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INVESTIGATION OF MECHANICAL PROPERTIES OF MWCNT INTEGRATED PA 66/GLASS FIBER COMPOSITES

Master's Thesis

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ÖZET

ÇDKNT ENTEGRE EDİLMİŞ PA 66/CAM ELYAF KOMPOZİTLERİN MEKANİK ÖZELLİKLERİNİN İNCELENMESİ

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Bu çalışmada, çok duvarlı karbon nanotüplerin (ÇDKNT), kısa cam elyafı (KCE) takviyeli Poliamit 66 (PA 66) kompozitlerinin(PA 66/KCE) çekme ve eğme davranışı üzerine etkisi incelenmiştir. Bu amaç doğrultusunda, PA 66/KCE granülleri ÇDKNT'ler ile manyetik bir karıştırıcı aracılığıyla etanol içinde karıştırılmıştır. Ardından, katkısız PA 66, PA 66/KCE ve PA 66/KCE/ÇDKNT'lü granüller, içerdikleri nemin uzaklaştılması amacıyla, bir fırında kurutma işlemine tabi tutulmuştur.

Plastik enjeksiyon kalıplama makinesi aracılığıyla katkısız PA 66, PA 66/KCE ve PA 66/KCE/ÇDKNT'den oluşan test numuneleri üretilmiştir. Elde edilen test numunelerinin çekme ve eğme davranışları, Ondokuz Mayıs Üniversitesi, Karadeniz İleri Teknoloji Araştırma ve Uygulama Merkezi'nde (KİTAM) bulunan Instron 5982 test cihazıyla karakterize edilmiştir.

Mekanik analizler sonucunda, en düşük elastik modül ve çekme dayanımının katkısız PA 66'dan oluşan numuneler tarafından, en yüksek elastik modül ve çekme dayanımının ise PA 66/KCE'dan oluşan numuneler tarafından sergilendiği görülmüştür. PA 66/KCE numunelerine kıyasla, PA 66/KCE/ÇDKNT'lü numunelerin çekme dayanımlarının % 13.4 oranında azaldığı, ancak elastik modüllerinin % 4.7 oranında arttığı tespit edilmiştir. Ayrıca, yapılan eğme testi sonuçları da ÇDKNT entegrasyonunun, PA 66/30KCE'nin eğme dayanımını ve eğme modülünü, sırasıyla, %1 ve %12 oranlarında artırdığını göstermiştir.

Anahtar Sözcükler: Kompozit malzeme, Poliamit 66, Cam lifi, Karbon nanotüp, Plastik enjeksiyon kalıplama

ABSTRACT

INVESTIGATION OF MECHANICAL PROPERTIES OF MWCNT INTEGRATED PA 66/GLASS FIBER COMPOSITES

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In this study, the influence of multi-walled carbon nanotubes (MWCNTs) on tensile and flexural behaviour of short glass fibre (SGF) reinforced Polyamide 66 (PA 66/SGF) was investigated. Upon this purpose, PA 66/SGF granules were mixed with MWCNTs in ethanol by means of a magnetic stirrer. Subsequently, neat PA 66, PA 66/SGF and PA 66/SGF/MWCNTs granules were dried in an oven so that the moisture they incorporate was avoided. Test specimens composed of neat PA 66, PA 66/SGF and PA 66/SGF/MWCNTs were produced using plastic injection moulding machine; and their tensile and flexural properties were characterized using Instron 5982 test machine in Central Laboratory (KITAM), Ondokuz Mayıs University (OMU).

Mechanical analyses revealed that neat PA 66 exhibited the lowest elastic modulus and tensile strength while PA 66/SGF exhibited the highest of the same mechanical properties. Comparing with PA 66/SGF, tensile strength of PA 66/SGF/MWCNTs decreased by 13.4 % while the elastic modulus increased by nearly 4.7 %. In addition, flexural test results revealed that the integration of MWCNTs increased the flexural strength and flexural modulus of PA 66/30SGF by 1% and 12%, respectively.

