecyl trimethyl ammonium bromide (DTAB) and sodium octanoate (SOCT)) and prepared solutions by using ultrasonic waves. They obtained homogenously dispersed MWCNTs by using both chemical approach (surfactant) and physical approach (ultrasonic mixer).

CHAPTER 3

METHODOLOGY

3.1. Materials

The experimental part of this work consists of five different composite production technique. In these productions, as a reinforcement phase, twill woven HexForce® E Glass Fiber is used. The properties of glass fiber are given below in **Table 3.1**. Also, schematic illustration of glass fiber is given in **Figure 3.1**.

Table 3.1 Properties of Supplied Glass Fibers

Reinforcement Phase	
Supplied from *	HexForce®
Type *	E Glass Fabric
Weave Style *	Twill Weave 2/2
Nominal Weight (g/m^2) *	390
Weight Distribution *	Warp: 53% Weft: 47%
Thickness (mm) *	0.30
Young Modulus (GPa) **	72 - 85
Tensile Strength (MPa) **	$1.95x10^3 – 2.05x10^3$
Flexural Modulus (GPa) **	72 - 85

* Data taken from HexForce® Datasheet, ** Data taken from CES Selector.

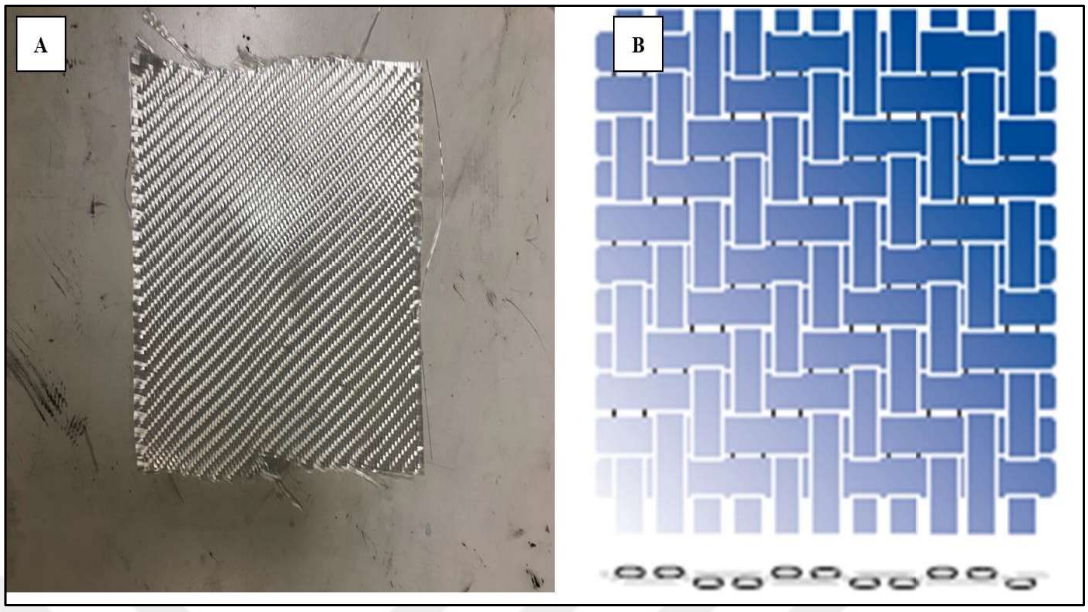

Figure 3.1 (A) E Glass Fiber Supplied From HexForce®, (B) Schematic Illustration of Twill 2/2

Epoxy is used as matrix phase in this study. The epoxy system is supplied from DURATEK®, "*Duratek Epoxy and Polyurethane Systems*". The properties of supplied system are given in **Table 3.2**. Considering the procedures to be performed, a slow curing hardener is preferred to prolong the processing time. Schematic illustrations of resin and hardener are given in **Figure 3.2**.

Table 3.2 Properties of Epoxy System Supplied from DURATEK

Matrix Phase*	
Supplied from	DURATEK® Epoxy System
Epoxy System	DTE 1000 (Resin (A)) + DTS 1105 (Slow Curing Hardener (B))
Density (kg/lt)	1.10 ± 0.05
Viscosity (mPas)	600 ± 200
Mix Life (23°C, 100ml) (min.)	360 ± 50

Matrix Phase*	
Resin to Hardener Ratio	4:1
Tensile Strength (N/mm^2) (at 100°C, 4 h)	71 - 76
Maximum Tensile Elongation (%) (at 100°C, 4 h)	3.8 – 4.3
Elastic Modulus (kN/mm^2) (at 100°C, 4 h)	3.2 – 3.5
Bending Strength (N/mm^2) (at 100°C, 4 h)	100 - 105
Water Absorption (mg) (at 100°C, 4 h)	47 - 52

* Data taken from DURATEK® Epoxy System Datasheet.

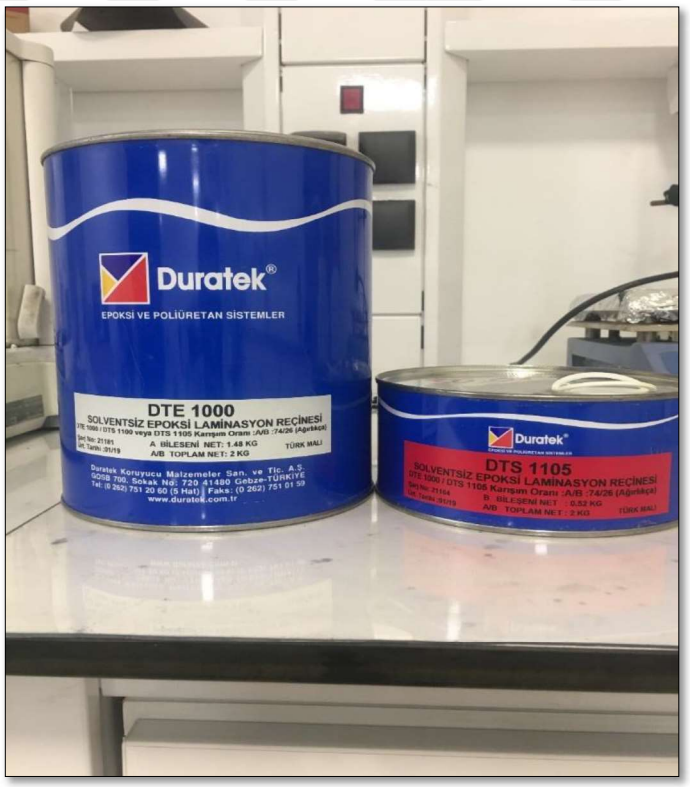

Figure 3.2 Epoxy System Supplied from DURATEK (DTE 1000 is resin (A) and DTS 1105 is slow curing hardener (B)).

Also, Multiwalled Carbon Nanotubes (MWCNTs) are used as additive to glass fiber reinforced epoxy composite materials. MWCNTs are supplied from HAZERFEN, "*Kimya Malzeme ve Enerji Teknolojileri Sanayi Ticaret A.Ş.".* The properties of supplied MWCNTs are given in **Table 3.3**. MWCNTs that have been used in this study are given in **Figure 3.3**.

Table 3.3 Properties of MWCNTs Supplied from HAZARFEN

Additive Nanoparticles*	
Supplied from	HAZARFEN
Type of Carbon Nanotubes	Multi-Walled Carbon Nanotubes
Diameter (nm)	50 – 85
Length (μm)	10 – 15
Nitrogen Surface Area (m^2/g)	60 – 90
Carbon Content (%)	> 94

* Data taken from HAZARFEN Datasheet.

Figure 3.3 Multi-Walled Carbon Nanotubes Supplied from HAZARFEN

MWCNTs have been supplied as non-functionalized, so, it should be functionalized to get better stability into matrix or solvent. Two methods of chemical modification to better disperse the CNTs were mentioned in Chapter 2. Conducted studies show that non-covalent modification is better than covalent modification. Based on these results, in this study, surfactant has been used to functionalized MWCNTs to get better homogeneity. Surfactants can be divided to two group: (a) ionic and (b) nonionic. Rastogi et al. [88] conducted comparative study on dispersion of MWCNTs with four different surfactants: (a) Triton X-100, (b) Tween 20, (c) Tween 80 and sodium dodecyl sulfate (SDS). The results of this study show that they reached maximum stability with Triton X-100. Also, Yeh [89] compared the Triton X-100 with sodium dodecylbenzene sulfonate (NaDDBS) and SDS in master thesis and obtained results showed that Triton X-100 is one of the best choices to get better homogeneity with CNTs. So, in this study, polyoxyethylene octyl phenyl ether (Triton X-100) has been used as surfactant that was supplied from MERCK. Properties of Triton X-100 is given in **Table 3.4**.

Table 3.4 Properties of Triton X-100 Supplied from MERCK [90]

Surfactant	
Supplied from	MERCK
Type of Surfactant	Nonionic
Name of Surfactant	Triton X-100
Chemical Formula	$C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$
CAS Number	9036-19-5
Boiling Point (°C)	>200
Density (g/cm^3)	1,07 (20 °C)
pH Value	5.0– 8.0 (10g/l, H_2O, 20 °C)

Surfactants are generally used with water or organic solvent to functionalize the CNTs. Vaisman et al. [14] in their review study concluded that in the literature generally, water/CNT solutions are chosen for ionic surfactant and, organic solvent/CNT solutions are generally chosen for nonionic surfactant. There are many organic solvents that are used to solve surfactants such as acetone, ethanol, tetrahydrofuran (THF), dichloromethane, N-methyl-2pyrrolodone (NMP), dimethylformamide (DMF), etc. Sun et al. investigated the effect of different organic solvent on dispersion of MWCNTs and they concluded that NMP, acetone, tetrahydrofuran and dichloromethane disperse MWCNTs better than water, ethanol and toluene. Due to this reason, acetone from MERCK has been chosen as organic solvent to functionalized MWCNTs with Triton X-100, because it is inexpensive chemical and compatible with the Triton X-100.

Mechanical mixing methods have been used in conjunction with non-covalent modification to distribute MWCNTs homogeneously. High shear mixer named High Speed Mixer^{TM} has been used in production of reference samples to mix the resin and hardener mixture. In other four composite productions with addition or attaching of MWCNTs, ultrasonic mixer has been used. Technical information of these two mixers is given in **Table 3.5** and **Table 3.6**.

Table 3.5 Technical Data of Speed Mixer

High Speed Mixer*	
Supplied From	Speed Mixer^{TM}
Speed Mixer Pattern	DAC 150.1 FVZ
Speed	Variable 300-3500 rpm
Mixing Time	5 seconds to 5 minutes
Mixing Capacity	5 grams to 100 grams
Voltage / Frequency	110V 60Hz
Power Consumption	500 W

***** Data taken from Speed Mixer^{TM} DAC 150.1 FVZ Datasheet.

Table 3.6 Technical Data of Ultrasonic Mixer

Ultrasonic Mixer*	
Supplied From	MTI Corporation
Ultrasonic Mixer Pattern	MSK-USP-12N
Voltage	AC 110V 50/60Hz
Power	1200W Max. – 20KHz
Timer	Adjustable from 1 second to 99 hours
Working Temperature	0-40 °C
Duty Rate	0%-100%
Sample Type	Solutions

* Data taken from MTI Corporation MSK-USP-12N Datasheet.

To improve z-axis or interlaminar properties of glass fiber epoxy matrix composites, MWCNTs have been attached onto glass fibers with aid of spray gun. Technical information of spray gun is given in **Table 3.7**.

Table 3.7 Technical Data of Spray Gun

Spray Gun*	
Supplied From	Mac Allister
Spray Gun Pattern	PLD 3020
Voltage	220 – 240V
Power	400W
Sound Level	96.1dB

* Data taken from Mac Allister PLD 3020 Datasheet.

In this study, five different glass fiber reinforced epoxy matrix composite techniques have been produced with/without MWCNTs addition which has been taken as 2.5 wt.% of total mixture (Epoxy System + MWCNTs). Also, since all the main parameters (type of glass fiber, dimensions of glass fibers and number of glass fibers used for a production) used in the study are the same, the same ratio was used in the attaching of MWCNTs onto the fibers. This ratio has been chosen from previous study results conducted in Bachelor Senior Thesis by Ozturk et al. [91]. In this thesis, different weight percentage ratio MWCNTs were used and three-point bending test was conducted to prepared samples and, results showed that the best result among the ratios used was obtained in the composite prepared with 2.5 wt.%. MWCNTs. Conducted manufacturing steps during this study are given in the flowchart below.

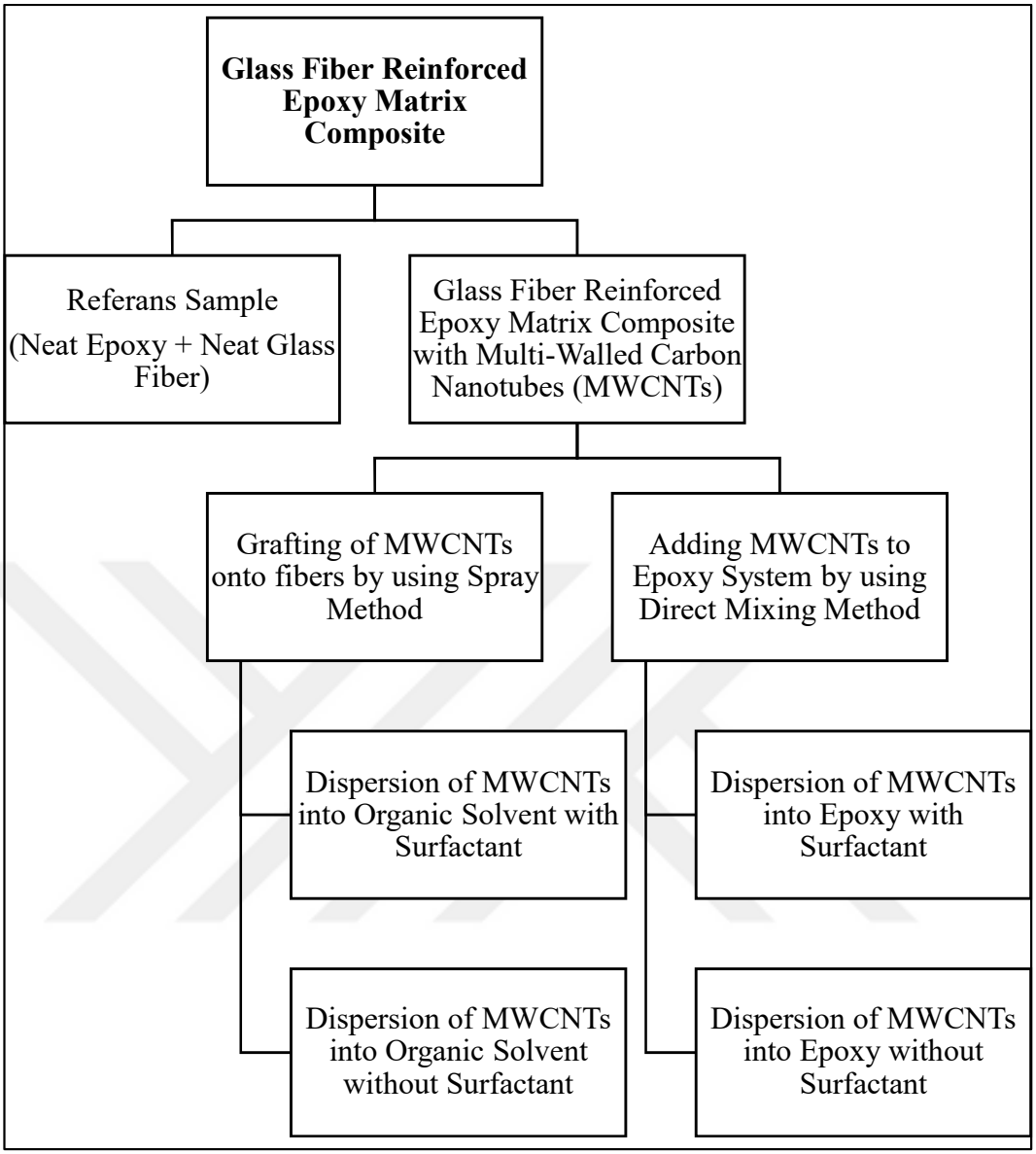

Figure 3.4 Followed Path for Production of Glass Fiber Composite Materials.

3.2. Composite Production

In this study, to see the effect of different production methods, epoxy (resin and hardener) mixture amount, carbon nanotube weight ratio, surfactant amount (used in only two composite production), number of glass layers, glass fiber dimensions and lamination sequence have been kept constant in all productions. Information of these parameters are given in **Table 3.8**:

- **Glass Fibers:** In order to achieve desired composite material thickness in line with "*ASTM D 7264 Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials"*, thickness of glass fabric has been measured as 0.31 mm. Composite laminates that produced in this study have been decided total fourteen plies of constant stacking sequence (without changing the laminate angle). Glass fabrics have been cut in accordance with the dimensions specified in ASTM D 7264. Also, the mass of fourteen glass fabrics to be used in composite laminates production has been measured as ~123g.
- **Epoxy System:** Resin and hardener ratio (4:1) have been decided in accordance with DURATEK® Epoxy Datasheet. Also, amount of resin and hardener has been calculated as totally 90 g (72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)) as a result of experiments.
- **Multi-walled Carbon Nanotubes:** The ratio of MWCNTs has been chosen as 2.5 wt.% based on study conducted by Öztürk et al. [91]. Amount of MWCNTs has been calculated as 2.3g in accordance with total mixture (resin, hardener and MWCNTs).
- **Surfactant:** Surfactant (Triton X-100) to MWCNTs ratio has been chosen as 5:1 based on studies conducted by Tang et al. [92]. Amount of surfactant has been calculated as 11.5g that is 5 times amount of MWCNTs.

Table 3.8 Information of Constant Parameter Used in Productions

	Production Methods				
Parameters	**Reference Sample**	**Direct Mixing with Surfactant**	**Direct Mixing without Surfactant**	**Spray Method with Surfactant**	**Spray Method without Surfactant**
Lamination and Stacking Sequence of Glass Fabrics	Total Fourteen Plies of Same Stacking Sequence	Total Fourteen Plies of Same Stacking Sequence	Total Fourteen Plies of Same Stacking Sequence	Total Fourteen Plies of Same Stacking Sequence	Total Fourteen Plies of Same Stacking Sequence
Dimensions of Glass Fabrics	150 mm x 150 mm	150 mm x 150 mm	150 mm x 150 mm	150 mm x 150 mm	150 mm x 150 mm
Mass of Glass Fabrics	~123 g	~123 g	~123 g	~123 g	~123 g
Type of Epoxy System	DURATEK®	DURATEK®	DURATEK®	DURATEK®	DURATEK®
Mass of Epoxy System	72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)	72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)	72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)	72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)	72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B)

	Production Methods				
Parameters	**Reference Sample**	**Direct Mixing with Surfactant**	**Direct Mixing without Surfactant**	**Spray Method with Surfactant**	**Spray Method without Surfactant**
Type of Carbon Nanotubes	NA	Multi-walled Carbon Nanotubes	Multi-walled Carbon Nanotubes	Multi-walled Carbon Nanotubes	Multi-walled Carbon Nanotubes
Mass of Carbon Nanotubes	NA	2.5 wt.% of total mixture – 2.3 g	2.5 wt.% of total mixture – 2.3 g	2.5 wt.% of total mixture – 2.3 g	2.5 wt.% of total mixture – 2.3 g
Type of Surfactant	NA	Triton X-100	NA	Triton X-100	NA
Mass of Surfactant	NA	11.5 g (5:1 Surfactant to MWCNTs Ratio)	NA	11.5 g (5:1 Surfactant to MWCNTs Ratio)	NA
Volume of Acetone	NA	100 ml	100 ml	250 ml	250 ml

3.2.1. Reference Sample Production

Reference sample has been produced with neat epoxy to compare the effects of MWCNTs onto glass fiber reinforced epoxy matrix composite materials. **Figure 3.5** shows steps during reference sample production.

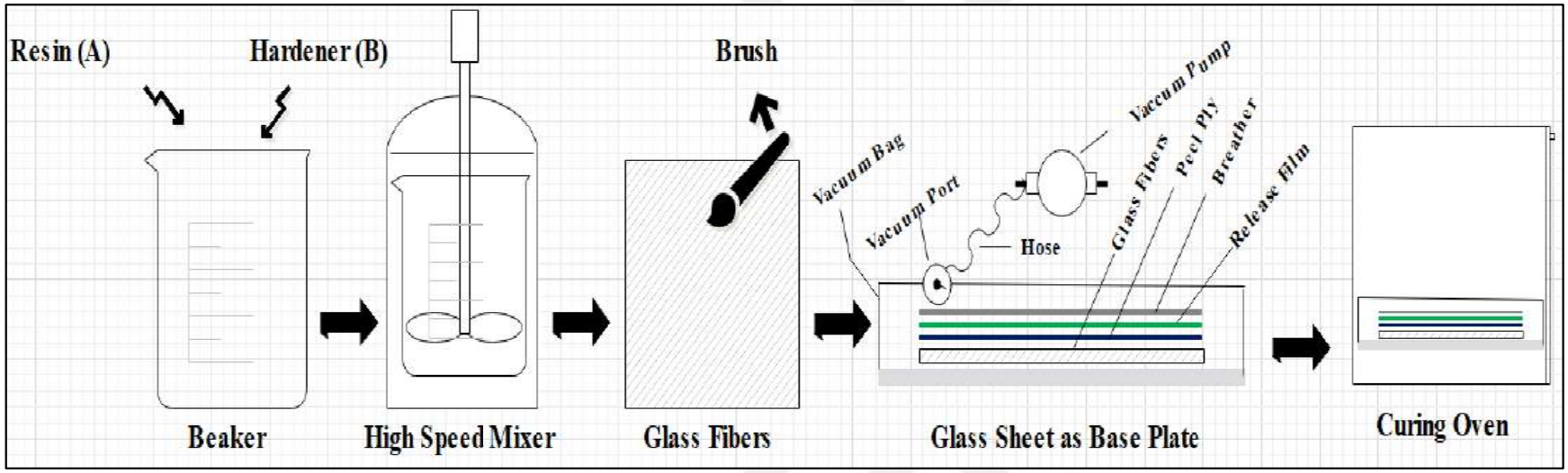

Figure 3.5 Followed Steps during Reference Sample Production

Also, steps followed during this production are given below:

1. The resin and hardener have been weighted (see **Figure 3.6**) in agitation vessel as 4:1 resin to hardener ratio that was specified by the manufacturer.

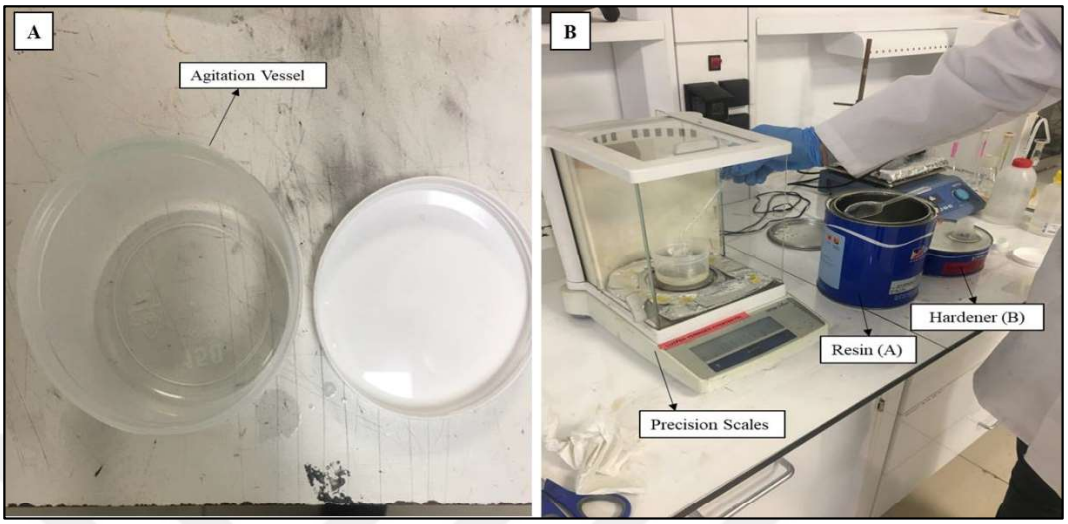

Figure 3.6 (A) Agitation Vessel, (B) Epoxy System Used in This Study.

2. 72 g DTE 1000 resin (A) and 18 g DTS 1105 slow curing hardener (B) have been mixed with the high speed mixer at 3500 revolution per minute (rpm), 2 minutes (see **Figure 3.7** (A)).
3. Epoxy mixture has been applied to every layer of composite laminates by using hand lay-up process. Laminates have been made with total fourteen plies of same stacking sequence. In hand lay-up process, glass sheet has been used as a base plate. Greaseproof paper has been used to prevent sticking of the fiber and resin mixture on the glass piece.
4. After hand lay-up process, vacuum bagging method has been utilized to remove voids and impurities between layers of fibers and, to absorb excess resin. Consumable materials for vacuum bagging process are given in **Figure 3.7** (B). These materials can be classified as:
    - **Peel Ply:** It is one of the most important parts of vacuum bagging process and placed onto the outer surface of glass fabrics. It is used to remove excessive resin and to get smooth surfaces after curing process. Also, it can be removed easily from composite surface.

- **Release Film:** Over the peel ply, perforated release film has been placed to prevent sticking of breather to the composite surface. Also, perforated film has been used to remove more excessive resin from glass fibers.
- **Breather/Bleeder Cloth:** On the top layer, breather cloth has been placed to access air passage and to absorb excess resin with impurities to get desired properties. Voids and impurities between glass fiber layers directly affect desired mechanical properties.
- **Vacuum Bag:** Vacuum bag has been used to surround all consumables and laminated materials and it provides a suitable vacuum environment thanks to the vacuum apparatus.

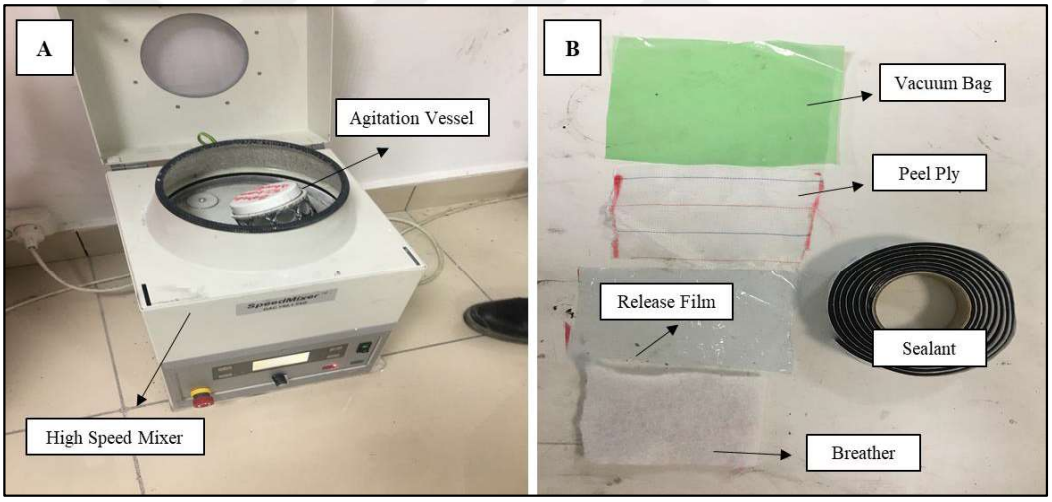

Figure 3.7 (A) Epoxy System Mixing into High Speed Mixer, (B) Vacuum Bagging Consumables

5. After vacuum bagging process, composite material has been cured in the curing oven at 100 °C, 4 hours. Curing temperature and curing time has been supplied by DURATEK®. Also, vacuum has been conducted during whole curing process see in **Figure 3.8**.
6. After curing process, reference sample has been removed from mold (see **Figure 3.9**).

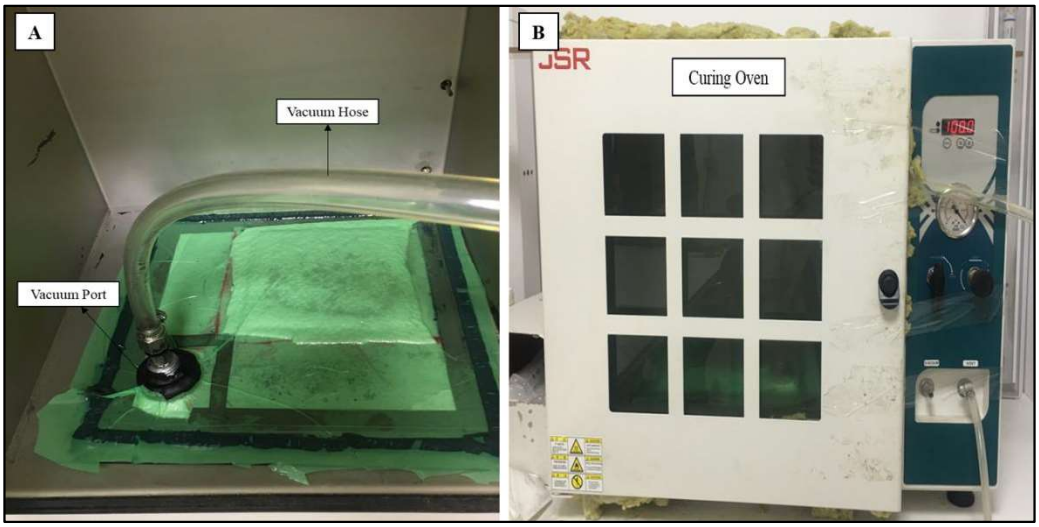

Figure 3.8 (A) Curing Process of Reference Sample and (B) Curing Oven

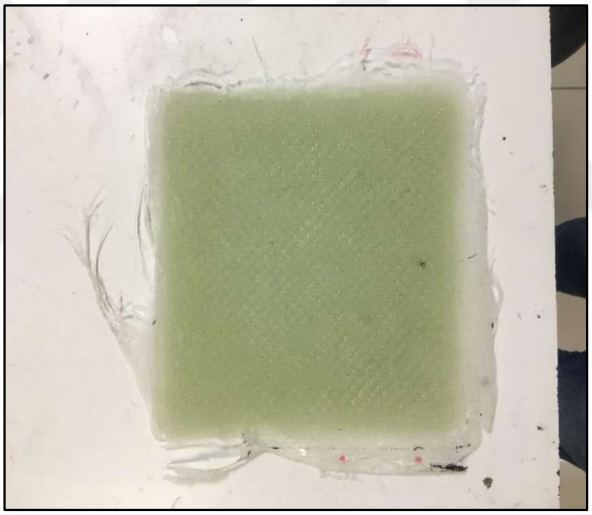

Figure 3.9 Reference Sample after Curing Process

3.2.2. Production of Glass Fiber Reinforced Epoxy Matrix Composites by Dispersing MWCNTs into Epoxy Matrix with The Aid of Surfactant

One of the production methods in this study is the production of glass fiber reinforced epoxy matrix composites by dispersing MWCNTs into epoxy matrix. In this process, surfactant is used to functionalize the MWCNTs to enhance dispersibility by preventing agglomerations. **Figure 3.10** illustrates the production of GFEC by dispersing MWCNTs into Epoxy matrix with the aid of surfactant.

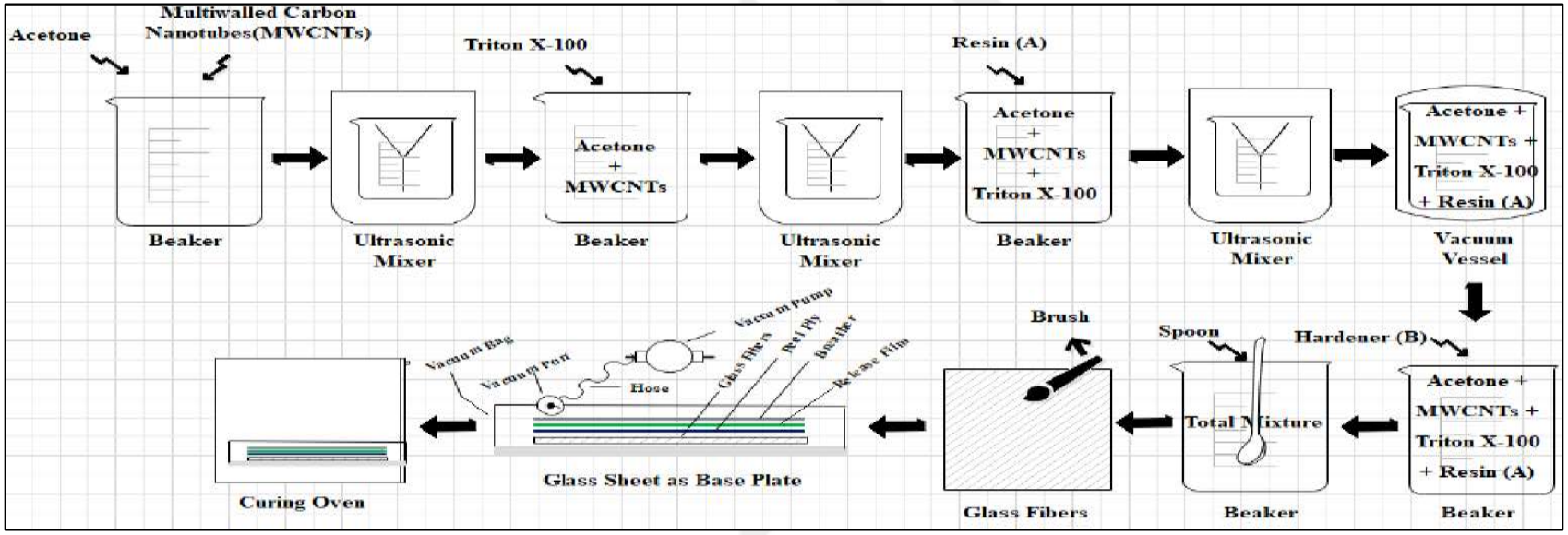

Figure 3.10 Followed Steps during Production of Glass Fiber Reinforced Epoxy Matrix Composites by Dispersing MWCNTs into Epoxy Matrix with The Aid of Surfactant.

Steps followed during this production are given below:

1. Acetone and MWCNTs have been put in the beaker and mixed with ultrasonic processor at 45% power for about 15 minutes. Working power of ultrasonic mixer has been determines based on studies conducted in the literature. Powers greater than 55% have not been used in mixing process, because the ultrasonic mixer can damage the structure of carbon nanotubes [73].
2. Triton X-100 has been added to Acetone + MWCNTs mixture and the new mixture has been mixed with ultrasonic mixer at 45% power for about 15 minutes.
3. Resin (A) has been included to Acetone + MWCNTs + Triton X-100 solution and mixed with ultrasonic mixer at 55% power for about 50 minutes. In this step, ultrasonic mixer has been adjusted to 30 seconds out of 50 seconds duration (see **Figure 3.11**).

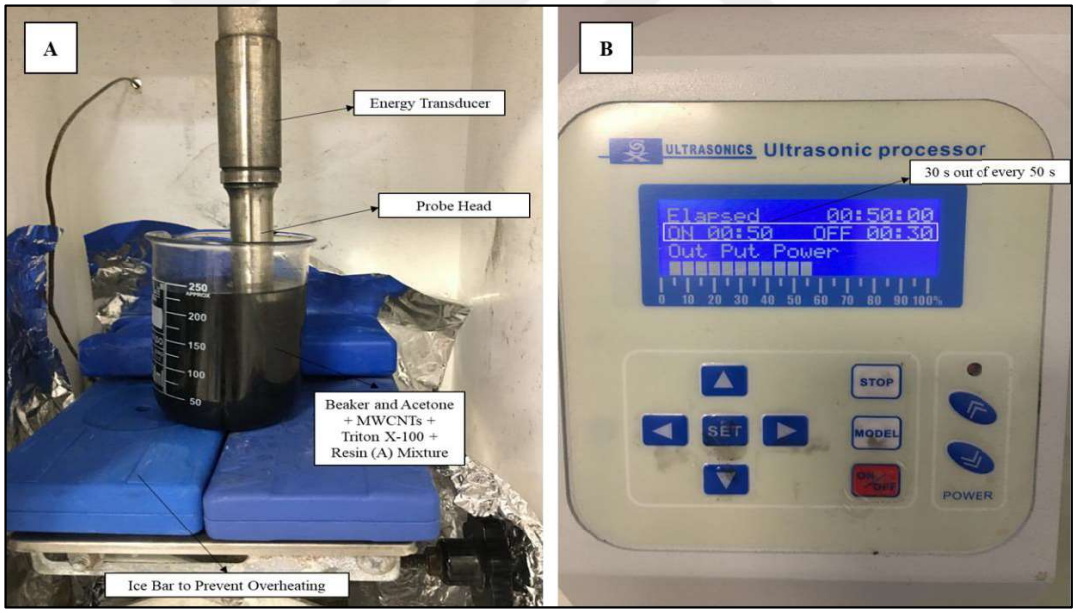

Figure 3.11 (A) Mixing Process of Acetone + MWCNTs + Triton X-100 + Resin (A) Mixture with the Aid of Ultrasonic Mixer, (B) Conducted Program in The Process

4. Acetone + MWCNTs + Triton X-100 + Resin (A) mixture has been kept in ambient atmosphere overnight. After that, 0.9 bar vacuum has been applied to

the mixture in vacuum vessel for about 2 hours to evaporate acetone from the total mixture (see **Figure 3.12**).

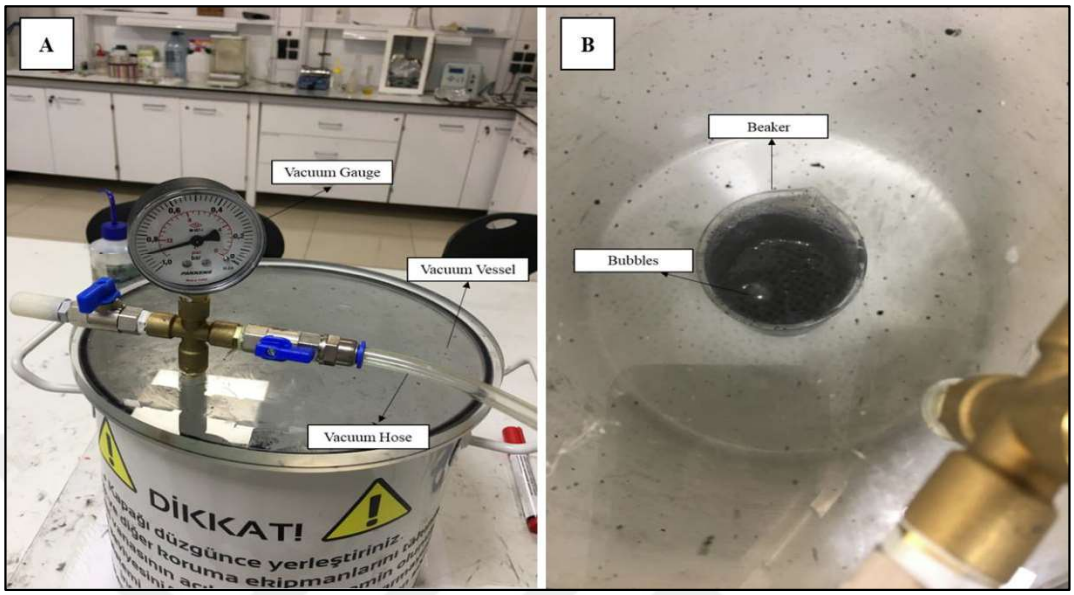

Figure 3.12 (A) Vacuum Vessel to Remove Acetone From Mixture, (B) Behavior of Mixture under Vacuum

5. After evaporation process, 18 g hardener (B) has been included to the mixture and mixed with stirring rod until homogeneity is obtained.
6. The mixture has been applied to every layer of composite laminates with the aid of brush. Laminates have been made with a total of fourteen plies of same stacking sequence.
7. After lamination process, vacuum bagging has been realized to laminates to eliminate excessive resin, voids and impurities. Vacuum has been kept during whole curing process.
8. Laminates have been cured at 100 °C, for 4 hours (see **Figure 3.13**).
9. After curing process, sample given in **Figure 3.14** has been removed from the mold.

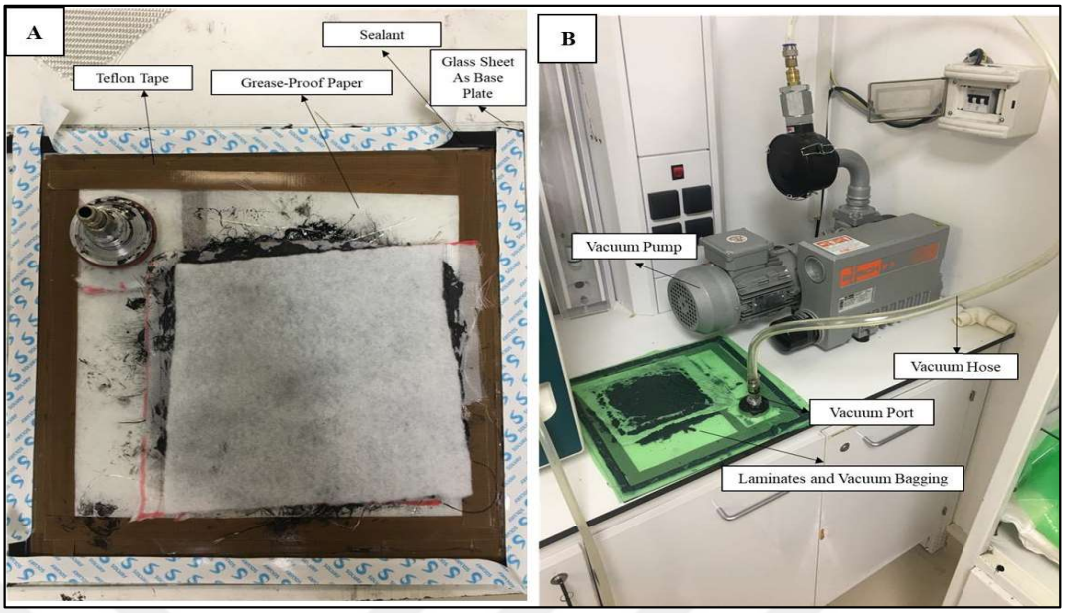

Figure 3.13 (A) Vacuum Bagging Process, (B) Vacuum Pumping of Laminates

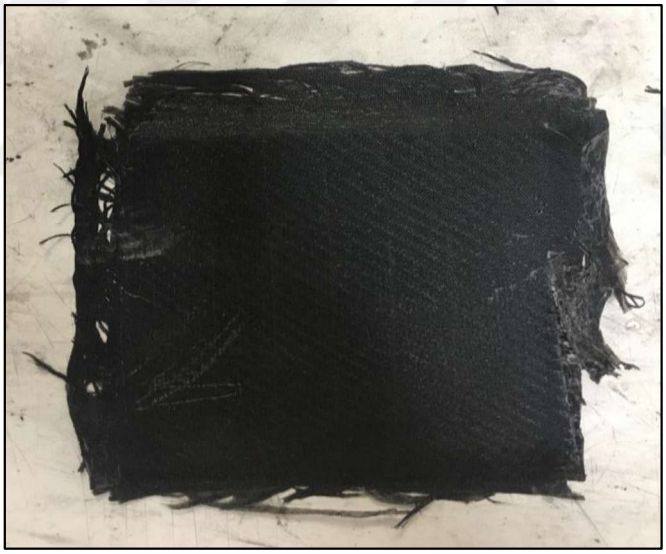

Figure 3.14 Glass Fiber Reinforced Epoxy Matrix Composite with Dispersion of MWCNTs into Epoxy System with the aid of Surfactant

3.2.3. Production of Glass Fiber Reinforced Epoxy Matrix Composites by Dispersing MWCNTs into Epoxy Matrix without The Aid of Surfactant

In this process, MWCNTs have been dispersed into Epoxy Matrix without the aid of surfactant. This process has been conducted to compare samples produced with surfactant and without surfactant. The steps given in **Figure 3.15** have been followed in this production.