Keywords: Composite material, Polyamide 66, Glass fiber, Carbon nanotube, Plastic injection moulding

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Fatma Burcu UZUNOĞLU

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ABBREVIATIONS

Al	Aliminum
C	Carbon
Ar	Argon
CaO	Calcium Oxide
CCC	Carbon-Carbon Composite
CF	Carbon Fiber
CFRC	Carbon Fiber Reinforced Composite
CMC	Ceramic Matrix Composite
CMNC	Ceramic Matrix Nanocomposite
CNT	Carbon Nanotube
Co	Cobalt
Cu	Copper
CVD	Chemical Vapor Deposition
Fe	Ferrrum (Iron)
FRC	Fiber Reinforced Composites
GF	Glass Fiber
GPa	Gigapascal
He	Helium
Mg	Magnesium
MMC	Metal Matrix Composite
MMNC	Metal Matrix Nanocomposite
MWCNT	Multi-walled Carbon nanotube
N	Nitrogen
Ni	Nickel
O	Oxygen
PA	Polyamide
PA 6	Polyamide 6
PA 66	Polyamide 66
PC	Polycarbonate
PE	Polystyrene
PMC	Polymer Matrix Composite
PMNC	Polymer Matrix Nanocomposite
PP	Polypropylene
PS	Polysyrene
PVC	Poly(vinyl chloride)
SEM	Scanning Electron Microscopy
SGF	Short Glass Fiber
Si	Silicon
SWCNT	Single-walled Carbon nanotube
Ti	Titanium
TPa	Terapascal

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CHAPTER 1

INTRODUCTION

The use of plastic materials reached up to 359 million tons in 2018 (Europe, 2019) and it was reported that 80% of all plastics used throughout the world are thermoplastics (Dynisco, 2018). Thermoplastics are commonly used in various industries such as automobile, aeronautic and aviation, defence, sports industry and so forth (Europe, 2019; Hv, 2016; Yern Chee, Chuah, Ching, Luqman Chuah, & Rahman, 2017). Some thermoplastics are recognized as suitable substitutes for metallic materials in industrial applications owing to their light weight, advatageous mechanical, thermal and chemical properties, easy machinability and relatively lower production expenditure (Gilbert, 2017). Nevertheless, despite their advantageous properties, thermoplastic materials tend to become deformed during the use or production. To prevent these deformations and to improve their mechanical properties, thermoplastics may be reinforced with microscale or nanoscale reinforcements such as glass fibers (GF), carbon nanotubes (CNTs), carbon fibres (CF), nanoclays etc. (Rajak, Pagar, Kumar, & Pruncu, 2019; Xanthos, 2010). Consequently, it is significantly essential to investigate and reveal the mechanical behaviour of these composites to obtain the desired design properties.

Polyamide 66 (PA 66) is one of the most outstanding thermoplastics used as engineering resin due to its good mechanical, chemical and thermal properties (Chow & Mohd Ishak, 2015; Vagholkar, 2016). Apart from neat PA 66, various types of polyamides reinforced with materials such as glass fibres are also commonly used in industry. A large number of studies revealed that inclusion of glass fibres results in enhancement in the mechanical performance of PA 66 matrix composites systems (Autay, Mars, & Fakhreddine, 2019; Çuvalci, Erbay, & İpek, 2014; Hsiung, Ren, Ning, & Chi, 2016; Javangula, Ghorashi, & Draucker, 1999; Kim, Kim, & Lee, 2012; Lingesh, Rudresh, & Ravikumar, 2014; Nuruzzaman, Iqbal, Oumer, Ismail, & Basri, 2016; Srivastava & Lal, 1991).

It has been known that the tensile behaviour of PA 66/GF composites is highly dependent on fibre fracture, diameter, length, orientation and interfacial strength

(Bernasconi & Cosmi, 2011; Sato, Kurauchi, Sato, & Kamigaito, 1988; Thomason, 2006, 2007). Moreover, it was revealed that injection parameters, such as mould temperature, injection pressure and speed, may affect the mechanical performance of the polymer matrix composite materials (Güllü, Özdemir, & Özdemir, 2006; Zainudin, Sapuan, & Imihezri, 2006).