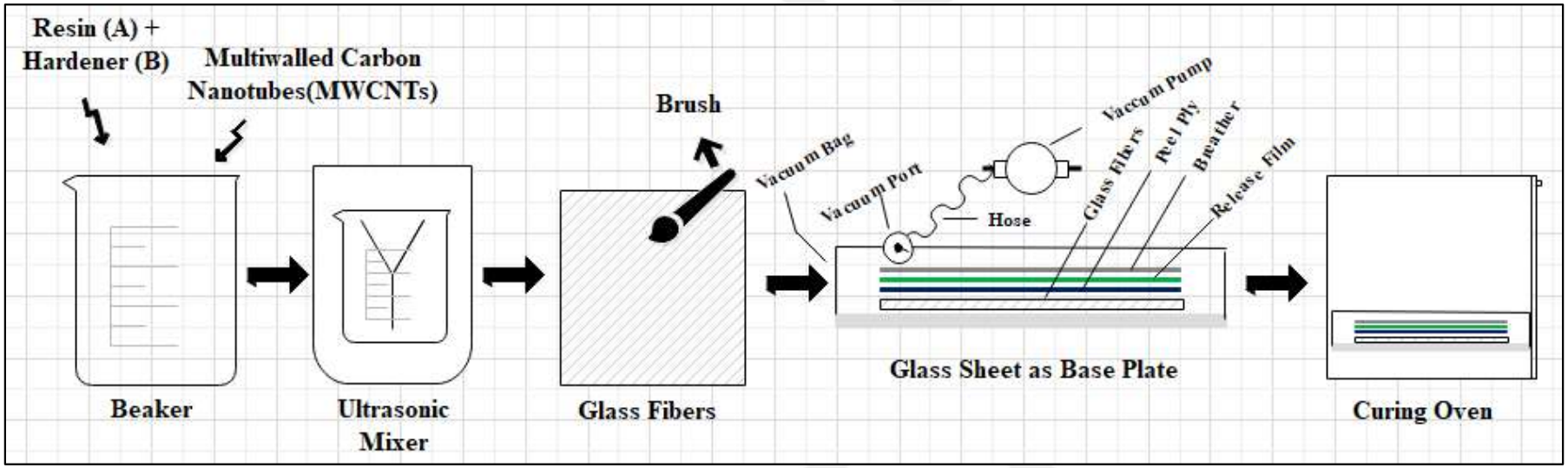

Figure 3.15 Followed Steps during Production of Glass Fiber Reinforced Epoxy Matrix Composites by Dispersing MWCNTs into Epoxy Matrix without the Aid of Surfactant

1. Resin, hardener and MWCNTs have been added into beaker and then, they have been mixed with ultrasonic mixer at 45% power for about 20 minutes (see **Figure 3.16** (A)).
2. After mixing process, prepared mixture has been applied to every layer of fibers with the aid of brush (see **Figure 3.16** (B)). As in the other process, laminates have been made with a total of fourteen plies of same stacking sequence.

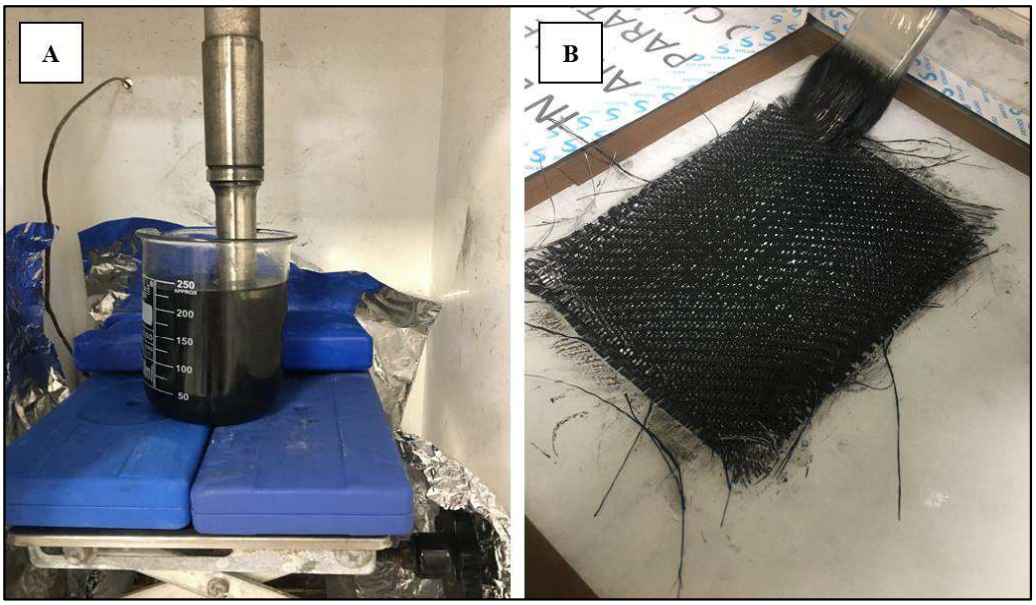

Figure 3.16 (A) Ultrasonic Mixing Process of Resin, Hardener and MWCNTs, (B) Application of Mixture to Every Layer of Glass Fabrics

3. Vacuum bagging process has been conducted to laminates to eliminate excessive resin, voids and impurities to get higher mechanical stability.
4. Laminates have been cured at 100 °C, 4 hours. Vacuum has been kept during whole curing process.
5. After curing process, cured composite sample is given in **Figure 3.17** has been removed from the mold.

Figure 3.17 Removing the Cured Composite Material from the Mold

3.2.4. Production of Glass Fiber Reinforced Epoxy Matrix Composites by Attaching MWCNTs onto Glass Fibers by Using Spray Method with The Aid of Surfactant

Another important method to produce MWCNTs enhanced GFEC is attaching the MWCNTs onto glass fibers by using spraying method. In this process, surfactant is used to enhance dispersibility of MWCNTs by preventing agglomerations. Followed steps in this production method have been given in **Figure 3.18**.

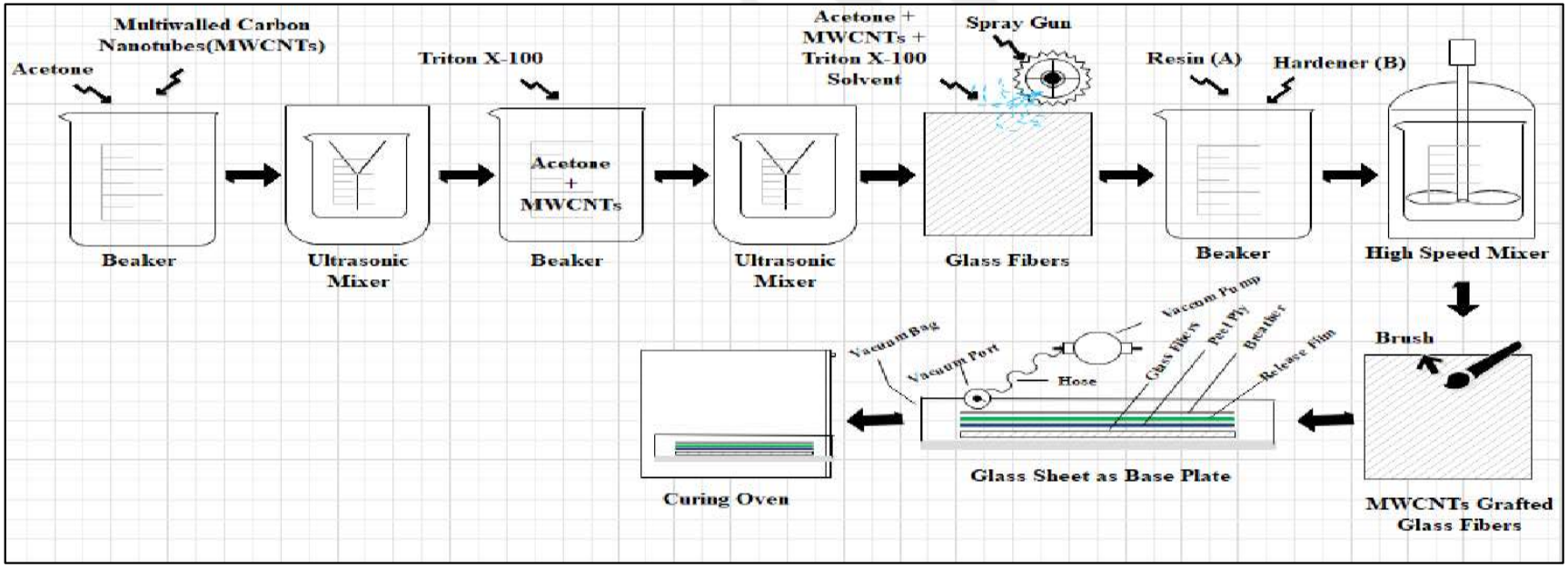

Figure 3.18 Followed Steps During Production of Glass Fiber Reinforced Epoxy Matrix Composites by Attaching MWCNTs onto Glass Fibers by Using Spray Method with The Aid of Surfactant

1. Acetone and MWCNTS have been combined in the beaker and mixed with the aid of ultrasonic processor at 45% power for about 15 minutes.
2. Triton X-100 is added to Acetone + MWCNTs mixture and ultrasonic waves have been used to attach surfactants onto MWCNTs' surfaces at 45% power for about 15 minutes.
3. Acetone + MWCNTs + Triton X-100 mixture has been filled into spray gun reservoir and mixture has been applied to both surface of fibers (see **Figure 3.19**).

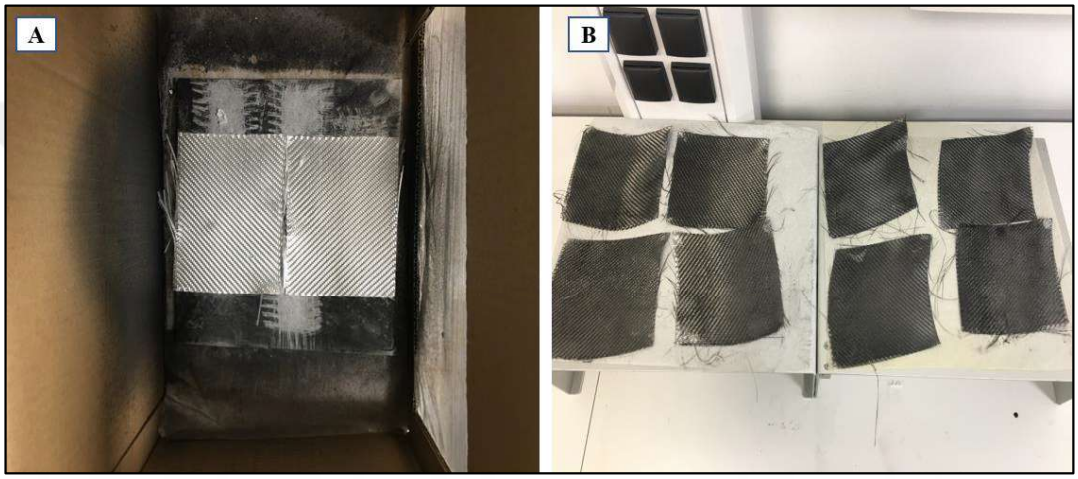

Figure 3.19 (A) Glass Fibers before Spraying Process, (B) Glass Fibers after Attaching MWCNTs with Spraying Process

4. Spraying process has been conducted under fume cupboard to prevent spraying effect of MWCNTs on human body. Also, the spraying process has been conducted in a sealed cardboard box (see **Figure 3.20**) to prevent the nanoparticles from scattering around during spraying.

Figure 3.20 (A) Sealed Cardboard Box for Spraying Process, (B) Spray Gun

5. During the whole spraying process, the same spherical shape nozzle type and the same spraying pattern have been used that are shown in **Figure 3.21**.

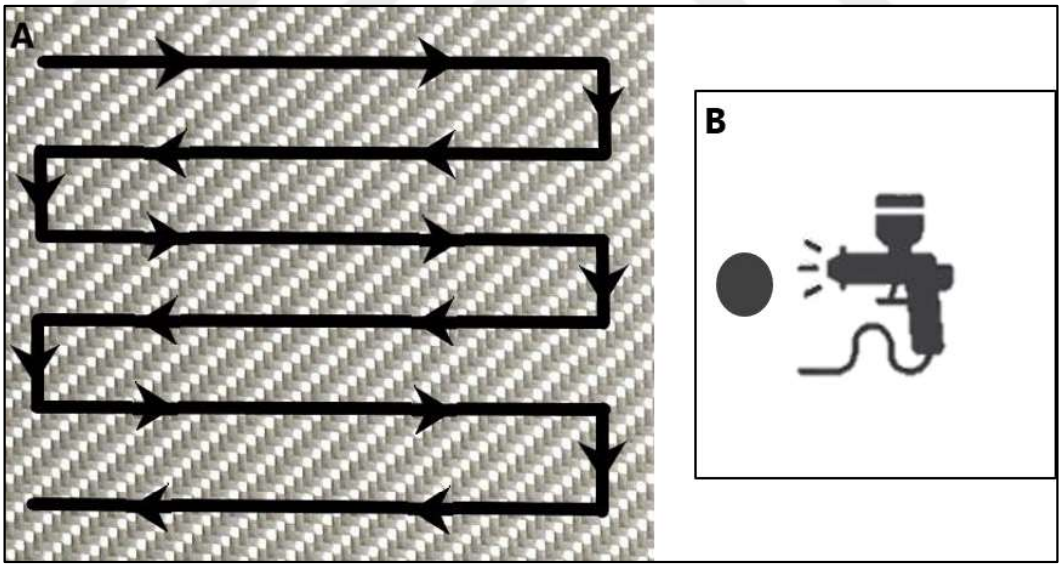

Figure 3.21 (A) Spraying Pattern That Has Been Applied onto Glass Fibers in This Production Method, (B) Shape of Nozzle That Has Been Used during Spraying Process

6. All treated fibers have been kept in the room condition overnight to evaporate acetone.

7. After evaporation process, resin and hardener have been mixed with high speed mixer at 3500 rpm for about 2 minutes.
6. Mixed epoxy system has been applied treated glass fibers by using brush. Laminates have been made with a total of fourteen plies of same stacking sequence.
8. After hand lay-up process, to get desired properties, treated glass fibers have been cured at 100 °C, for 4 hours under vacuum environment (see **Figure 3.22** (A)).
9. After curing process, cured composite sample given in **Figure 3.22** (B) has been removed from mold.

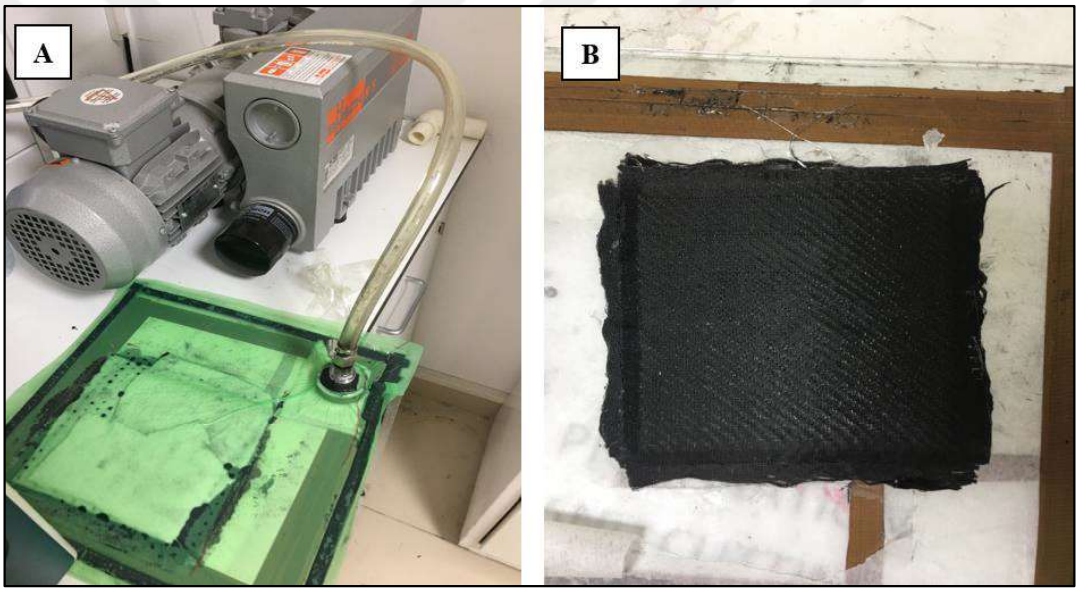

Figure 3.22 (A) Vacuum Process after Hand Lay-up, (B) Product after Curing Process

3.2.5. Production of Glass Fiber Reinforced Epoxy Matrix Composites by Attaching MWCNTs onto Glass Fibers by Using Spray Method without The Aid of Surfactant

In this production process, spraying method has been conducted same as in the production method given in above, but the surfactant (Triton X-100) has not been used in the mixture (Acetone+MWCNTs). The flowchart given in **Figure 3.23** has been followed in this process.

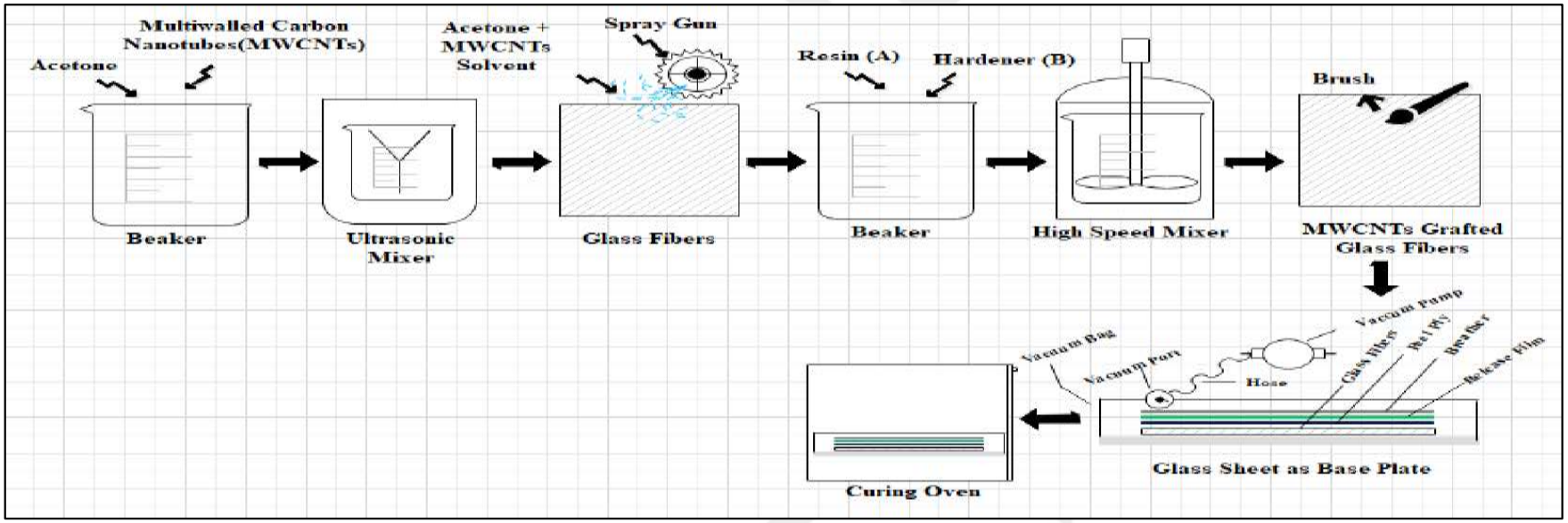

Figure 3.23 Followed Steps During Production of Glass Fiber Reinforced Epoxy Matrix Composites by Attaching MWCNTs onto Glass Fibers by Using Spray Method without The Aid of Surfactant

1. Acetone and MWCNTs have been put in the beaker to get homogenous mixture by the aid of ultrasonic processor (see in **Figure 3.24** (A)). Ultrasonic mixer power has been set 45% and mixing process has been continued for about 15 minutes.
2. Acetone + MWCNTs mixture has been filled in reservoir of spray gun (see **Figure 3.24** (B)) and spraying process has been conducted on both surface of glass fibers. The same as the other spraying process, necessary precautions have been taken to prevent harm to human health, also, spraying pattern and shape of nozzle given in **Figure 3.21** have been conducted on all glass fibers.

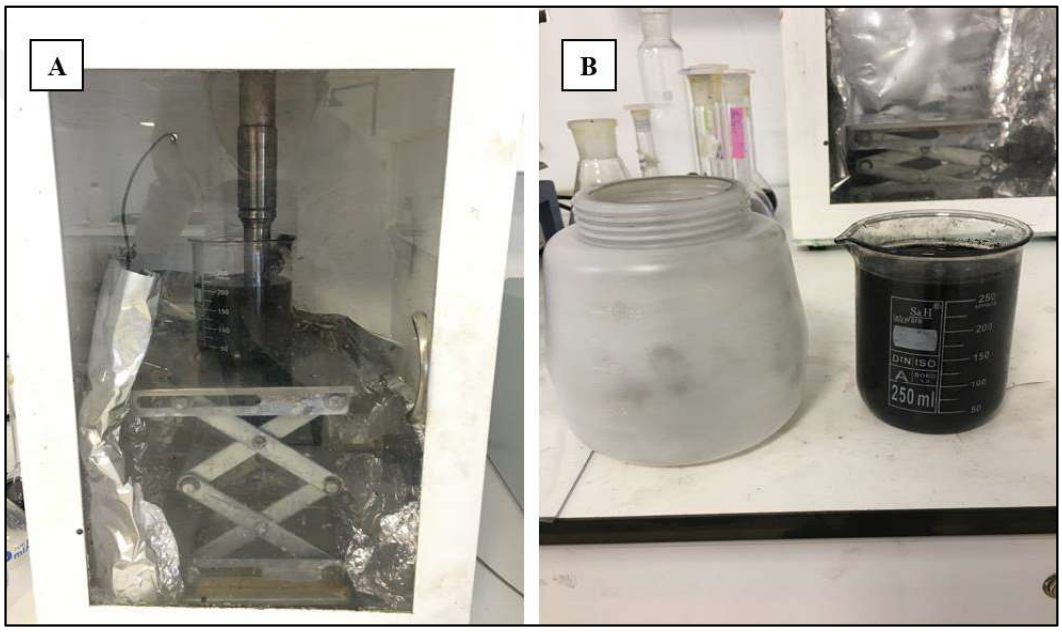

Figure 3.24 (A) Ultrasonic Mixing Process of Acetone + MWCNTs Mixture, (B) Spray Gun Reservoir and Acetone + MWCNTs Mixture

3. After spraying process, all glass fibers have been kept in the room condition overnight to evaporate acetone contained in fibers.
4. After evaporation process, resin and hardener have been mixed with high speed mixer at 3500 rpm for about 2 minutes.
5. Mixed epoxy system has been applied treated glass fibers by using hand lay-up process. Laminates have been made with a total of fourteen plies of same stacking sequence (0°).

6. After hand lay-up process, to get desired properties, treated glass fibers have been cured at 100 °C, for 4 hours. Also, vacuum environment has been maintained throughout the entire curing cycle (see **Figure 3.25** (A)).
7. After curing process, cured composite sample given in **Figure 3.25** (B) has been removed from the mold.