Today, nanoscale materials, namely nanomaterials, too are being utilized as reinforcement so as to acquire better mechanical performance of composite systems; and one of the most prominent of them are certainly carbon nanotubes (CNTs) (Baughman, Zakhidov, & Heer, 2002; J. N Coleman, Khan, & Gun'ko, 2006). CNTs are simply divided into two simple categories according to the number of their walls: The first category includes multi- walled CNTs (MWCNTs), which was initially explored by (Iijima, 1991), and the second category includes single- walled CNTs (SWCNTs), which was later studied out by (Iijima & Ichihashi, 1993). The reason why MWCNTs are utilized as nanofillers is that they exhibit extraordinary mechanical properties such as ultra high tensile strength varying between 11-63 GPa (M. F. Yu et al., 2000) and e-modulus, which is approximately 1 TPa (Salvetat et al., 1999; M. F. Yu et al., 2000). These superior characteristics of MWCNTs made them highly promising reinforcing fillers for improving polymers, ceramics and metals. Nevertheless, polymer matrices have aroused a great deal of interest for industrial applications owing to the light weight, easy machinability and production costs (Du, Bai, & Cheng, 2007; Sahoo, Rana, Cho, Li, & Chan, 2010; Shankar & Rhim, 2016; Song et al., 2013).

To prepare high-performance CNTs/polymer composites, many studies have been performed to date (Arash, Wang, & Varadan, 2014; Chen, Liu, Wang, Zhang, & Zhang, 2018; Jonathan N. Coleman, Khan, Blau, & Gun'ko, 2006; Hassani, Mohd Ishak, & Mohamed, 2014; F.-L. Jin & Park, 2011; W. Khan, Sharma, & Saini, 2016a; Moniruzzaman, Chattopadhyay, Billups, & Winey, 2007; Sahoo et al., 2010; Spitalsky, Tasis, Papagelis, & Galiotis, 2010; Tarfaoui, Lafdi, & El Moumen, 2016; Zabegaeva et al., 2016; J. Zhang et al., 2019). Majority of these studies reported that CNTs is able to upgrade the mechanical behaviour of polymeric composite systems. Coleman et al. (J. N Coleman et al., 2006) and Miyagawa et al. (Miyagawa, Misra, & Mohanty, 2005) provided comprehensive reviews regarding reinforcing polymers by the use of CNTs.

It is stated that good-dispersion of CNTs and efficient CNT-matrix interaction are critical parameters so as to obtain a penetrating stress or load transmission from continuous phase to the filler network and hence to control some of the mechanical characteristics of the composite system. Therefore, several studies focused on CNT-polymer matrix interaction and crack behaviour of CNTs/polymer composites (Gorga, Lau, Gleason, & Cohen, 2006; Gupta & Harsha, 2014; Y. Kuronuma, Shindo, Takeda, & Narita, 2010; Yu Kuronuma, Shindo, Takeda, & Narita, 2011; Shindo, Kuronuma, Takeda, Narita, & Fu, 2012; Takeda, Shindo, Naraoka, Kuronuma, & Narita, 2013).

(Ajayan, Schadler, Giannaris, & Rubio, 2000) analyzed the morphology of fractured epoxy/SWNTs composites by means of SEM and monitored SWCNTs bridging across a crack opening in the epoxy resin.

(Liu, Phang, Shen, Chow, & Zhang, 2004) examined the surface characteristics and mechanical performance of MWCNTs reinforced Polyamide 6 (PA 6) and obtained the SEM micrographs of microcracks which were linked by multiple bridged nanotubes as well as their agglomerates within fractured PA 6 matrix. The authors also noted that e-modulus and strength of the specimens enhanced by approximately 214% and 162 %, respectively , after including merely 2 wt. % MWNTs content. However, they reported a 26% decline in tensile strength and attributed this failure to the brittleness of polymer matrix after the addition of MWCNTs.