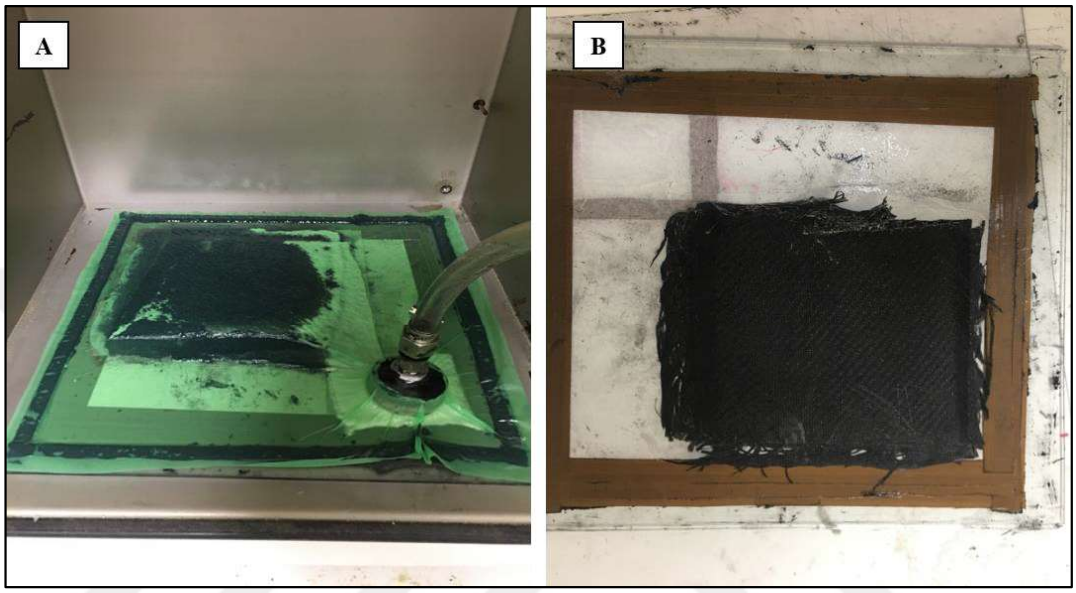

Figure 3.25 (A) Vacuum Environment in Furnace, (B) Produced Composite Sample after Curing Process

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1. Three Point Bending Test

To see the effects of MWCNTs and different composite production methods along the z-axis/through thickness properties of glass fiber composite materials, Three-Point Bending Test has been conducted to composite specimens in accordance with ASTM D 7264 Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials- Procedure A. This test is applied to determine flexural properties of polymer matrix composite materials. Procedure A is defined in standard as *"the bar rests on two supports and is loaded by means of a loading nose midway between the supports [93]"*. **Figure 4.1** gives loading diagram of ASTM D 7264 – Procedure A (P represents applied load and L represents support span).

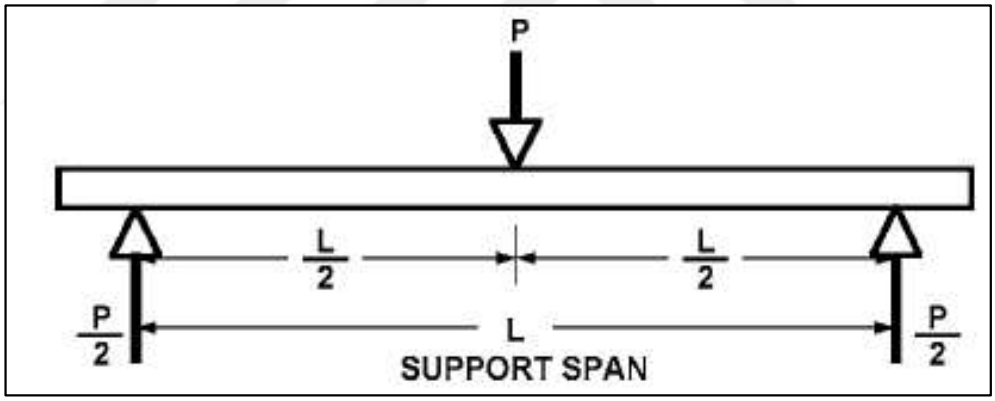

Figure 4.1 Loading Diagram of ASTM D 7264 Procedure A [93]

Composite plates have been cut by waterjet to suitable specimen size (see **Figure 4.2**) given in applicable standard. Also, the standard span to thickness ratio has been chosen as 16:1 as given in ASTM 7264.

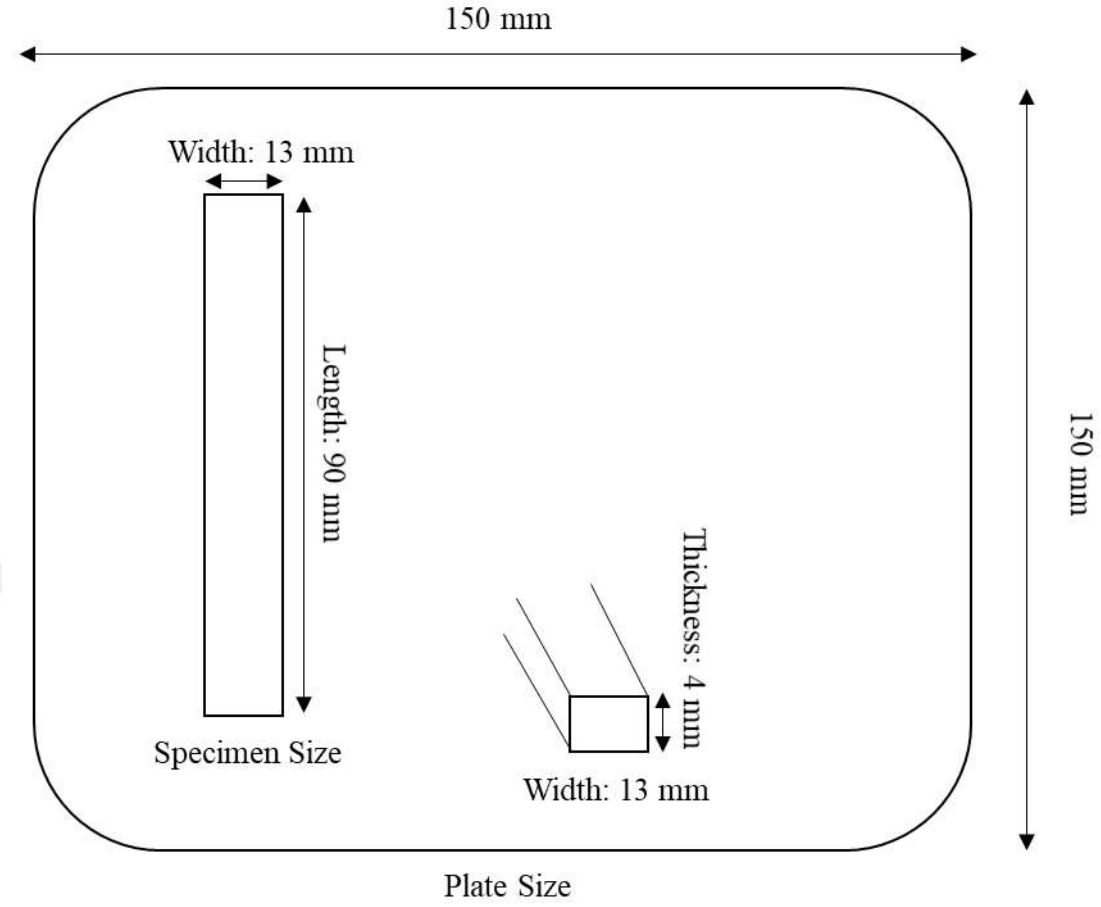

Figure 4.2 Three Point Bending Specimen Size According to ASTM D 7264

The tests have been carried out at Türkiye Bilimsel ve Teknolojik Araştırma Kurumu (TÜBİTAK) Savunma Sanayii Araştırma ve Geliştirme Enstitüsü (SAGE) Infrastructure facility by using Zwick Roell Test Machine. Three specimens from each plate have been tested. Video extensometer has been used to measure flexural properties. Also, speed of testing has been set at a crosshead movement of 1 mm/min in accordance with ASTM 7264 [93]. **Figure 4.3** illustrates three-point bending test of reference sample.

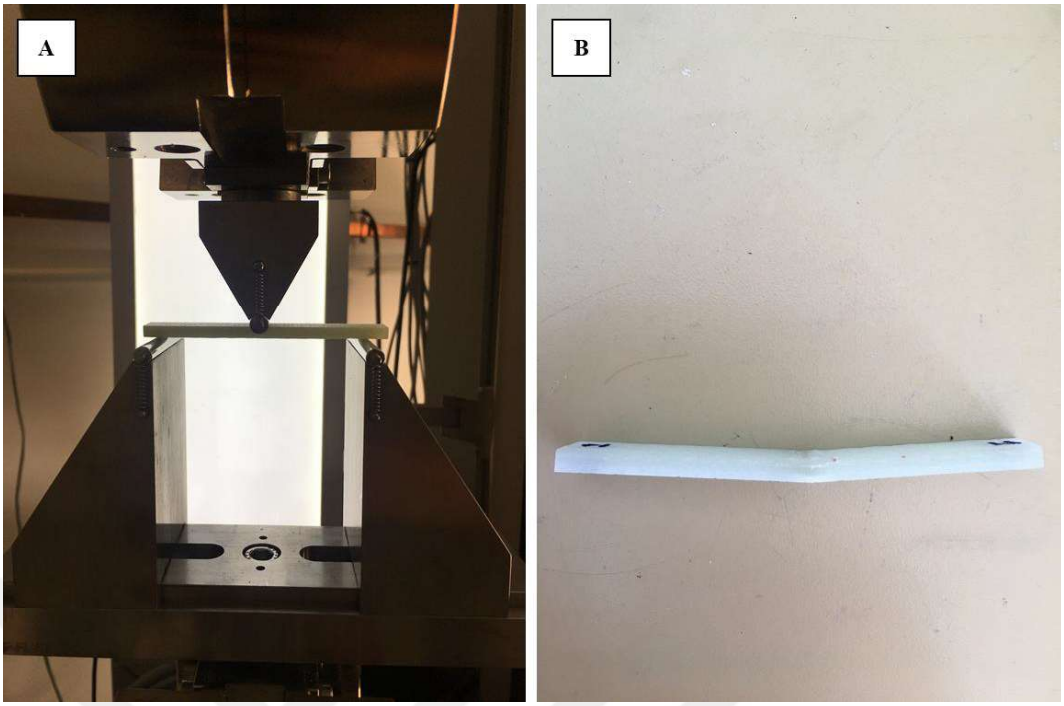

Figure 4.3 (A) Three-Point Bending Test Fixture with Located Specimen, (B) After Three-Point Bending Test Bending Test

Flexural Stress values are calculated for any point on the load-deflection curve by the following equation given in Equation (4.1) [93]:

$$\sigma = \frac{3PL}{2bh^2} \quad \textbf{(4.1)}$$

where;

σ is the stress at the outer surface at mid-span, MPa [psi],

P is the applied force, N [lbf],

L is the support span, mm [in.],

b is the width of the beam, mm [in.],

h is the thickness of the beam, mm [in.].

Flexural Modulus values are calculated according to following equation that is given in Equation (4.2) [93]:

$$E_f^{secant} = \frac{L^3 m}{4bh^3} \quad \textbf{(4.2)}$$

where;

E_f^{secant} is the flexural secant modulus of elasticity, MPa [psi],

L is the support span, mm [in.],

b is the width of the beam, mm [in.],

h is the thickness of the beam, mm [in.],

m is the slope of the secant of the force – deflection curve.

4.2. Hardness Test

To see the effect of MWCNTs on the hardness of composite materials, Shore Hardness and Vickers Microhardness Tests have been conducted in accordance with ASTM D 2240 – Standard Test Method for Rubber Property – Durometer Hardness and ASTM E384 – Standard Test Method for Micro indentation Hardness of Materials.

Shore hardness measures resistance of materials against applied pressure with indentation. There are different types of Shore Hardness to measure hardness of different materials such as Shore 00, Shore A and Shore D. According to Shore Hardness Scales given in **Figure 4.4**, Shore D Hardness has been used in this study [94].

Figure 4.4 Shore Hardness Scale [94]

Shore D hardness values have been taken from three different point on each different composite specimens. The test has been carried out at TUBİTAK SAGE Infrastructure facility by using PosiTector® Shore Hardness Durometer. The measurement has been conducted with needle at the end of the gauge. When pressure is applied to composite materials, needle has penetrated to materials. The device gives the Shore D Harness value after penetration process. The process is shown in **Figure 4.5**.

Figure 4.5 (A) Shore D Hardness Test, (B) After Indentation to Composite Material

Vickers Microhardness Test has been conducted for three different point on composite materials produced by different production method. The test has been carried out at TUBİTAK SAGE Infrastructure facility by using DuroScan Microhardness Tester. Test force has been chosen as 5.0 kgf. The process is shown in **Figure 4.6**.

Figure 4.6 (A) Vickers Hardness Test, (B) After Indentation to Composite Material

4.3. Fractographic Analysis

Scanning Electron Microscopy (SEM) has been used for the following purposes:

- To evaluate distribution of MWCNTs in epoxy system and on glass fibers,
- To see the effect of MWCNTs to mechanical properties of GFEC,
- To identify damage and degradation micro-mechanisms for deformed composite materials.

The analysis has been carried out at Middle East Technical University Metallurgical and Materials Engineering Department Electron Microscopy Laboratory by using FEI Nova Nano SEM 430. Analysis has been carried out to one specimen of each plate.

Before the analysis, all samples have been covered with gold to provide the conductivity to get desired image. Gold-plated specimens are given in **Figure 4.7**.

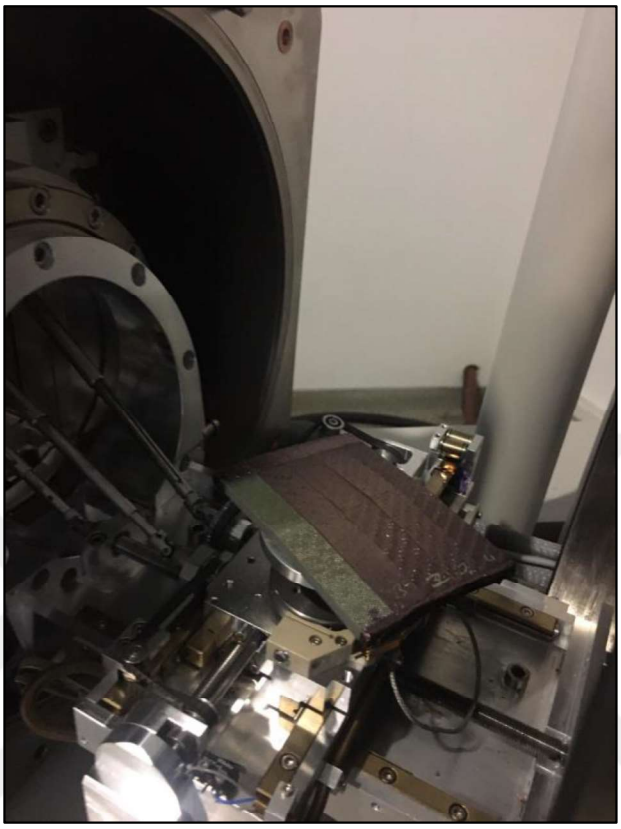

Figure 4.7 Gold-Plated Composite Specimens for SEM Analysis

CHAPTER 5

RESULT AND DISCUSSION

5.1. Three-Point Bending Test Results and Comparison Plots

Three-Point Bending Test has been conducted to determine flexural properties of composite materials that are significant data to understand fiber/matrix interfacial interaction through the thickness direction. In this study, Three-Point Bending Test has been conducted to see the effects of different production methods on through thickness/z direction properties of Multi-walled Carbon Nanotubes grafted and non-grafted glass fiber reinforced epoxy matrix composites. This test has been applied to three specimens of each series and results are given in **Table 5.1**.

Table 5.1 Three-Point Bending Test Results of Specimens Produced with Different Production Methods

Production Methods	Specimens	E_H (GPa)	S_M (MPa)	r_{max} (mm)	L (mm)	h (mm)
Control Samples	Specimen-1	16.736	398.006	5.472	70.400	4.480
	Specimen-2	16.635	379.179	4.837	70.400	4.470
	Specimen-3	17.181	394.266	5.258	70.400	4.440
Direct Mixing Method with Surfactant	Specimen-1	16.490	323.716	3.577	64.000	3.980
	Specimen-2	19.828	350.944	3.803	62.400	3.900
	Specimen-3	17.915	396.094	4.160	64.000	3.970
Direct Mixing Method without Surfactant	Specimen-1	17.585	361.269	4.662	69.280	4.280
	Specimen-2	16.570	356.797	6.048	69.280	4.320
	Specimen-3	17.353	366.031	5.608	69.280	4.300
Spray Method	Specimen-1	20.097	404.125	4.492	62.020	3.800
	Specimen-2	20.779	407.582	3.857	62.020	3.800

Production Methods	Specimens	E_H (GPa)	S_M (MPa)	r_{max} (mm)	L (mm)	h (mm)
with Surfactant	Specimen-3	19.683	422.221	4.005	62.020	3.880
Spray Method without Surfactant	Specimen-1	17.389	360.061	4.280	67.200	4.190
	Specimen-2	17.099	376.265	5.393	67.200	4.180
	Specimen-3	16.978	366.424	5.423	67.200	4.250

In this study, three-point bending tests have been conducted for three specimens of each production methods to get valid test results. Results given in **Table 5.1**show the highest flexural strength value of control samples with neat epoxy has been obtained as 398,006 MPa in three-point bending tests.

Three-point bending results of MWCNTs grafted GFEC produced by Direct Mixing Method with surfactant (Triton X-100) indicate that the highest flexural strength value has been obtained as 396.094 MPa. Also, the highest flexural strength has been obtained as 366.031 MPa from samples of MWCNTs grafted GFEC produced by Direct Mixing Method without aid of surface-active agent.

Also, in this study, Spray Method has been used to produce GFECs with/without aid of surfactant. The results given in **Table 5.1** show that the highest flexural strength value among samples of MWCNTs grafted GFEC produced by spraying process with aid of surfactant has been obtained as 422.221 MPa. Also, MWCNTs grafted GFEC produced by spraying process without aid of surfactant. Three-point bending test results of this series show that the highest flexural strength has been obtained as 376.265 MPa.

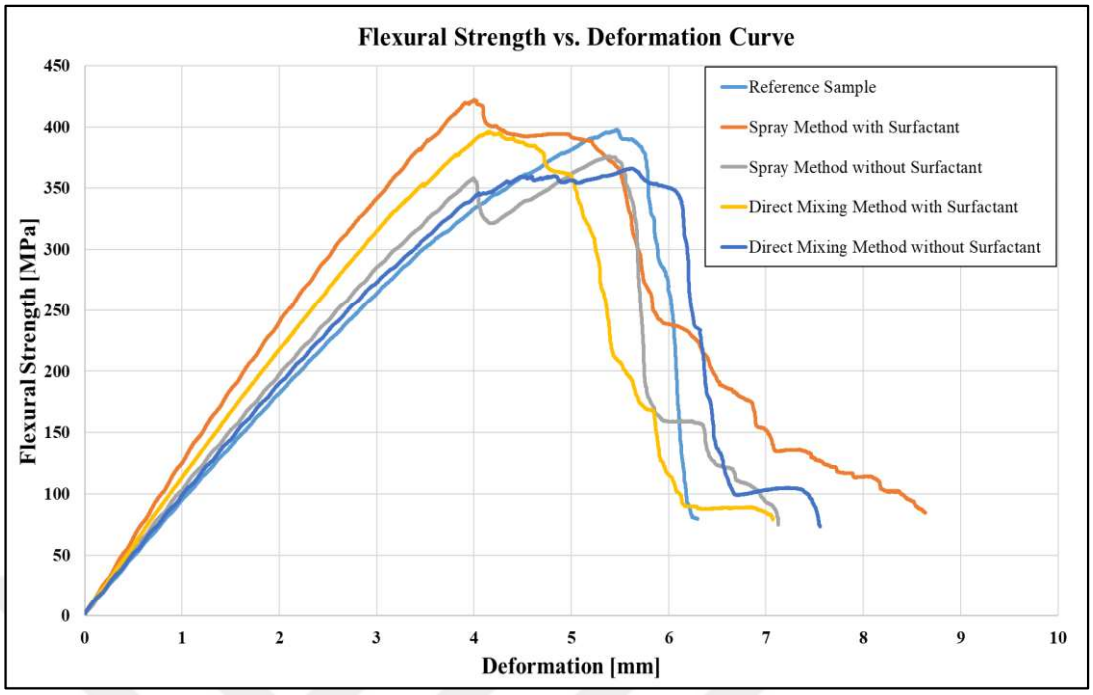

Figure 5.1 Flexural Strength vs. Deformation Curve for Samples

It is observed that from Flexural Strength (MPa) vs. Deformation (mm) curves given in **Figure 5.1**, the composite material produced with neat resin quickly failed after reaching its maximum strength value. This is due to fiber breakage during loading which related to matrix cracking and widening of local delamination. When MWCNTs have been added to GFECs, it is observed on composite materials produced by different production methods that slight decrease in load after reaching its maximum strength value. Although decreasing in the flexural strength of composite materials produced by other methods except for the composite material produced by spray method with surfactant, it is considering that slight decrease in the load because of local increases in the strength which correspond with reduction of matrix cracking and local delamination between interfaces [95-96]. Also, it is observed from Flexural Strength (MPa) vs. Deformation (mm) curve of sample produced by Spray Method without aid of surfactant that the maximum strength value has been reached after primary load fall. This situation indicates that there is a strong adhesion locally between the fiber and the matrix phases [96].

When the force is applied to the specimen surface in Three-Point Bending Test, two different stresses are generated on the both side of the specimen surfaces. These stresses are compressive stress on concave face and tensile stress on convex face. Also, there is neutral axis in mid-plane of specimens where there is no direct stress. The stresses generated during bending test are illustrated in **Figure 5.2**. Curves obtained from mechanical tests (tensile, compressive, bending etc.) can show linear or non-linear behavior. It is clearly seen that Standard Force (MPa) vs. Deformation (mm) curves given in **Figure 5.1** show non-linear behavior. This indicates that crack is initiated from tension side (opposite to loading direction) and it propagates from bottom surface to compression side (upper surface). Then, crack reaches the neutral axis where the interlaminar shear stresses increase with the decreasing tensile stress. Crack initiation from tension side shows that specimens start to lose their strength and Standard Force [MPa] vs. Deformation [%] curves approaches to non-linearity [97], [98].

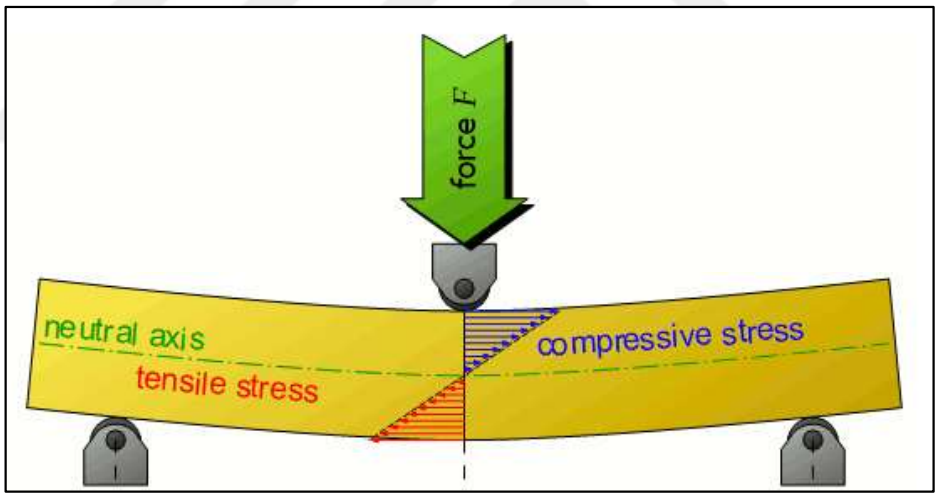

Figure 5.2 Stresses Generated During Three-Point Bending Test [99]

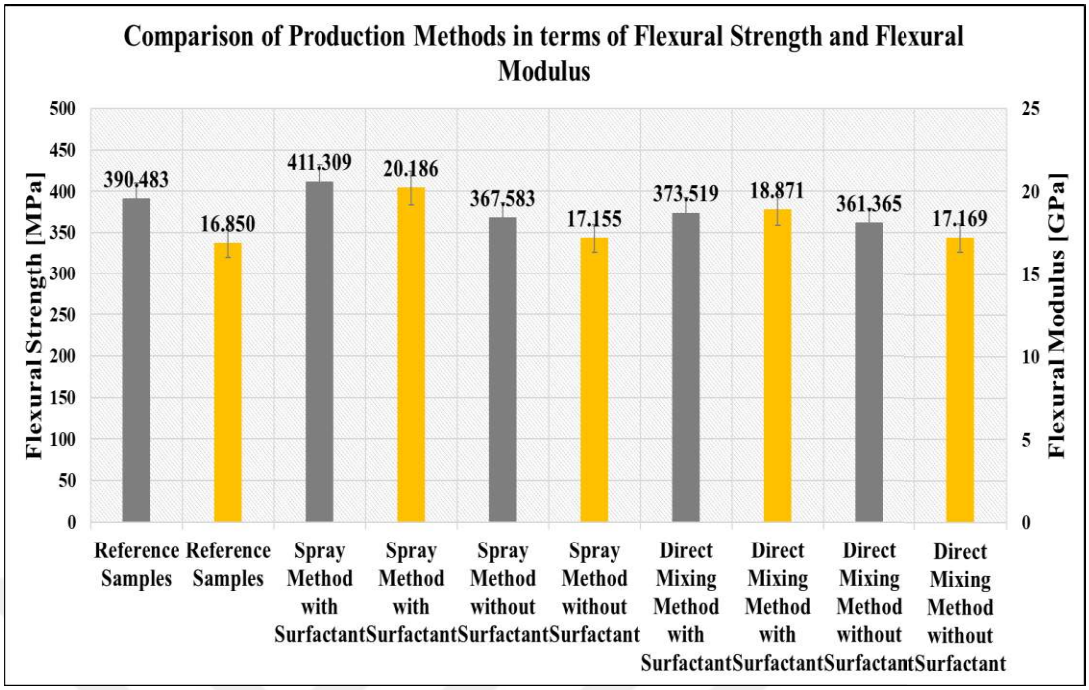

Figure 5.3 Comparison of Specimens Made by All the Utilized Techniques in the Study in Terms of Flexural Strength and Flexural Modulus

In **Figure 5.3**, all results from different production methods are compared in terms of Flexural Strength (MPa) and Flexural Modulus (GPa). When all results are examined, it is clearly seen that the best average flexural strength and average flexural modulus values are obtained as 411.309 MPa and 20.186 GPa from the sample produced by the Spray Method with aid of Triton X-100. The results show that flexural strength and flexural modulus are increased about 5.33% and 19.79% respectively when compared with the control samples. Dalina et al. [100] produced MWCNTs/Carbon Fiber/Epoxy laminated composites by using spraying method. They used Triton X-100 in their productions to improve dispersion of MWCNTs, but their results showed that flexural strength of samples produced by spraying with Triton X-100 decreased when they compared with control samples. On the contrary to study of Dalina et al., the best results are obtained from samples produced by using spraying and Triton X-100 in this study. This indicates that the best homogeneous MWCNTs distribution has been achieved by using spray method in this study. The most homogenous distribution of MWCNTs in structure has been observed by using Scanning Electron Microscopy (SEM). The images obtained from SEM are given in Section 5.3. Homogenously

distributed functionalized MWCNTs with Triton X-100 on the glass fiber surfaces create stronger interface between fiber and matrix phases. This lead to better load transfer from matrix to reinforcement phase and improve the through thickness properties, as observed in the study of Sánchez et al. [95]. They produced carbon fiber reinforced epoxy matrix composited with the different non-functionalized and functionalized carbon nanotube contents. Their results showed that composites with functionalized carbon nanotubes shows better results than non-functionalized carbon nanotube which shows lower interface than composites with functionalized carbon nanotubes.

When the results of composite materials produced by Direct Mixing Method with/without Surfactant and Spray Method without Surfactant are compared with results of control sample, decreases are observed in terms of flexural strength and increases are observed in terms of flexural modulus. The test results of composite material produced by Direct Mixing Method with the aid of Triton X-100 shows that flexural strength is decreased about 4.541% and flexural modulus is increased about 12%. The composite sample produced by Direct Mixing Method without the aid of Triton X-100 shows decreases in flexural strength about 8% and 2% increment in flexural modulus. Also, composite material produced by Spray Method without the aid of surface-active agent shows decreases in flexural strength about 6.2% and increases in flexural modulus about 2%. To improve the mechanical strength of MWCNTs grafted composite materials, CNTs must be dispersed in polymer matrix/organic solvent very well because Van der Waals forces between them increases the tendency of nanotubes to agglomerate. That is lead to poor interfacial interaction between fibers and matrix phase and hinder load transferring from matrix phase to reinforcement phase. The decreases in flexural strength observed in composite materials produced by Direct Mixing Method with/without Surfactant and Spray Method without Surfactant are thought to be due to poor dispersion of MWCNTs in epoxy resin and organic solvent. Poor dispersion forms agglomerated MWCNTs/entangled MWCNTs between epoxy and fibers. Agglomerated MWCNTs have been observed by using Electron Microscope and images are discussed in **Section 5.3**. These regions may act as stress concentration points. Weak matrix/reinforcement interface due to poor dispersion of nanofillers have been reported by many researchers in literature. Panchagnula et al.

[37] studied effects of MWCNTs on mechanical properties of glass fiber reinforced polymer composites. They used different weight ratio of MWCNTs in epoxy matrix. The materials' mechanical properties decreased about 12.02% with the addition of 0.2% MWCNTs as compare to control samples due to poor dispersion. Also, Singh et al. [97] produced different amount MWCNTs grafted glass fiber reinforced polymer composites (GFRP) by hand lay-up and vacuum bagging technique in their study. Their results show that with the addition of 0.5% MWCNTs to glass fiber reinforced polymer composite, decreases in flexural strength were observed about 31% as compare to neat GFRP. Reason of this results were explained with in fractography as poor fiber/matrix interfacial strength.

In the composite materials produced with these methods mentioned above, increases have been observed in flexural modulus while flexural strength has been decreased. Flexural modulus gives the stiffness of the composite materials. CNTs are nanoparticles with excellent stiffness property. It is believed that nanoparticles, which are locally homogeneously distributed between the laminas, increase the modulus value. Sapiai et al. [101] worked on mechanical properties of Kenaf/Glass Fiber hybrid composites with different amount CNTs. Bending test on the five samples from each series shows that flexural strength decreases with increasing CNTs content, but the flexural modulus increases with increasing CNTs content.

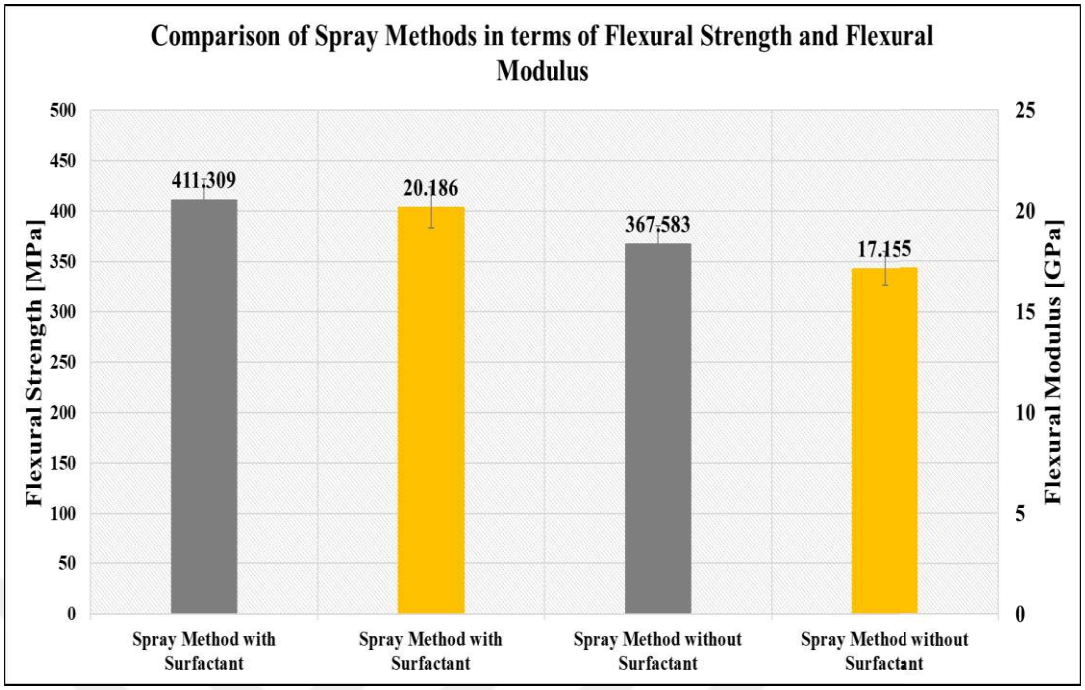

Figure 5.4 Comparison of Spray Method with/without Surfactant in terms of Flexural Strength and Flexural Modulus

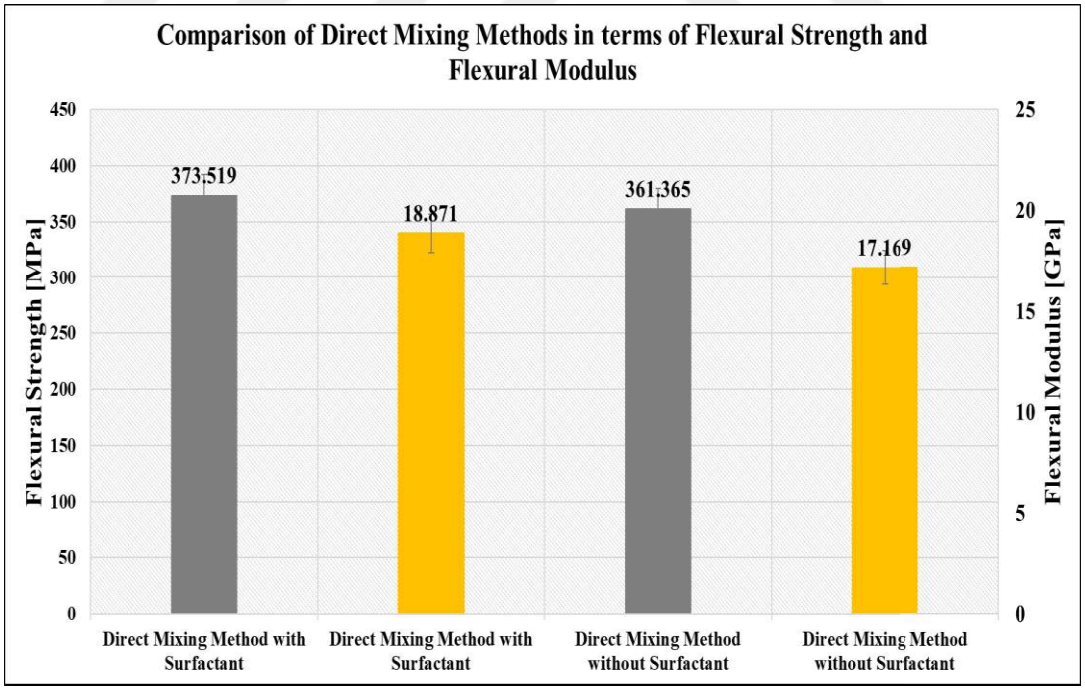

Figure 5.5 Comparison of Direct Mixing Method with/without Surfactant in terms of Flexural Strength and Flexural Modulus

In this study, MWCNTs have been dispersed in epoxy/organic solvent with/without Triton X-100 to see the effect of surfactant on dispersion. It has been aimed to distribute CNTs more homogeneously by lowering the surface tension of MWCNTs with using non-ionic surfactant (Triton X-100) which is one of the non-covalent physical processes. Considering the average flexural strength and average flexural modulus values given in **Figure 5.4** and **Figure 5.5**, composite materials produced with the aid of Triton X-100 showed better flexural strength and flexural modulus than composite materials produced without the aid of Triton X-100. In addition, best flexural strength and flexural modulus values have been obtained on composite materials produced by Spray Method with the aid of Triton X-100. Also, Geng et. al [102] enhanced dispersion of CNTs in epoxy matrix and mechanical properties of CNT/epoxy nanocomposites by using Triton X-100.

Even if the mechanical properties of the composite material produced by the Direct Mixing Method with the help of surfactant are higher than that of the composite materials produced by Spray and Direct Mixing Methods that are not produced with surfactant, decreases in flexural strength is observed about 4.541% as compared to control samples. Also, the bending tests performed on the three samples taken from this composite material, it has been observed that the distribution of results are not close to each other. This is thought to be because of local residual acetone remain in polymeric network which cannot be easily detected during manufacturing [103-104]. Galtieri et al. [104] worked on how the solvent affects the mechanical behavior of resin/CNTs nanocomposites. They concluded in their study that small amount of residual acetone in epoxy network can decrease the flexural strength.

5.2. Hardness Tests Results and Comparison Plots

In this study, Shore D and Vickers Hardness Tests have been conducted to see the effect of same amount of MWCNTs on surface hardness of the composite materials produced by different methods. **Table 5.2** gives the hardness values read from devices and their mean hardness values. Also, **Figure 5.6** and **Figure 5.7** give hardness tests results comparison charts.

Table 5.2 Shore D and Vickers Hardness Tests Values

Shore D Hardness					
#	Control Samples	Direct Mixing - with Surfactant	Direct Mixing - without Surfactant	Spray Method - with Surfactant	Spray Method - without Surfactant
1	86	92	90	90	90
2	84	90	90	91	89
3	87	92	89	87	89
Average	85.7	91.3	89.7	89.3	89.3
Vickers Hardness (HV5)					
#	Control Samples	Direct Mixing - with Surfactant	Direct Mixing - without Surfactant	Spray Method - with Surfactant	Spray Method - without Surfactant
1	52.6	62.8	67.4	61.5	62.3
2	50.2	67.9	65.8	62.7	64.2
3	54.7	68.9	63	66.8	62.1
Average	39.375	49.9	49.05	47.75	47.15

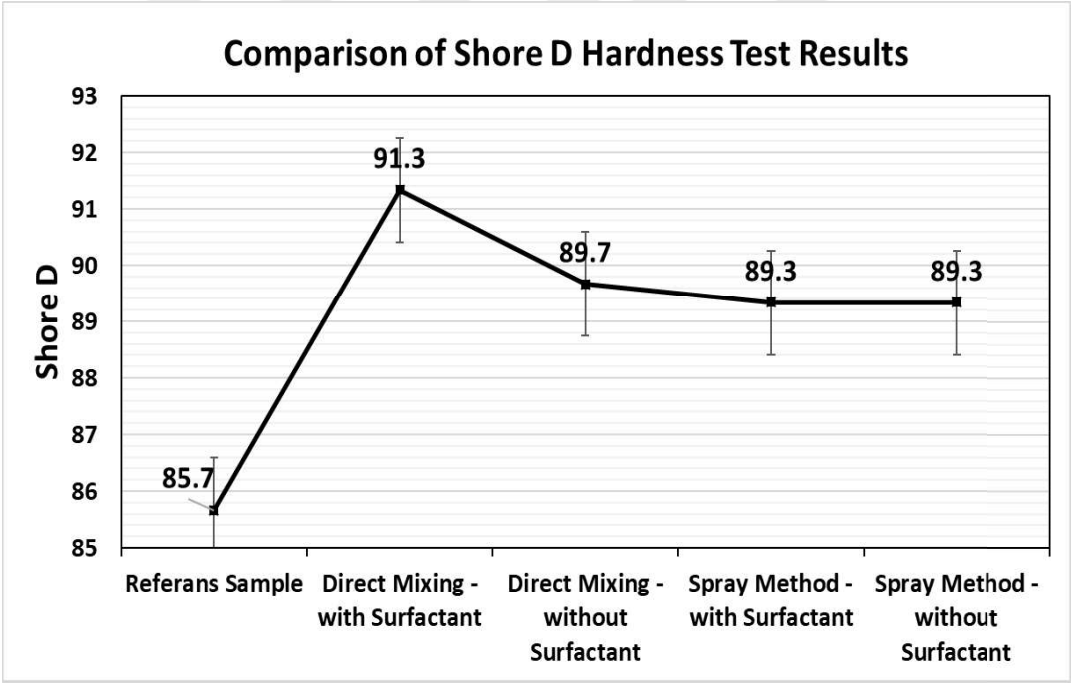

Figure 5.6 Comparison of Shore D Hardness Test Results

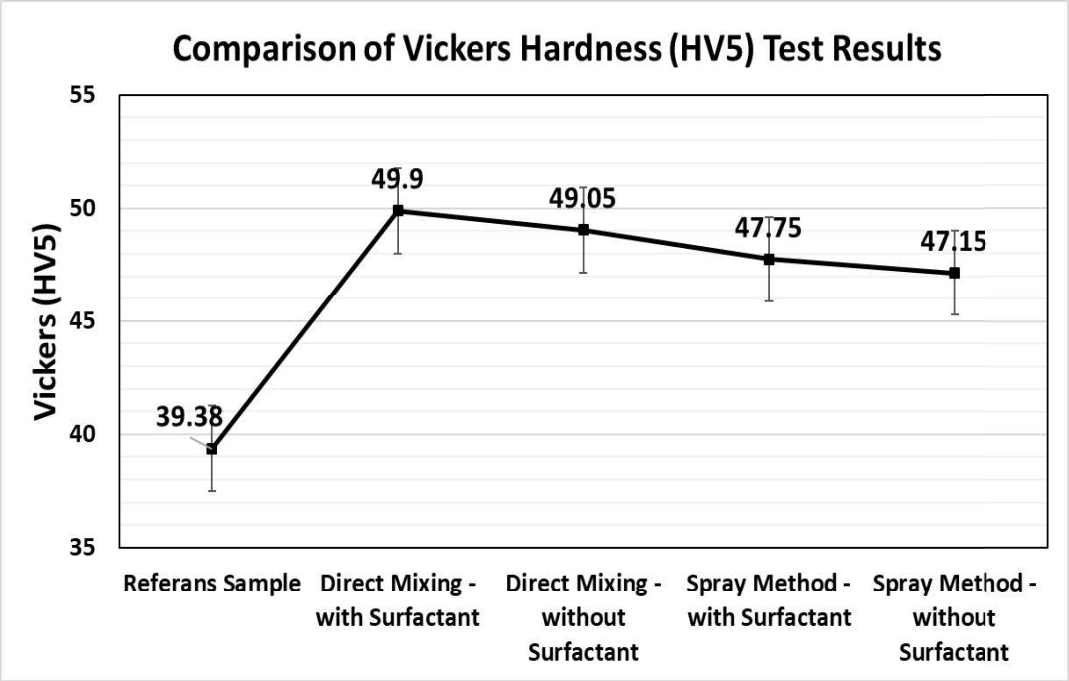

Figure 5.7 Comparison of Vickers Hardness Test Results

It is clearly seen from the Shore D and Vickers hardness test results that increases in hardness are observed with addition of MWCNTs to the GFECs. When the test results are investigated, best surface hardness values are obtained in composite material produced by Direct Mixing Method with Surfactant for two different measurement methods. Increases in hardness values are observed about 6.5% for Shore D Hardness and about 26% for Vickers Hardness as compared to control sample. When the hardness values obtained from the production methods are compared with each other, there was not much difference between the two measurement methods in terms of hardness values. The reason for this is thought to be keeping the amount of MWCNTs constant in all production methods. Also, when the direct mixing method is compared with the Spray Method, the composite materials produced by the Direct Mixing Method showed a slight increase in hardness. It is believed that this is due to directly mixing of MWCNTs with epoxy. In addition to this, although the MWCNTs have been sprayed on the glass fibers by spray method, it is believed that applied resin to each fiber by hand lay-up process forms a network between matrix and MWCNTs. This situation causes an increase in hardness. Also, conducted studies in literature [105-107] show that with the addition of CNTs to polymer composite materials enhance the

hardness performance of composite materials. This situation is explained in literature that CNTs in polymer matrix increase the viscosity of polymer material that leads to reduction on the movement of polymer molecules. This leads to increases material resistance against indentation and improve hardness of polymer matrix materials [108].

5.3. Scanning Electron Microscopy Analysis

To see the effect of Spray Method with/without Triton X-100 and Direct Mixing Method with/without Triton X-100 on the dispersion of MWCNTs on the glass fiber and in epoxy system and to identify damage and degradation micro-mechanisms for produced composite materials, Scanning Electron Microscopy has been used. In this analysis, images have been taken from the fractured surface of the specimens.