According to the study carried out by (Ferreira, Paiva, & Pontes, 2013), incorporating CNTs within Polyamide 6 notably rises the tensile strength and e-modulus values of the bulk composite. (Chopra, Deshmukh, Deshmukh, & Peshwe, 2018) confirmed that including MWCNTs could increase tensile strength of Polyamide 6 by nearly 12%, which was explained by the efficient PA 6-MWCNT facial interaction as well as well-dispersed MWCNTs within PA 6 resin. Similarly, (Kartel, Sementsov, Mahno, Trachevskiy, & Bo, 2016) investigated the tensile performance of PA 6/CNTs; however, they noticed that tensile properties of the system exhibits non-linear dependency by the inclusion of CNT-content, however, these properties exhibit a decreasing trend after the addition of 0.5 wt. % CNT content. The authors also reported that PA 6 matrix composites incorporating 0.25 wt. % CNTs exhibit the highest tensile strength.

Despite the fact that a large number of studies subjected polymer/CNT composites are available in literature, there are not sufficient amount of studies focused on the hybrid reinforced polymer systems wherein both microscale and nanoscale fillers are used together as reinforcement (Mahato, Rathore, Prusty, Dutta, & Ray, 2017; Nguyen-Tran, Hoang, Do, Chun, & Yum, 2018).

Majority of the studies focused on polymer/CNTs point out that mechanical performance of polymer/CNT systems are considerably dominated by CNT dispersion within polymeric continuous phase as well as CNT-matrix facial interaction during the mixing process of the composite constituents (Jogi, Sawant, Kulkarni, & Brahmankar, 2012; Pötschke et al., 2005).

The study of (Arao et al., 2013) regarding mechanical properties of SCF filled PP/MWCNTs hybrid composite systems revealed that the incorporation of 1 wt.% MWCNTs-content led to an increasing trend in e-modulus and tensile strength comparing PP/SCF without MWCNTs. The authors attributed this effect to improved interfacial shear strength. However, they also stated that increasing MWCNTs-content from 1 to 4 wt. % led to failure in the tensile strength, which was explained by presence of MWCNT agglomerates within polymer matrix.

In spite of the theorical and experimental studies carried out by scientist and engineers so far, the full potential of nanofillers and the properties of their combinations with other reinforcement materials, such as glass fibres, have not fully discovered yet. Thus, this study aims to introduce tensile and flexural properties of MWCNTs-integrated Polyamide 66/SGF nanocomposites. The results obtained from this study are expected to make a great contribution in designing brand-new high-performance materials offering superior advantages over their counterparts.

CHAPTER 2

COMPOSITE MATERIAL

2.1. Definition

A composite is described as a combined materials often composed of at least 2 materials with different chemical, physical and mechanical characteristics, such as high tensile and flexural strength, long fatigue life, resistance against chemical substances, stiffness, light weight, resistance against impact, favorable thermal conductivity and so forth (Vinson & Sierakowski, 2008). This combined product, namely the composite, exhibits improved properties than those of its individual constituents while these constituents retain their chemical, physical or mechanical properties. The use of composites over their traditional counterparts is due to the fact that they improve the performance properties of their base materials and offer some qualifications such as light weight and relatively low cost.

Composites consist of two main phases: a) matrix (binder) phase, b) dispersed (reinforcement) phase. Matrix phase, which is often continuous, holds the dispersed phase and protects it from the environmental damage; and also, absorbs the stress resulting from the applied load to the composite and transfers it to other constituents. Dispersed phase, on the other hand, is imbedded within the matrix. Since this phase generally exhibits higher strength than the matrix does, it is also named as "reinforcement phase". Dispersed phase is usually discontinuous; however, materials in continuous forms can also be used as reinforcement. The properties of composite materials are usually anisotropic; therefore, unlike isotropic materials, most of the composites exhibit different properties in different directions. Moreover, properties of a composite is known to be dependant on the characteristics and amounts of each phase as well as the geometry of reinforcement such as shape, size, orientation and distribution of reinforcing material in matrix. These characteristics can be seen in Figure 2.1.