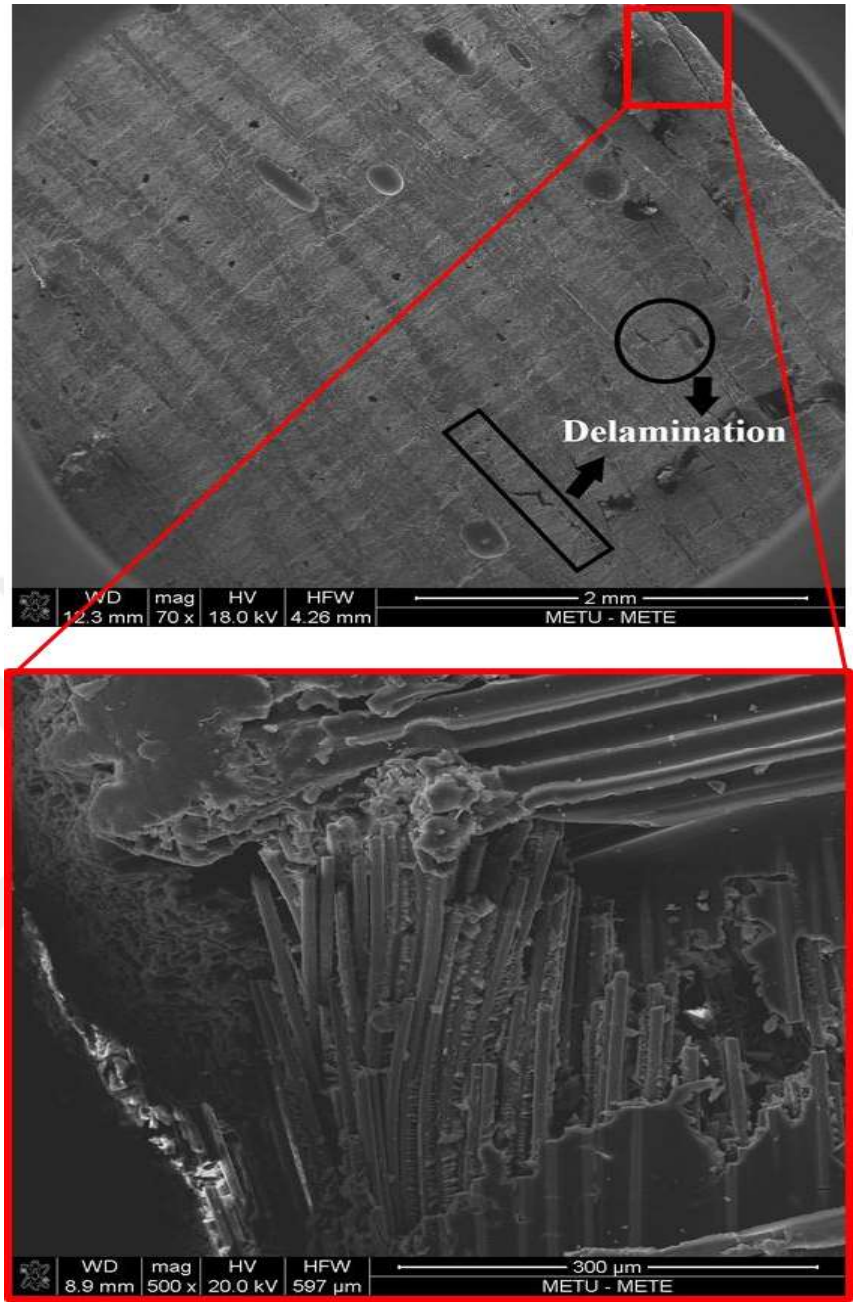

Figure 5.8 SEM Images of Neat GFRC Showing Fractured Glass Fibers and Delamination

Figure 5.8 and **Figure 5.9** show the SEM images of neat Glass Fiber Reinforced Epoxy Matrix Composite (GFRC) material from the fractured surface of specimen. **Figure 5.8** shows failure behavior of neat GFRC materials after three-point bending test. In this composite material, it is clearly seen that there is a slight separation between the laminates. This failure mode encountered in unfilled GFRC is delamination or ply splitting which occurs between laminates due to the interlaminar

shear forces. Delamination generally occurs due to matrix dominated fracture and fiber/matrix interfaces. Once the bending force is applied to composite materials, crack is developed on the matrix phase due to weak fiber and matrix interface. This situation causes the delamination between laminates. Delamination can affect through thickness properties of composite materials. Also, fractured fiber bundles on the surface of unfilled GFRC material are given in **Figure 5.8**. Epoxy-free regions are easily visible on the broken fiber bundle. This situation causes debonding between fibers and weak fiber-matrix interface [97-98, 109].

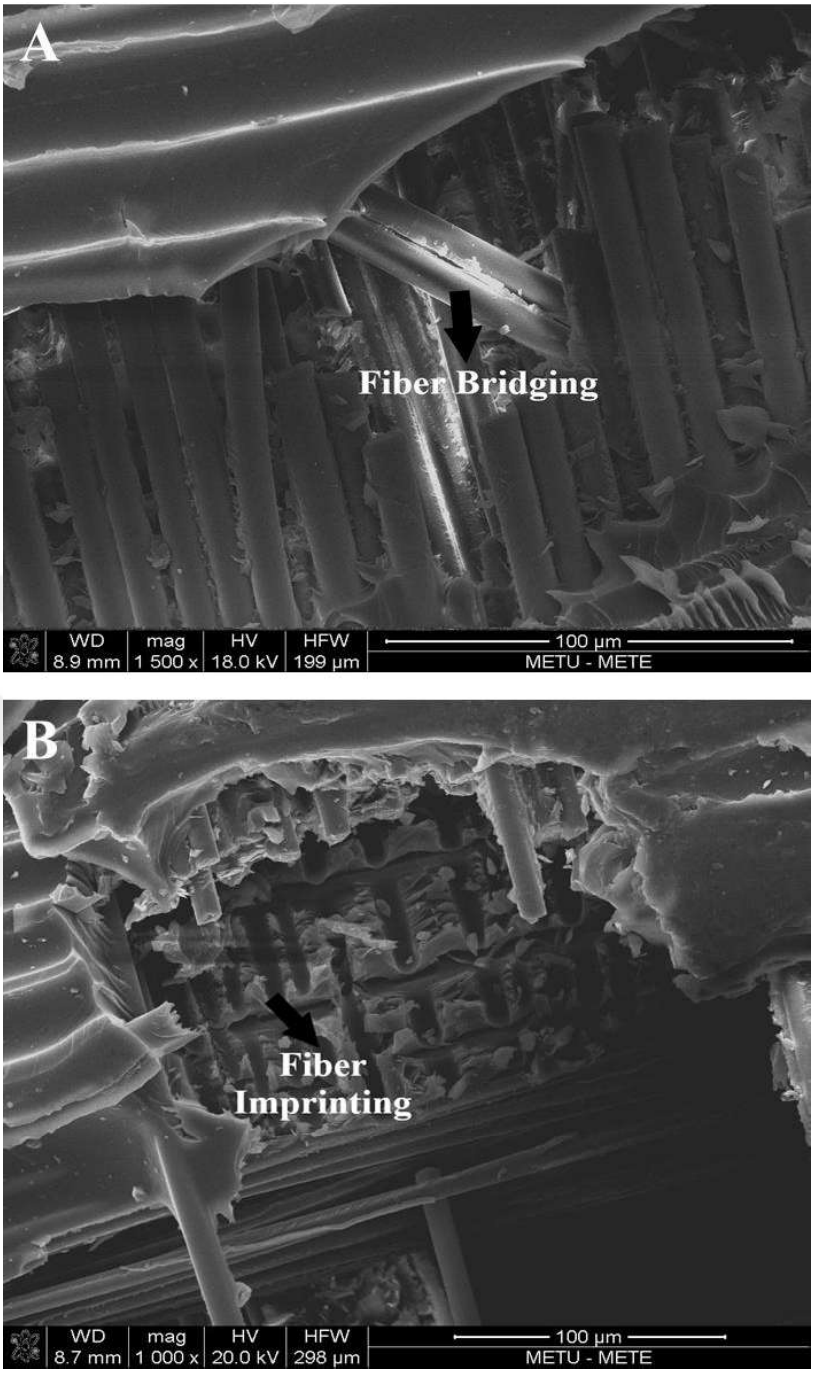

Figure 5.9 SEM Images of Neat GFRC Showing (A) Fiber Bridging and (B) Fiber Imprinting

Fiber bridging and fiber imprinting are important phenomenon in fractured surface of the GFRCs. **Figure 5.9** (A) shows the fiber bridging that create resistance mechanism against to delamination between laminates. In the fiber bridging phenomenon, fibers create bridges between adjacent plies that increases inter-laminar properties and

improve the resistance to delamination. Khan [110] showed effect of fiber bridging in composite materials in his review study. **Figure 5.9** (B) gives the fiber imprinting where delamination between matrix and fiber clearly seen. Fiber imprinting is brush like failure that is due to weak bonding strength between fiber and matrix materials [109]. Singh et al. [97] defended in their thesis that fiber imprints in longitudinal direction gives us the direction of crack propagation in matrix dominated failures. It is believed that the direction of crack propagation is parallel to the fiber imprints.

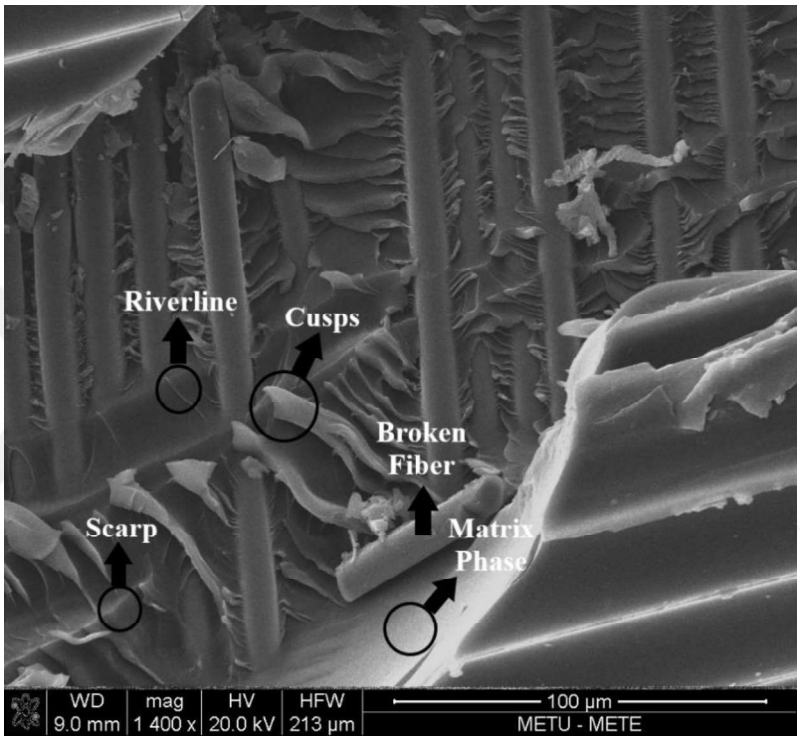

Figure 5.10 Characteristic Features of unfilled GFRC

In **Figure 5.10**, some important matrix dominated fractographic features emerged with the shear forces are given. These features give the information on crack growth and shear direction. One of these characteristic features is cusp that become visible as raised outgrowth on the fractured surface. The cusps give the evidence to determine shear direction are clearly seen on the SEM images from **Figure 5.10**. Greenhalgh [109] explained how to determine the shear direction by using cusps in her study. According to Greenhalgh, fractured surface moves in the opposite direction of cusps orientation. **Figure 5.11** gives schematically appearance of cusps. In **Figure 5.10**, it is clearly seen from rounded area that cusps orientation is to the left direction,

considering the study in the literature, the direction of the shear forces formed here is thought to be to the right.

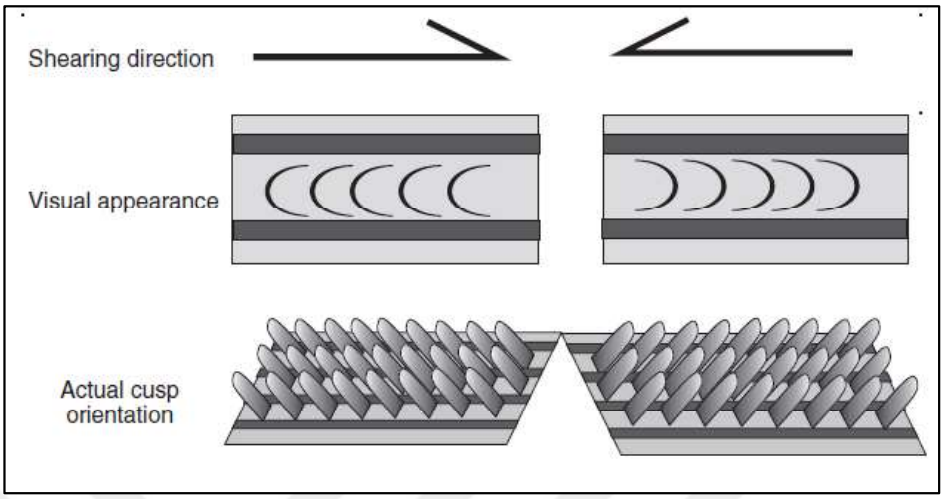

Figure 5.11 Relation Between Cusp Orientation and Shearing Direction [109]

Another important feature in the fractured surface of neat GFRC is the riverline formation that is a significant sign of the local crack growth direction. The riverlines converge into one crack plane that give the direction of crack growth. Boundary of two crack planes form another crucial feature, scraps that show tendency to be aligned parallel with crack growth direction [109]. In **Figure 5.10**, scrap is rounded that shows us the crack growth line that is thought to be parallel to the scrap alignment. As a result of SEM images, it is believed that main fracture mechanism in unfilled GFRC is matrix dominated due to cohesive failure in the matrix phase that covers the fibers.

In this study, one of the production methods is Direct Mixing Method without Surfactant where MWCNTs have been directly mixed with matrix material without surface active agent by using shear forces. **Figure 5.12** to **Figure 5.15** give the images of SEM analysis of composite materials produced by Direct Mixing Method without Triton X-100.

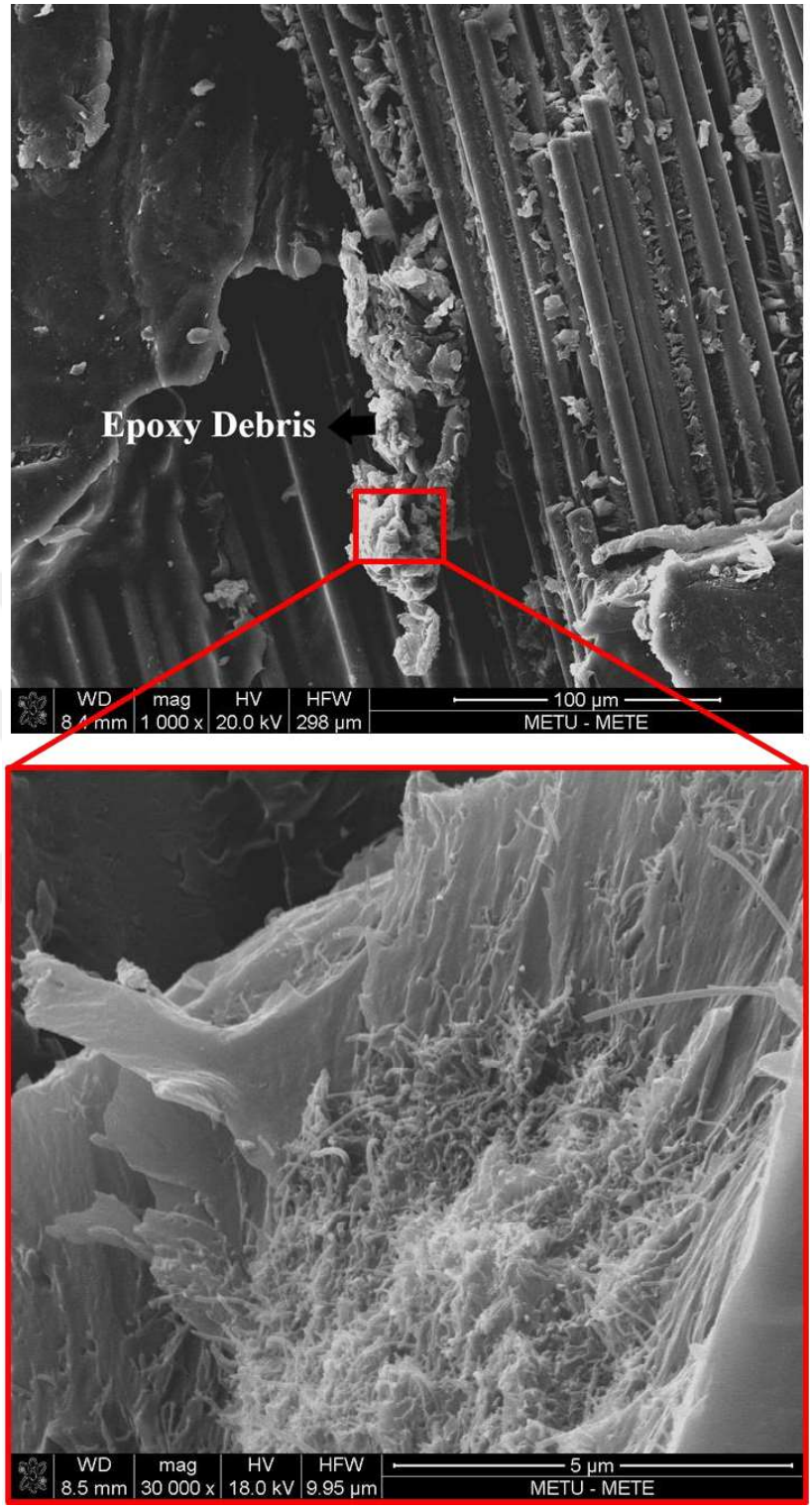

Figure 5.12 SEM Image of Composite Material Produced by Direct Mixing Method without Surfactant Showing Epoxy Debris and MWCNTs Agglomeration

In the production of MWCNTs doped GFRC material by Direct Mixing Method without the aid of surfactant, CNTs have been directly mixing with epoxy matrix. In **Figure 5.12**, epoxy matrix micrograph from SEM analysis is investigated. It is clearly seen from image that a lot of matrices residue/debris is holding on the glass fibers surfaces. If MWCNTs are dispersed homogeneously, it is expected that the matrix residues provide a better adhesion to glass fibers surfaces that causes strong fiber/matrix bonding and increases in flexural properties. Singh et al. [97] obtained images of surface debris/matrix residues in their composite materials by using SEM and they concluded that matrix residue/surface debris supply better sticking to fiber surface that causes better bonding strength between polymer matrix and fiber surfaces. But in this study, matrix residues are thought to have the opposite effect due to the agglomeration of MWCNTs that is clearly seen in **Figure 5.12**. It is anticipated that the agglomerated MWCNTs create a stress-increasing zone in the matrix phase, resulting in composite materials produced by Direct Mixing Method without Surfactant having less flexural strength as compared to the unfilled GFRC.

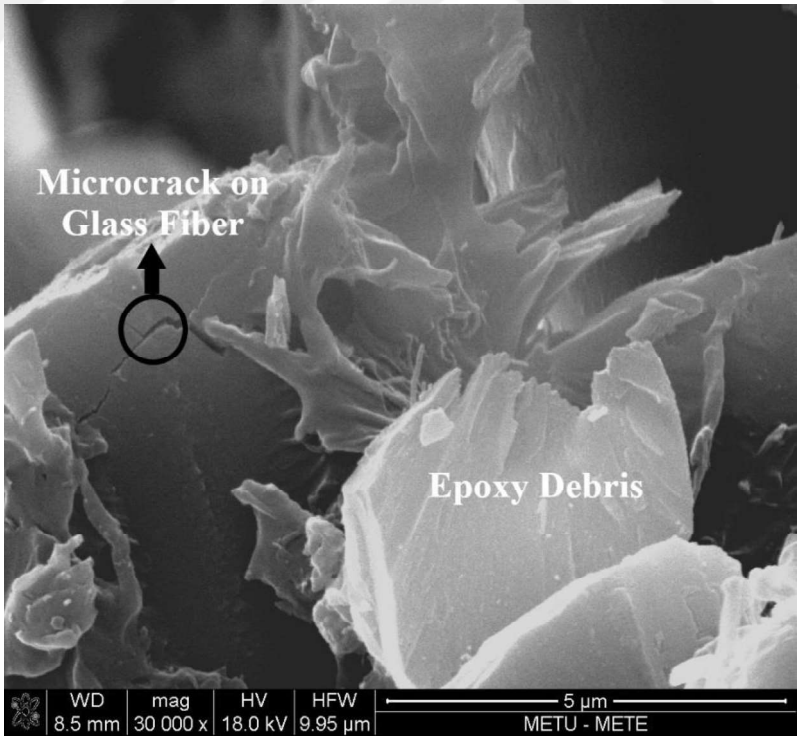

Figure 5.13 SEM Image of Composite Material Produced by Direct Mixing Method without Surfactant Showing Microcrack Mechanism on Glass Fiber

Figure 5.13 shows microcrack on the glass fiber that gives a significant failure mechanism, translaminar fracture that is fiber dominated failure mechanism. The microcrack seen on the glass fiber of the composite material produced by Direct Mixing Method without Triton X-100 indicates that there is strong fiber-matrix strength in the region where microcrack is seen on the glass fiber. This mechanism and its effects are explained by Greenhalgh [98] in her study.

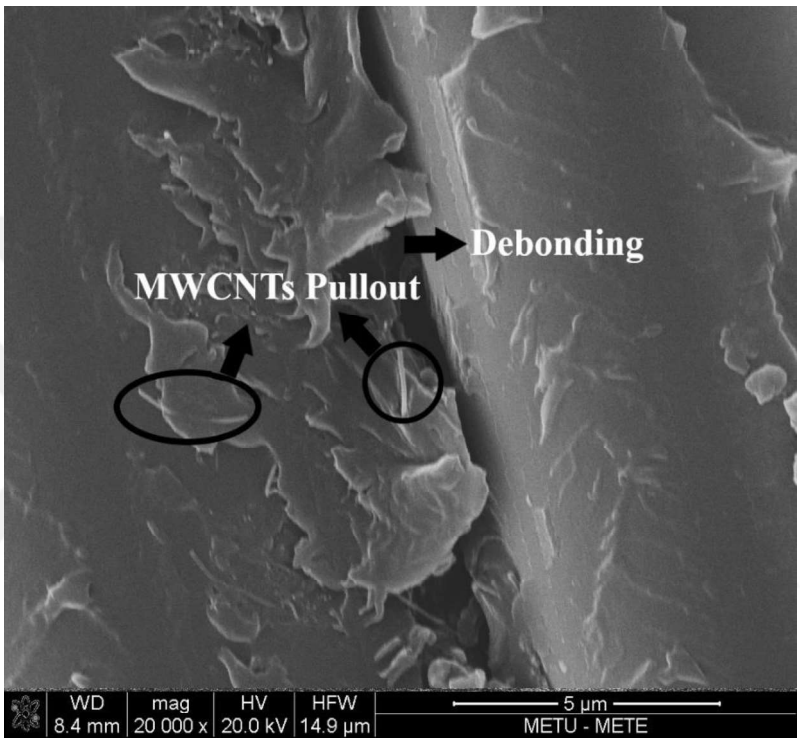

Figure 5.14 SEM Image of Composite Material Produced by Direct Mixing Method without Surfactant Shows MWCNTs Behavior

Figure 5.14 reveals the behavior of MWCNTs in the epoxy matrix that directly mixed with epoxy and depicts debonding between glass fibers. It is clearly seen on SEM image that MWCNTs come out and are lying on the surrounding matrix. This situation directly affects the mechanical through thickness properties of MWCNTs filled GFRC material because these carbon nanotubes cannot improve the interfacial bonding between fiber and matrix phases. Therefore, CNTs cannot effectively transfer the stresses coming into the epoxy to the glass fibers, resulting in poor fiber matrix interphase. This causes the reduction in the flexural properties. In addition to MWCNTs pullout, interfacial debonding mechanism is observed from the SEM image

of composite material produced by Direct Mixing Method without Surfactant. Interfacial debonding between the glass fibers is matrix dominated failure and is the indication of poor fiber-matrix interfacial strength that causes decreasing in through thickness properties of MWCNTs filled GFRC. This situation is directly related to dispersion of MWCNTs into epoxy matrix [97].

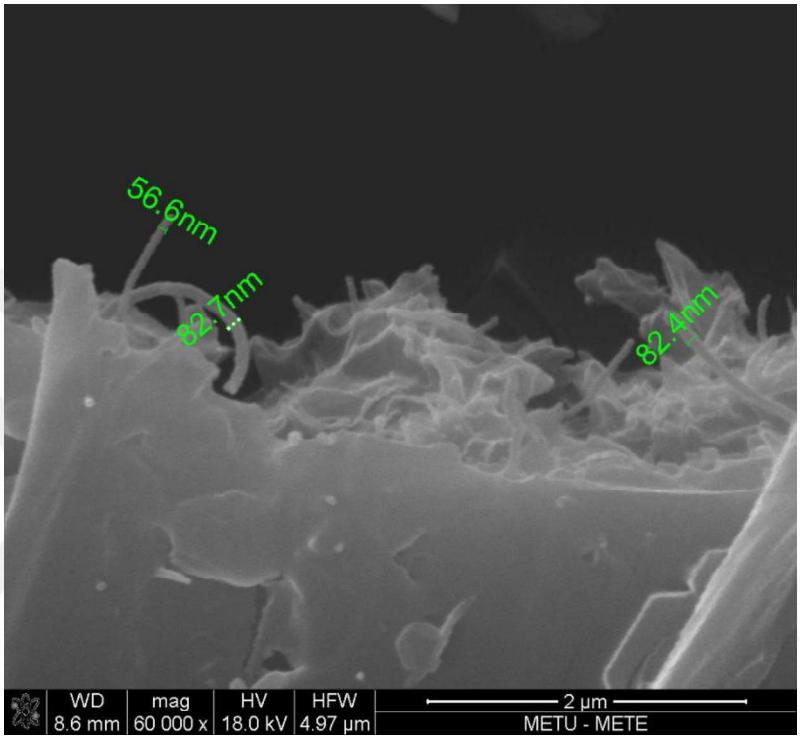

Figure 5.15 SEM Image of Composite Material Produced by Direct Mixing Method without Surfactant Showing Dimensions of MWCNTs

Diameters of MWCNTs have been measured by using SEM image from composite material produced by Direct Mixing Method without Surfactant. **Figure 5.15** gives diameters of three MWCNT as 56.6 nm, 82.7 nm and 82.4 nm. When the results are compared with the diameters by HAZARFEN, it is observed that the diameters of MWCNTs are within the range guaranteed by the manufacturer.

Triton X-100 nonionic surface-active agent has been used in production of composite material by Direct Mixing Method to see the effects on dispersion of MWCNTs in epoxy and organic solvent. In **Figure 5.16**, fracture mechanism and fractographic

features are depicted and **Figure 5.17** gives SEM image about the effects of surfactant on the dispersion of MWCNTs in epoxy matrix.

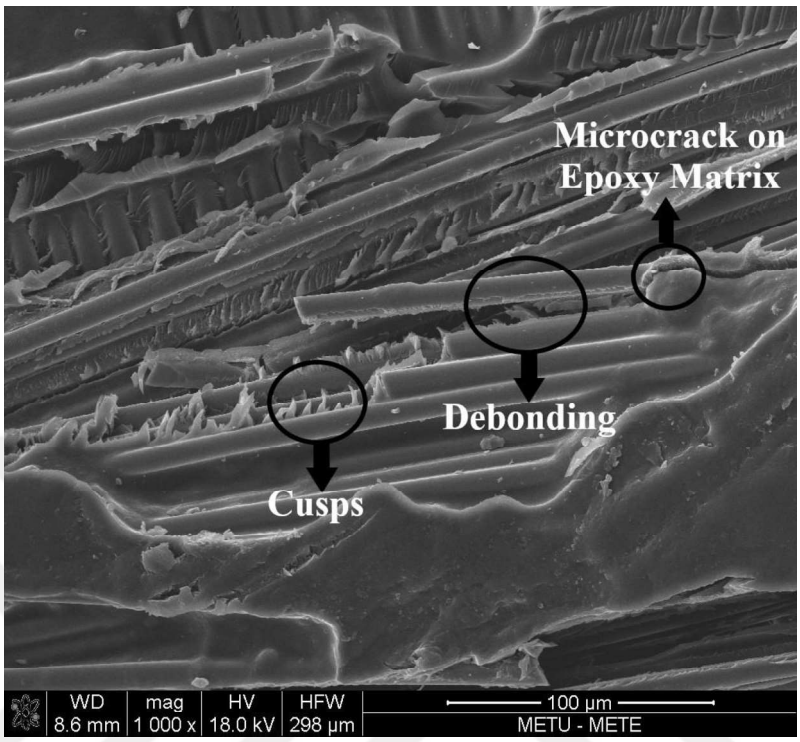

Figure 5.16 SEM Image of Composite Material Produced by Direct Mixing Method with Surfactant Showing Fractographic Features and Fracture Mechanisms

In **Figure 5.16**, cusps are clearly seen on fractured surfaces. They give information on direction of shear forces. In the SEM image, it is seen obviously that cusps are directed to right side which means the direction of the shear forces formed here is thought to be to the right. Also, **Figure 5.16** reveals fracture micro mechanism which is matrix dominated failure. It is clearly seen that microcrack is generated by applied load in the epoxy matrix. It is believed that these microcracks coalesce to form unstable macrocracks. When macrocracks reach to glass fiber, shear stresses are generated between fiber/matrix interface which causes debonding between fibers. This situation indicated that weak bonding between fiber and matrix phases negatively affect through thickness properties of composite material.

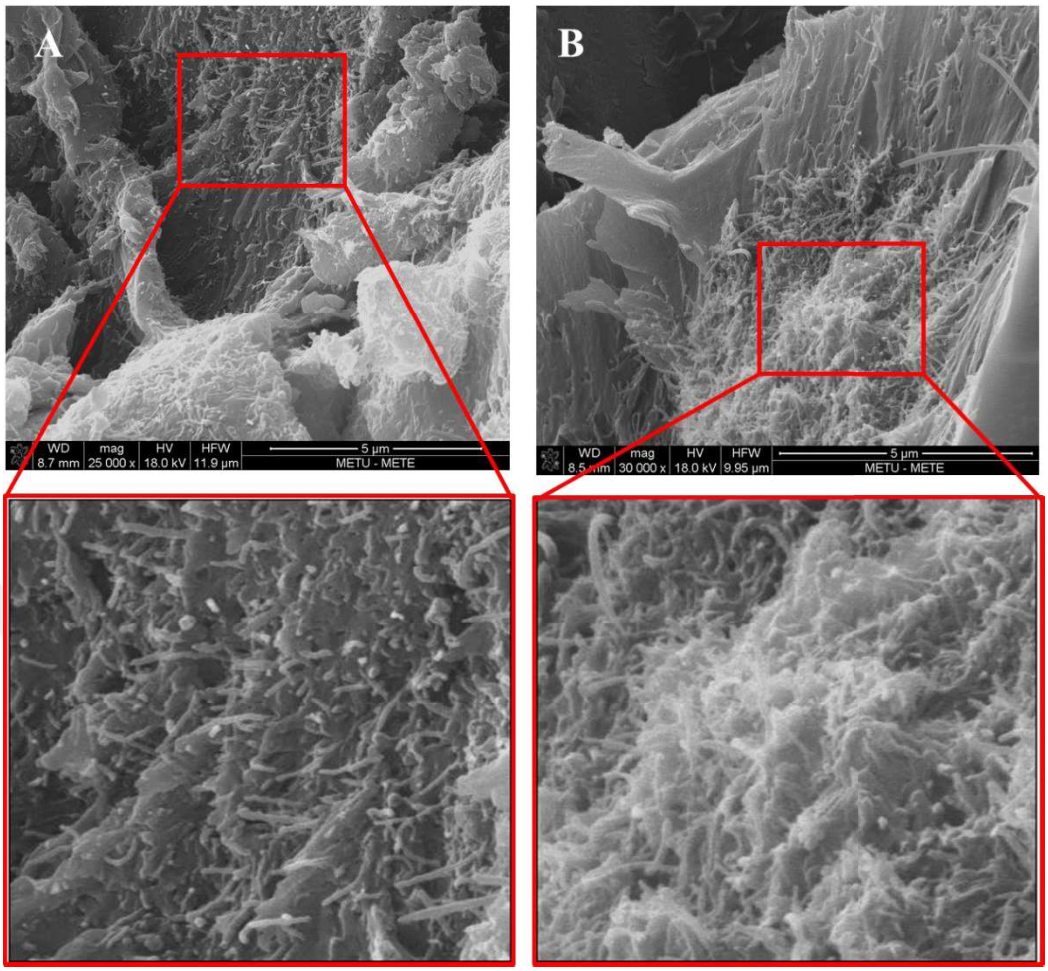

Figure 5.17 Effect of Surfactant on Dispersion of MWCNTs in Epoxy Matrix, (A) SEM Image of Composite Material Produced by Direct Mixing Method with Triton X-100 and (B) SEM Image of Composite Material Produced by Direct Mixing Method without Triton X-100

Figure 5.17 reveals the effect of Triton X-100 that is non-ionic surfactant on the dispersion of MWCNTs in epoxy matrix. In this study, CNTs have been directly mixed with epoxy matrix using two different techniques. These are production with surfactant and production without surfactant. The reason for this is that it is desired to see the effect of the surfactant on the homogeneous mixing of MWCNTs in epoxy matrix and see the effect of surfactant on through thickness properties. ImageJ image processing tool has been used on SEM images of composite materials obtained from two different production methods and the amount of MWCNTs in the same area was examined. It is seen obviously from SEM image obtained from composite material produced with Triton X-100 that MWCNTs show more homogenous distribution. When the SEM

images obtained from the composite material produced without the use of Triton X-100 are examined, the agglomeration of MWCNTs formed in the epoxy matrix due to the Van der Waals forces between tubes can be easily seen. Randhawa et al. [87] in their studies showed the effects of Triton X-100 on the dispersion of MWCNTs. They concluded that MWCNTs show better functionalization after the dispersion of MWCNTs with Triton X-100 than samples produced without surfactant. These situations directly affect the flexural properties of these composite materials. The results of three-point bending test performed on these composite materials to obtain flexural properties overlap with the SEM images obtained. The results (see **Figure 5.3**) of the composite material produced by Direct Mixing Method with the aid of Triton X-100 shows that flexural strength increases about 3.25% and flexural modulus increases about 9.01% as compared to composite material produced by Direct Mixing Method without the aid of Triton X-100.

In this study, one of the production routes of MWCNTs grafted GFRC materials is attachment of MWCNTs onto glass fiber surfaces by using spray method. In this method, organic solvent that contained MWCNTs has been sprayed onto both surfaces of glass fibers. Then, epoxy matrix has been applied by hand lay-up method to produce GFRC materials. As in Direct Mixing Method, productions in Spray Method have been made both by the aid of Triton X-100 and without Triton X-100 to see the effects of Triton X-100 on the dispersion of MWCNTs in organic solvent.

Figure 5.18 and **Figure 5.19** give the SEM images taken from composite material produced by Spray Method without using Triton X-100.

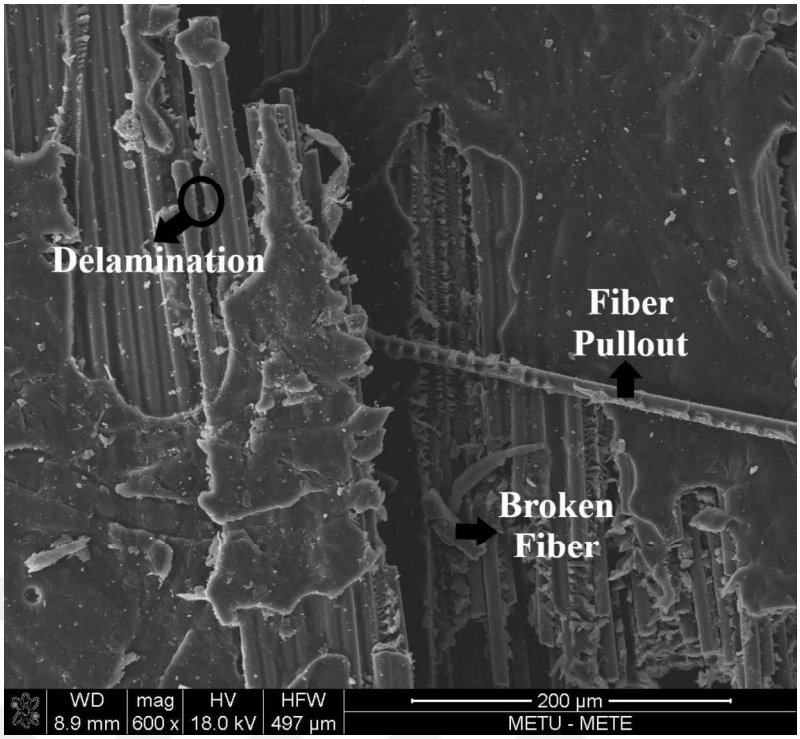

Figure 5.18 SEM Image of Composite Material Produced by Spray Method without Surfactant Showing Fractographic Features and Failure Mechanisms

Figure 5.18 reveals one of the failure mechanisms that is fiber pull-out in the fiber reinforced composite materials. Fiber pull-out mechanism is related to debonding, fiber imprinting and fiber bridging mechanisms. This mechanism is generated during the debonding that is due to the weak bonding between fiber and matrix phases and lead to separation of fiber bundles. Also, fiber pull-out causes the fiber imprinting on the laminates and fiber bridging between plies. All these mechanisms are due to the weak fiber/matrix interfaces. Mechanisms other than fiber bridging have negative effects on flexural properties of composite materials [110-112]. Also, broken fiber is clearly seen on fractured surface in the micrograph given in **Figure 5.18** that is due to the weaker interfacial bonding between glass fiber and matrix materials. It is believed that debonding, fiber pull-out and fiber breakage mechanisms causes reduction in flexural properties of composite material produced by Spray Method without using Triton X-100. Singh et al. [97] revealed these mechanisms on MWCNTs grafted GFRC by using SEM analysis and concluded in their study that these mechanisms

cause the reduction in interlaminar shear strength (ILSS) as compared to neat GFRC material.

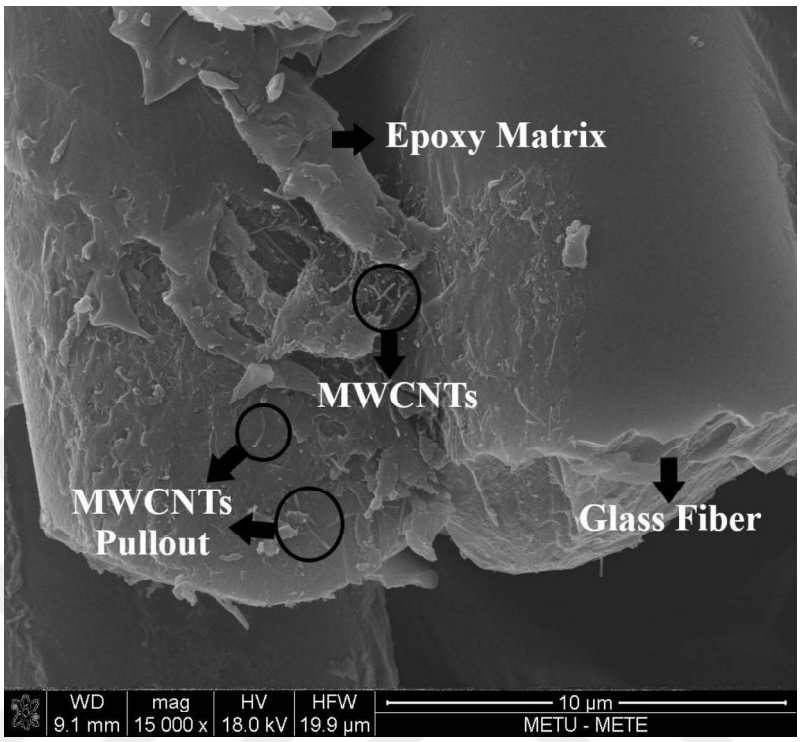

Figure 5.19 SEM Image of Composite Material Produced by Spray Method without Surfactant Showing Dispersion of MWCNTs

During the SEM analysis of the composite material produced by Spray Method without the aid of Triton X-100, MWCNTs could hardly be visualized as compared to composite materials produced by Direct Mixing Method. This is because MWCNTs have been applied directly onto glass fibers. This situation can be clearly seen in **Figure 5.19**. It is believed that the first layer of epoxy applied onto sprayed glass fibers interact with the MWCNTs, so CNTs can be seen in the very thin epoxy layer on the fibers. When SEM image taken from composite material is investigated, it is obviously seen that MWCNTs are distributed onto glass fibers surfaces. Also, **Figure 5.19** shows MWCNTs that lie down onto glass fiber surfaces that is called as MWCNTs pull-out. It is believed that this type of CNTs directly affects the stress transfer capacity of epoxy matrix to glass fibers that causes reduction in the flexural strength of composite material [45, 97]. Singh et al. [97] showed the effect of MWCNTs pull-out mechanism on the flexural properties of MWCNTs grafted GFRC materials and they concluded

that MWCNTs pull-out represents a weak interfacial bonding between carbon nanotubes and epoxy matrix. Also, Shan et al. [45] produced MWCNTs grafted carbon fiber reinforced epoxy composite by using spraying technique and they believed that pulled out MWCNTs can cause agglomeration into epoxy matrix and affect mechanical properties.

Another method that has been used to produce composite material is Spray Method with using Triton X-100. In this study, it was planned to distribute CNTs more homogeneously and to get desired mechanical properties by using surfactant. Also, the best flexural properties have been obtained with the composite material produced by this production method. SEM images taken from composite materials produced by Spray Method with the aid of Triton X-100 are given in **Figure 5.20** to **Figure 5.22**.

Interface between glass fibers and epoxy matrix is given in **Figure 5.20**. Through thickness properties of composite materials are directly related to bonding between fiber and matrix phases. When this bonding is strong where matrix phase can transfer stresses coming from outside sources to the reinforcement phase, better mechanical properties are achieved. In composite material produced by Spray Method, interface between glass fiber and epoxy matrix is believed to be achieved by spraying MWCNTs onto the fiber surface homogenously. It is believed in **Figure 5.20** that MWCNTs onto glass fiber surfaces generate strong chemical bonding and strengthen the interface between glass fiber and epoxy matrix. This is one of the key factors to get better flexural properties as compared to other composite materials produced by different production routes. Davis et al. [43] produced carbon fiber reinforced epoxy composite materials with functionalized carbon nanotubes (f-CNTs) by using spraying methodology. The believed from their study that f-CNTs create strong bond between carbon fiber and epoxy matrix and strengthen the interface between fiber and matrix phases.