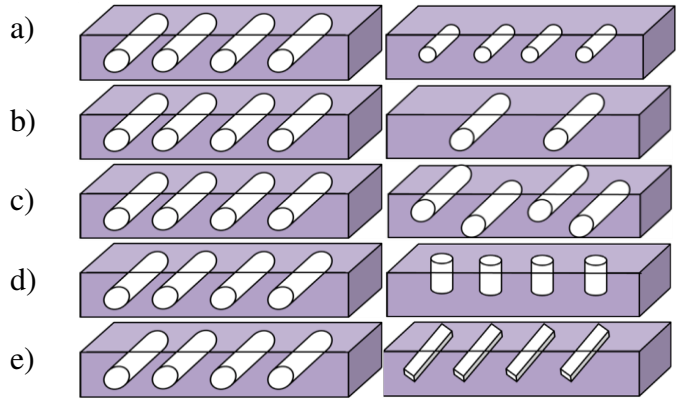

Figure 2. 1. Geometry of reinforcing fillers based on their (a) size, (b) concentration, (c) distribution, (d) orientation and (e) shape (Callister & Rethwisch, 2011).

2.2. Classification of Composite Materials

Figure 2.2 represents the classes and subclasses of composite materials with regard to their their constituents.

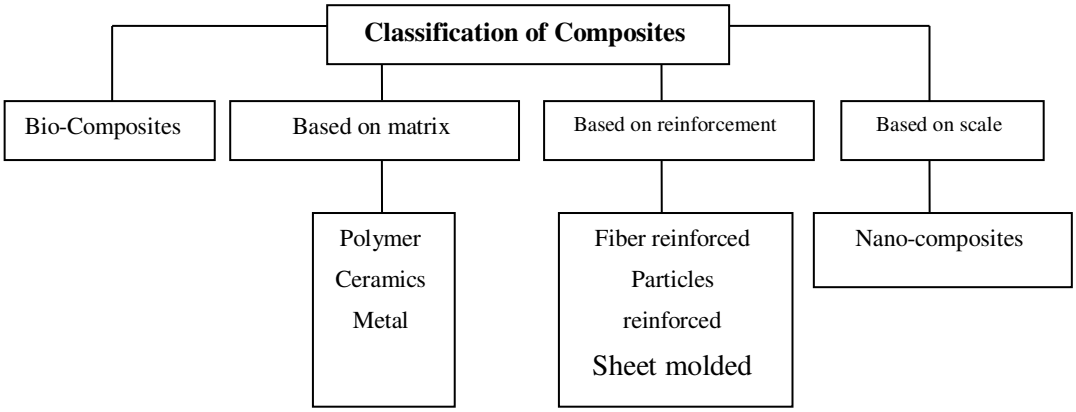

Figure 2. 2. Classification of composite materials (Rajak et al., 2019).

2.2.1. Classification of Composites Based on Reinforcement

This level of classification is based on the structure of the reinforcing materials and divided into three main classes as: i) particle reinforced, ii) fiber reinforced and iii) structural composites. The classes and subclasses of composites based on the forms of reinforcement are shown in Figure 2.3. The main purpose of utilizing reinforcing materials is to improve mechanical properties; however, depending on

the requirements of the desired design, they may also contribute to chemical, electrical, thermal performance of materials. Reinforcing materials should be stronger and stiffer than the matrix so that they are able to change to failure mechanism for the favor of the composite.