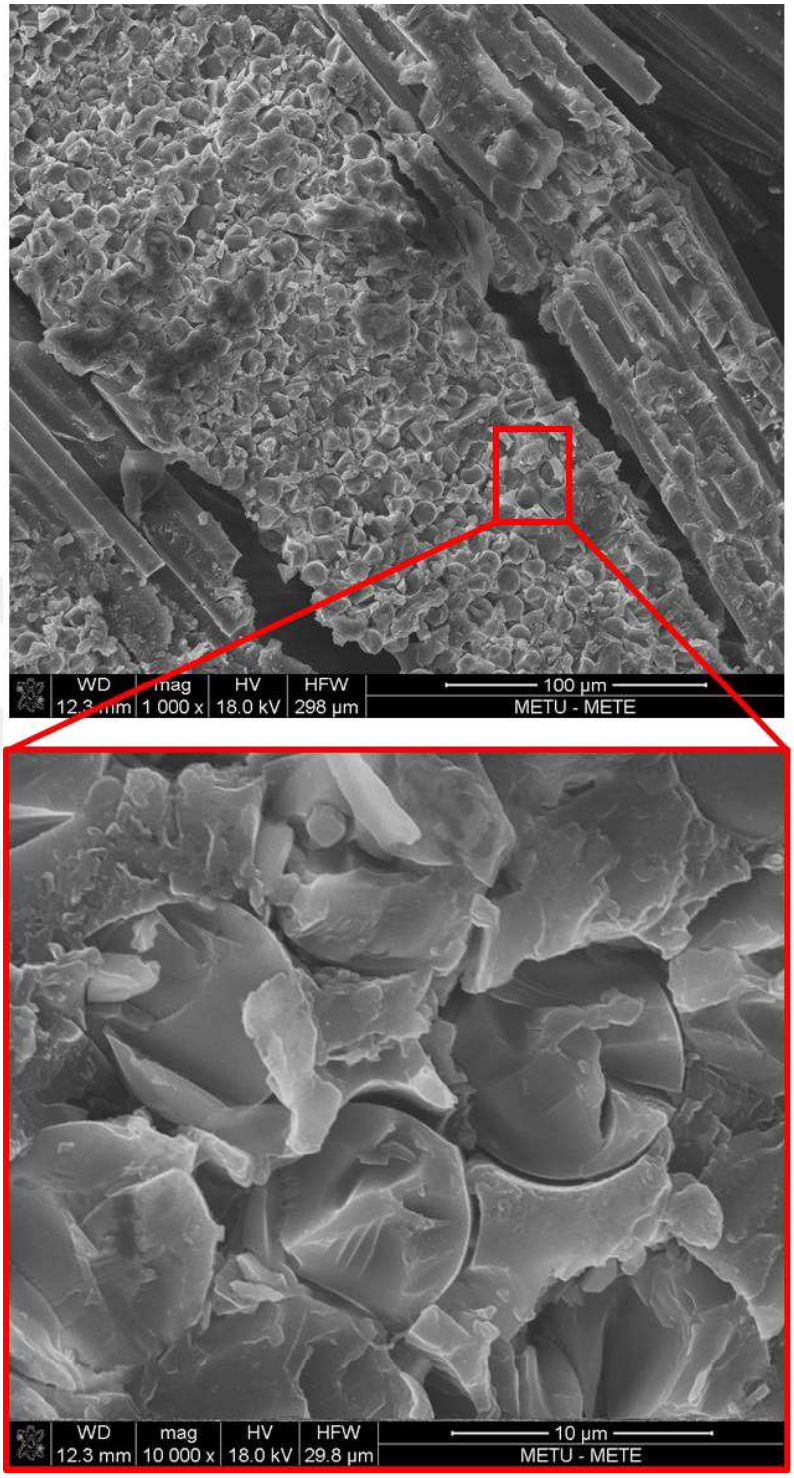

Figure 5.20 SEM Image of Composite Material Produced by Spray Method with Surfactant Showing Fiber/Matrix Interface

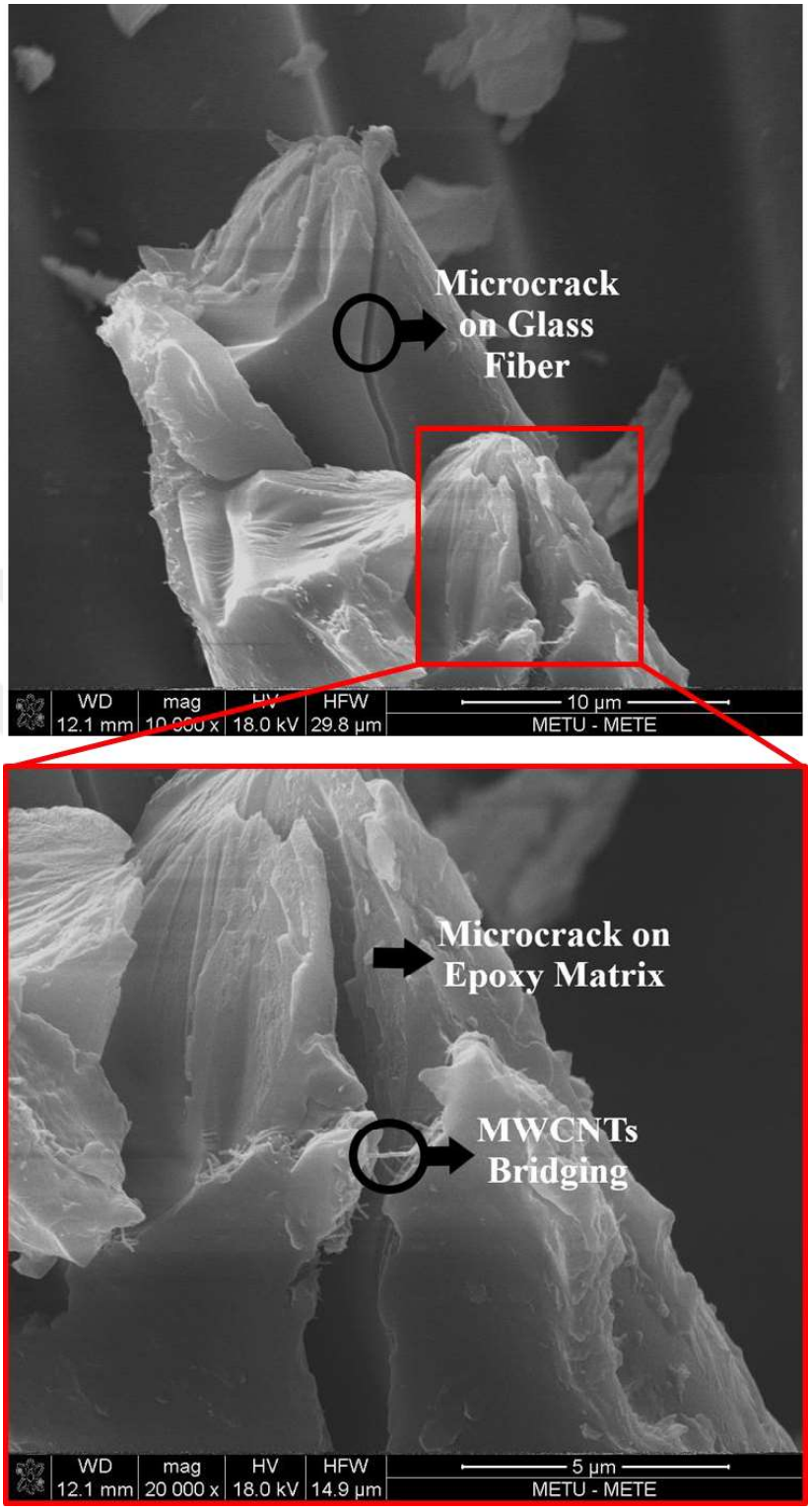

Figure 5.21 SEM Image of Composite Material Produced by Spray Method with Surfactant Showing Fracture Mechanisms and MWCNT Bridging

Figure 5.21 reveals one of the most important fibers dominated failure mechanism that is translaminar fracture. In this type of fracture, microcrack is initiated on the matrix phase and propagates through fiber material. It is clearly seen on SEM image that microcrack on the epoxy matrix propagates through glass fiber, this is because of strong fiber/matrix bonding [98]. It is believed that this situation directly positively affects the flexural properties of the composite material produced by Spray Method by using Triton X-100.

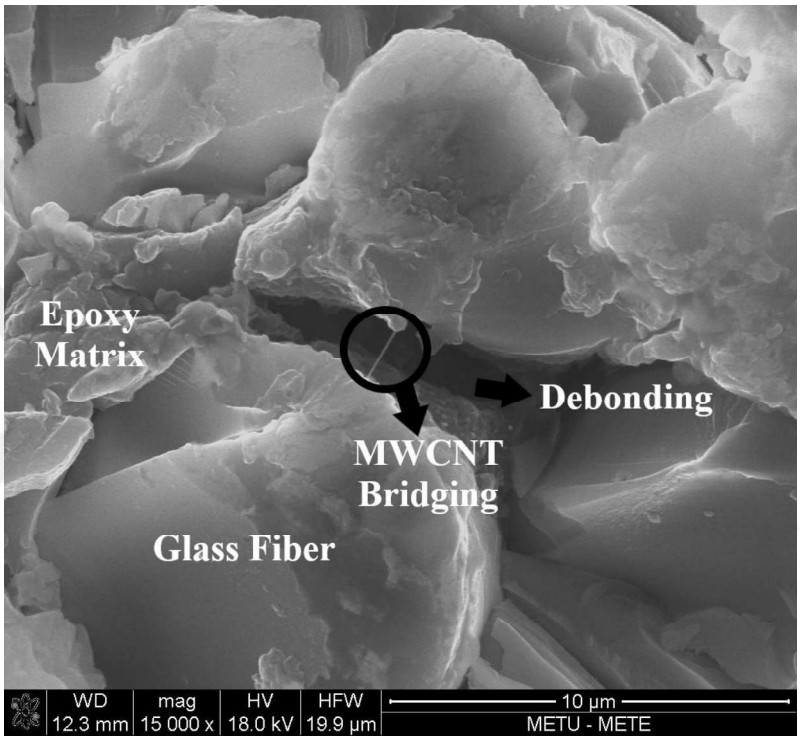

Figure 5.22 SEM Image of Composite Material Produced by Spray Method with Surfactant Showing Debonding Between Fiber and Matrix, and MWCNT Bridging

Figure 5.21 and **Figure 5.22** show MWCNTs bridging on two fractured end of epoxy matrix and between fibers where debonding is dominant. It is believed that MWCNTs bridging is one of the most important toughening mechanisms between interfaces that causes reduction in crack propagation and prevent crack growth and causes increase in flexural properties [32, 97].

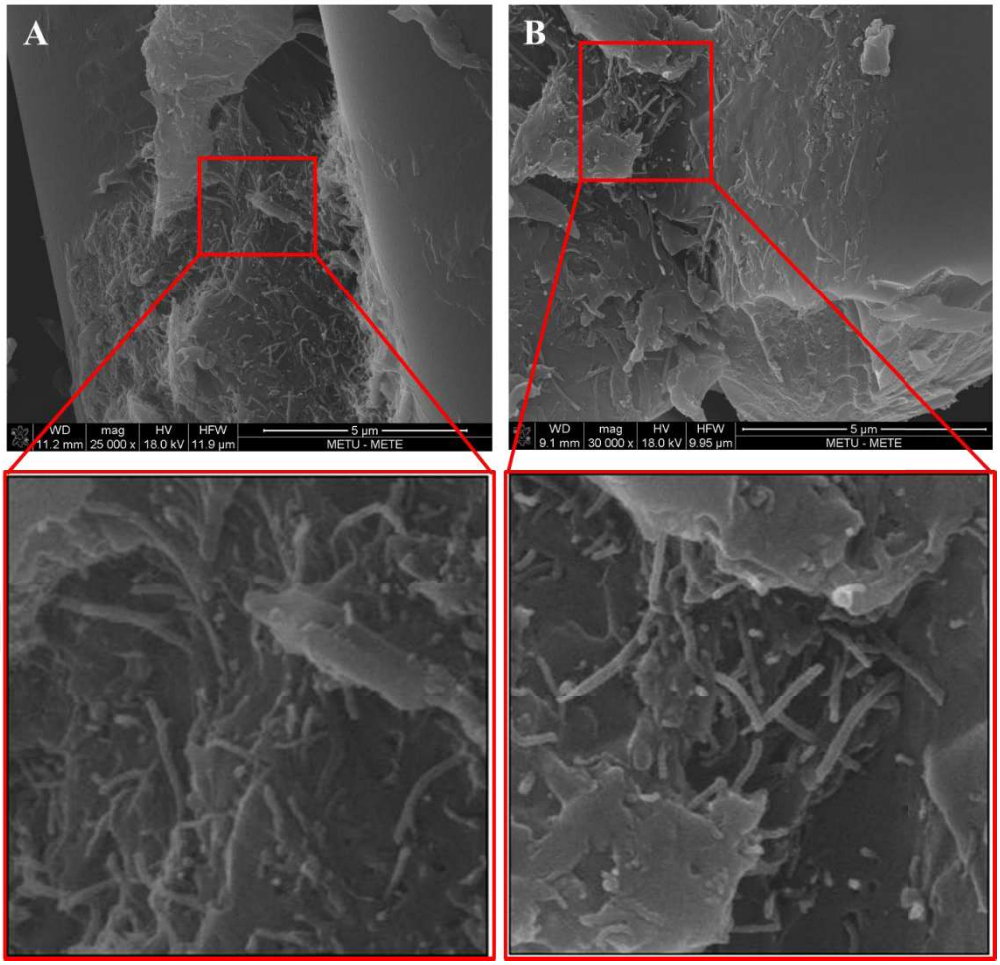

Figure 5.23 Effect of Surfactant on Dispersion of MWCNTs in Epoxy Matrix, (A) SEM Image of Composite Material Produced by Spray Method with Triton X-100 and (B) SEM Image of Composite Material Produced by Spray Method without Triton X-100

Effects of Triton X-100 on the dispersion of MWCNTs in organic solvent is given in **Figure 5.23**. While Triton X-100 has been used in one of the composite materials produced by the Spray Method, it was not used in another composite material produced by Spray Method. It is obviously seen that MWCNTs are found less frequently in the structure in the production involved Triton X-100. In the production where Triton X-100 is not used, it seems that MWCNTs forms a mass like structure. This is an indication that better flexural properties are obtained with the composite material using Triton X-100 in three-point bending tests as compared to the composite material does not contain surface active agent.

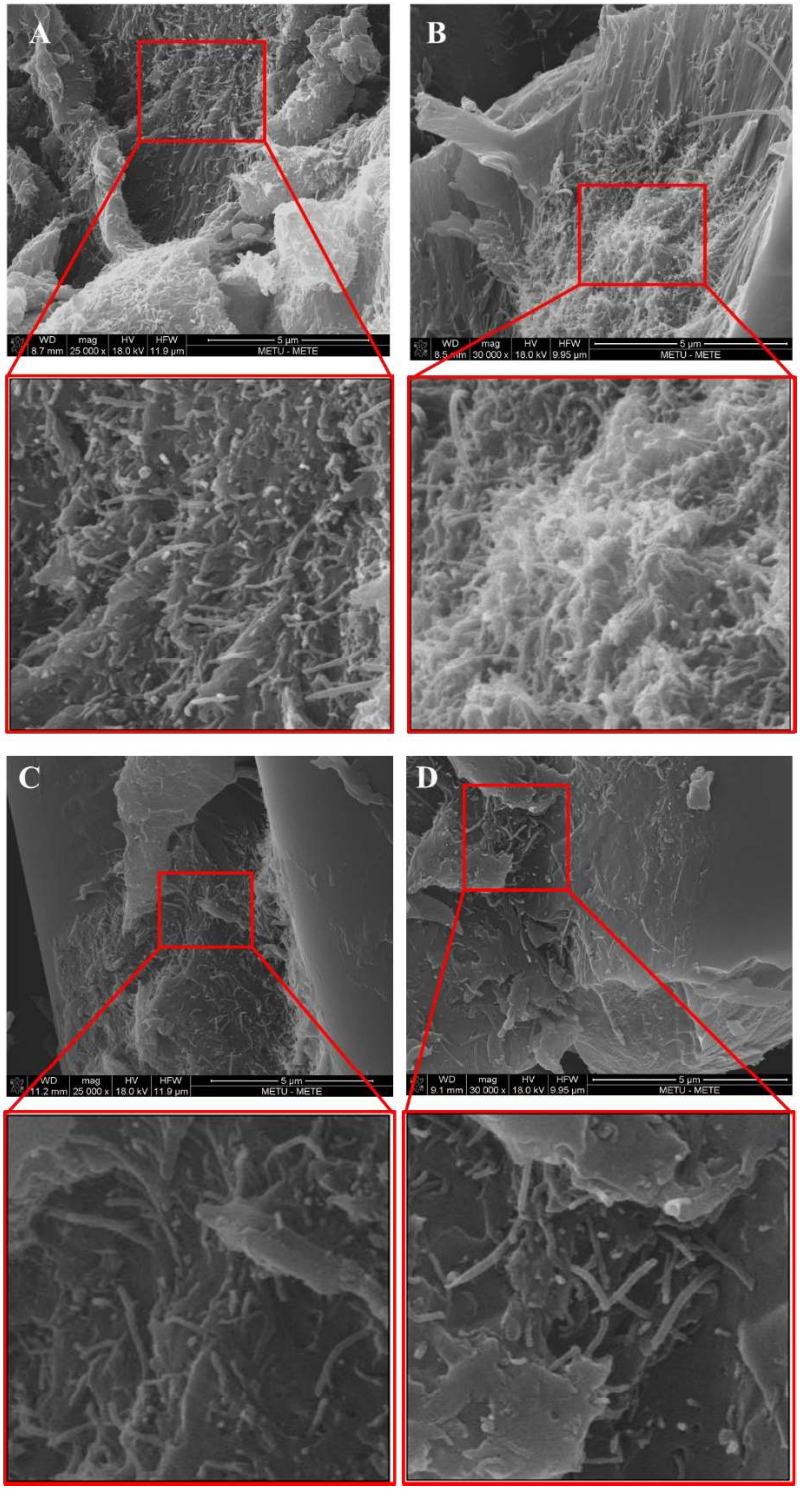

Figure 5.24 Effects of Surfactant on Dispersion of MWCNTs in Epoxy Matrix, (A) SEM Image of Composite Material Produced by Direct Mixing Method with Triton X-100, (B) SEM Image of Composite Material Produced by Direct Mixing Method without Triton X-100, (C) SEM Image of Composite Material Produced by Spray Method with Triton X-100 and (D) SEM Image of Composite Material Produced by Spray Method without Triton X-100

In this study, MWCNTs have been directly mixed with epoxy matrix in Direct Mixing Method and have been sprayed onto glass fibers before hand lay-up process in Spray Method. SEM analysis have been conducted to see the effects of these methods with/without Triton X-100 on the dispersion of MWCNTs are given in the **Figure 5.24**. In composite materials produced by Spray Method, SEM images of MWCNTs have been hardly taken. This is thought to be due to MWCNTs being sprayed onto the glass fibers. Also, image processing tool (ImageJ) is used in proportion to the magnification of the images taken from composite materials to see the distributions of MWCNTs. When SEM images given in **Figure 5.24** are examined, it is clearly seen that in both Spray and Direct Mixing Methods, distributions of MWCNTs are more uniform in composite materials produced by using Triton X-100. This situation also coincides with the flexural properties given in **Figure 5.3**, and the composite materials produced by using Triton X-100 have better flexural properties than that of the composite materials produced without using Triton X-100. Also, it is obviously seen that best homogeneous distribution is obtained with composite materials produced by Spray Method with the aid of Triton X-100 that is also conforming to the flexural properties given in **Figure 5.3**. When the flexural strength and flexural modulus values obtained in this study are compared, the best results have been obtained with the composite material produced by this method. The reason is believed to be the tendency of MWCNTs to create agglomerates that is higher in the epoxy matrix material than organic solvent because of the structure of the epoxy. On the other hand, with the dispersion of MWCNTs in suitable organic solvent it is thought that more homogenous distribution is obtained and, with the spraying process of this organic solvent, higher loading and better dispersion are provided.

CHAPTER 6

CONCLUSIONS

In this work, Multi Walled Carbon Nanotubes (MWCNTs) grafted Glass Fiber Reinforced Epoxy Matrix Composite (GFECs) materials have been produced by using two significant routes to enhance the through thickness properties of GFECs. Also, it has been aimed to see the effects of production methods used on the distribution of MWCNTs in the composite structure. One of the two production methods used in this study is the Direct Mixing Method. With this method, MWCNTs have been directly mixed with/without Triton X-100 in epoxy matrix by using ultrasonic mixer. Another production method is Spray Method. With this method, MWCNTs have been dispersed in organic solvent with/without Triton X-100 and sprayed directly onto glass fiber surfaces. To see the effects of these methods on the composite materials Three-Point bending test, Shore D and Vickers hardness tests and, SEM Analysis have been conducted. In the view of the results, the following conclusions have been drawn:

- The average test results taken from three-point bending test have been compared among composite materials produced by different methods and control sample. While the best flexural strength and flexural modulus are obtained with the composite material produced by the Spray Method with the aid of Triton X-100, the results of composite materials produced by other methods show that decreases in flexural strength and increases in flexural modulus. It is believed that decreases in flexural strength as compared to control sample is due to the agglomeration of MWCNTs inside the increases composite structure. Also, it is believed that increases in flexural modulus while flexural strength decreases due to locally homogeneously dispersed nanoparticles. According to test results:
    - The best flexural strength and flexural modulus are obtained as 411.309 MPa and 20.186 GPa taken from composite material produced by the Spray Method with the aid of Triton X-100 respectively. Also, flexural

strength and flexural modulus are increased about 5.33% and 19.79% respectively as compared to control sample.

- The test results of composite material produced by Direct Mixing Method with the aid of Triton X-100 shows that flexural strength is decreased about 4.541% and flexural modulus is increased about 12% as compared to control sample.
- The composite plate produced by Direct Mixing Method without the aid of Triton X-100 shows decreases in flexural strength by about 8% and 2% increment in flexural modulus as compared to control sample.
- The composite material produced by Spray Method without the aid of surface-active agent shows decreases in flexural strength about 6.2% and increases in flexural modulus by about 2% as compared to control sample.
- Also, higher flexural properties have been obtained in composite materials produced by using surfactant than that of those produced without surface active agent. Although it can't completely prevent agglomeration problem, this indicates that Triton X-100 has played an important role on the distribution of MWCNTs in epoxy matrix/organic solvent.
- The test results obtained from three test samples of composite material produced by Direct Mixing Method with the help of Triton X-100 show nonuniformity and decreasing in flexural strength as compared to control sample. The reason is thought to be due to local residual acetone remained in epoxy matrix. Acetone has been used to mix MWCNTs, Triton X-100 and resin.

- Hardness test results were compared among composite materials produced by different methods and control sample. In this study, the best hardness value in both Vickers and Shore D Hardness results have been obtained in the composite material produced by Direct Mixing Method with the aid of Triton X-100 as compared to control sample. Also, increases in hardness observed in the composite materials produced by other production methods. When the test

results obtained from Shore D and Vickers are compared, the same rising trend is obtained in both measurement methods. According to test results:

- The hardness test results of composite material produced by Direct Mixing Method with the aid of Triton X-100 shows increase in Shore D hardness was about 6.5% and in Vickers Hardness about 26% as compared to control sample.
- Also, Shore D and Vickers Hardness results obtained from MWCNTs grafted GFECs produced by different methods show that there is no big difference between the hardness values. It is believed that this is due to the constant amount of MWCNTs.

- SEM has been used to investigate the distribution of MWCNTs in composite structure and reveals effect of Triton X-100 on the dispersion of MWCNTs. Also, fracture mechanisms of composite materials after three-point bending tests are examined. According to SEM images taken from composite materials:
  - SEM images taken from MWCNTs rich regions show that the most uniform distribution of MWCNTs are obtained from composite materials produced by Spray Method with the aid of Triton X-100. This observation also conforms to flexural properties. This shows that MWCNTs sprayed on the glass fiber surfaces have created a better interface between epoxy and glass fibers than other methods.
  - Also, in this study, composite materials produced with Triton X-100 show more homogeneous dispersion to composite materials that were not produced with Triton X-100. This indicates the positive effects of Triton X-100 on mechanical properties by improving the distribution of MWCNTs. It is obvious that this situation is reflected in flexural properties.

In the light of all this results, it was observed that, the Spray Method used to produce composite materials by using Triton X-100 shows better performance to enhance through thickness properties. The most important reason is that MWCNTs which are homogeneously distributed in the organic solvent with the help of Triton X-100, adhere well to the fiber surfaces and form strong bonds between the glass fibers and epoxy matrix.

6.1. Future Works

In this study, hand lay-up method has been conducted for production processes. In this method, epoxy is applied with a brush between layers. Therefore, in this method, the amount of resin applied to each layer cannot be adjusted exactly equally, also, the success of the method depends largely on operator's skill. This situation directly affects desired mechanical properties of composite materials. In order to prevent this situation in the future studies, it is planned to use Vacuum-assisted Resin Transfer Molding (VARTM) which is an alternative production method. The studies conducted in the literature show that composite materials produced by VARTM technique show better mechanical properties and more lightweight with a better fiber to resin ratio. In the future studies, it is planned to produce composite materials by using Spray Method and Direct Mixing Method with VARTM technique to see the effect of VARTM on the mechanical properties of composite materials produced by Direct Mixing and Spray Methods.

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