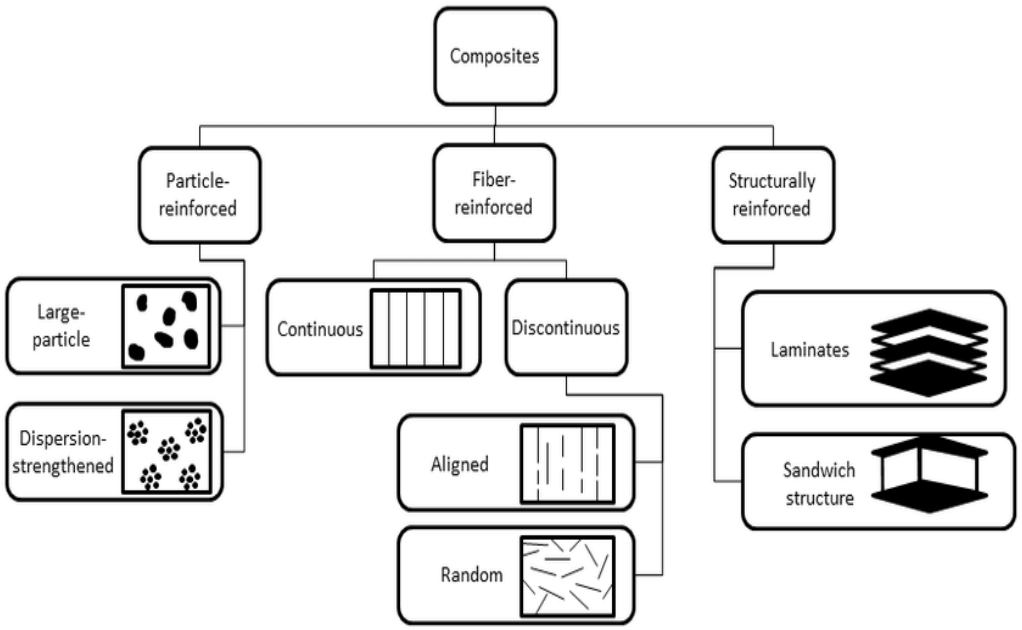

Figure 2. 3. Classification of composites based on type of reinforcement (Callister & Rethwisch, 2011).

In particle reinforced composite systems, particulates used as reinforcement could be at micro or nanoscale, as shown in Figure 2.4. However, since their strengthening mechanism is different, it is more appropriate to locate the nano-sized particulates in another category of reinforcing materials. In large particulate reinforced composites, the particles are major load bearers and they are prone to restraining matrix deformation at the vicinity of their surfaces, which explains the

main strengthening mechanism in large particle composites (M. Egbo, 2020). However, in nano-scale particle reinforced composites, the matrix is major load bearer of the external stress applied to the composite. In this case, the strengthening mechanism occurs in the atomic level and the nano particles enhance the strength by preventing the crack opening and crack propagation along the matrix during the fracture.

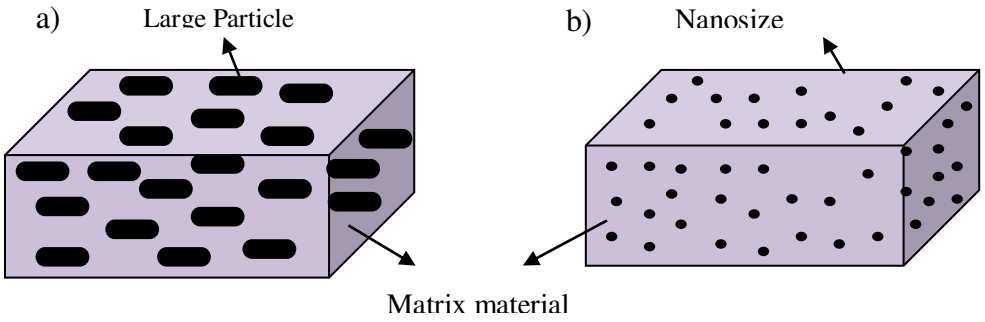

Figure 2. 4. Illustration of (a) microscale reinforcement, (b) nanoscale reinforcement (M. Egbo, 2020).

Second type of composites based on reinforcement is fiber reinforced composites (FRCs). These composite systems are the most famous and preferred type of composite materials. This system consists of fibrous materials such as glass fibers; and a matrix made of metal, polymer or ceramic. The presence of fibers in composites results in improved performance properties, which means that they may improve the strength, e-modulus, resistance against chemical substances, resistance against temperature and wear. The resulting strength of the fiber reinforced composites is related both to properties of the individual constituents and to length/diameter ratio of the fibers used in the dispersed phase (Fu & Lauke, 1996). Considering the length/diameter ratio and fiber orientations, FRCs are simply divided in three main classes as shown in Figure 2.5. First type of FRC is filled with continuous fibers which are usually long and aligned. Second type of FRC is filled with discontinuous fibers, which are usually short and aligned. And thirth type of FRC is filled with discontinuous fibers which exhibit random orientation throughout the matrix.

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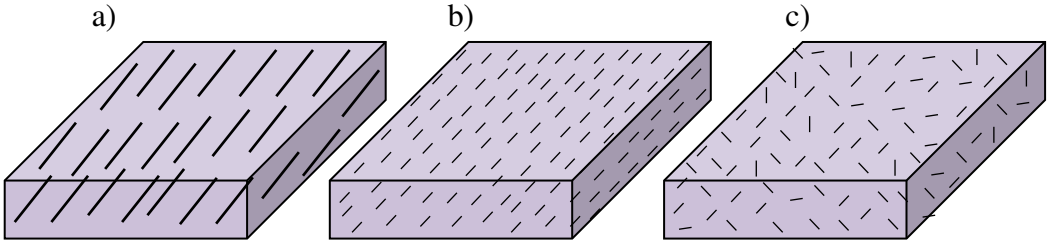

Figure 2. 5. Illustration of FRCs filled with (a) continuous and aligned fibers, (b) discontinuous and aligned fibers, (c) discontinuous and randomly oriented fibers (Callister & Rethwisch, 2011).

Third type of the composites based on reinforcement is structural composites (See Figure 2.6.). A structural composite is an engineered material which is composed of different composites and homogenous materials. The resulting performance properties of structurally reinforced composite systems are dependant not only on the characteristics of compositions of each constituent but also on their geometry such as shape and size.

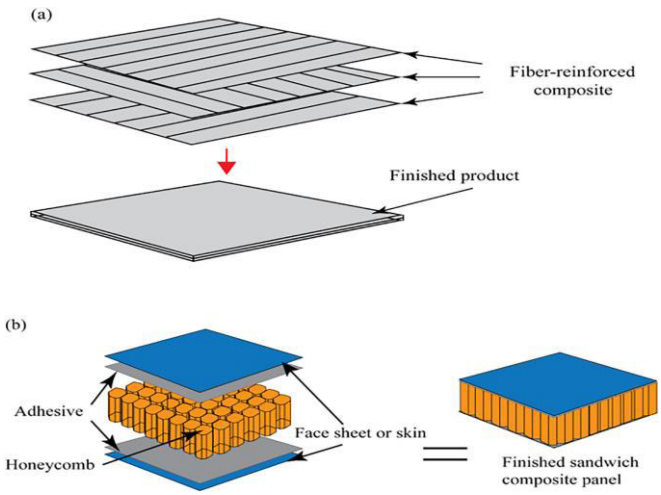

Figure 2. 6. Illustration of structural composites: (a) laminar composite (b) sandwich panel (M. K. Egbo, 2020).

2.2.2. Classification of Composites Based on Matrix

Considering the material types used as matrix, composites are divided into four subclasses following as; i) Polymer matrix composites (PMCs), ii) Metal matrix composites (MMCs), iii) Ceramic matrix composites (CMCs) and iv) Carbon

carbon composites (CCCs). Figure 2.7 represents the classes and sublasses of composite materials based on matrix material.

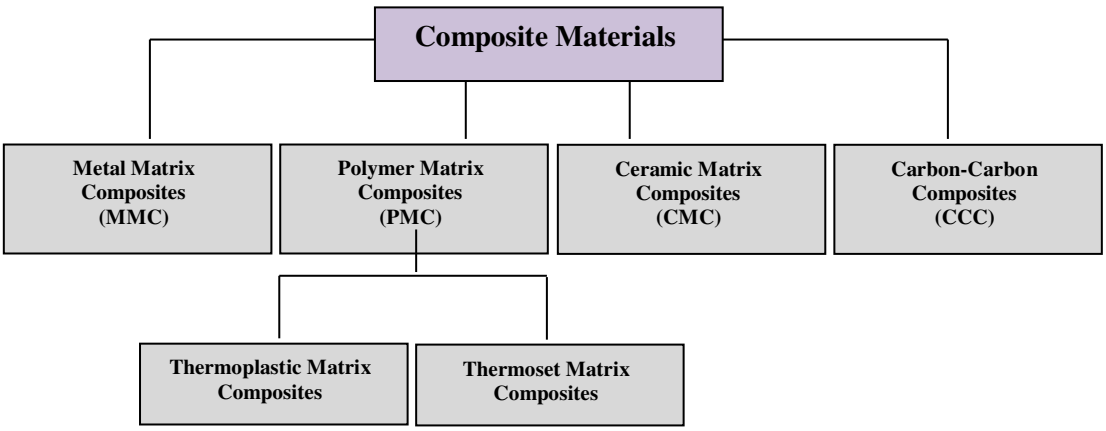

Figure 2. 7. Classes and subclasses of composites based on matrix type.

Polymer matrix composites are typically made out of thermosetting or thermoplastic matrix a reinforced with a man-made or natural fiber, such as carbon, glass, Kevlar, metal fibers. In this type of composites, mechanical properties of the fibers are usually much higher than the matrix; therefore, fibers are considered to be the main load bearers in the system. Yet, the matrix is expected to have good adhesion properties in order to hold the fibers. Moreover, the performance of fibers, matrix and the facial interaction between them highly influence the performance of PMCs (Wang, Zheng, & Zheng, 2011).

Polymers are typically organic substances whose chemisty is based on carbon, hydrogen and other elements. They possess fairly large, repeating chain-like compounds with a backbone of C atoms. Majority of polymers are rather ductile and pliable, which gives them the ability of being easily formed into complex shapes (M. Khan & Srivastava, 2018). PMCs are one of the most preferred composites which are used in many applications due to a number of advantages they posses such as high tensile and flexural properties, high stiffness, abrasion resistance, corrosion resistance, low density or light weight, easy machinability and low processing cost.

Polymer matrices are commonly grouped into two types following as: i) Thermosets and ii) Thermoplastics. The primary difference between thermosets and thermoplastics is their reaction to the application of heat.

Second type of composites with respect to matrix is MMCs. Matrix material of MMCs, as the name indicates, is composed of metallic matrix such as aluminum, magnesium, copper or titanium. On the other hand, the reinforcement may be ceramic or metal oxide in the form of fiber, whisker or particle. MMCs are lightweight structural materials used in a small number of applications in aviation industry. Low density metal alloys are commonly used as matrix in MMC systems. Metal matrices offer high strength, high stiffness, electrical conductivity and ductility. Yet, since they have relatively high density and complex processing techniques, they are not as widely used as polymer matrices.

The third type of composites based on matrix is ceramic CMCs. A CMC consists of a ceramic matrix and reinforcing materials such as particulates, fibers or whiskers. These reinforcing materials prevent or block crack propagation during the fracture and thus improve the mechanical characteristics of the composite system. Indeed, ceramics already have advantageous properties; yet, they are rather vulnerable due to lack of toughness, which may cause catastrophic failures. In other words, CMCs can be easily damaged during the fabrication or use. In order to overcome this disadvantage, ceramics are often toughened by incorporation of fibers. On the other hand, CMCs differ from other types of composites in terms of their reinforcing mechanism. In non-ceramic matrix composites, fibers are the primary load bearers and the external load applied to the system is shared between the matrix and fibers depending on content ratio of the fibers and e-modulus of the matrix (Chawla, 2012). Therefore, CMCs are also referred as *inverse composites*. They are quite suitable for high temperature applications; and they provide high hardness, low density, and superior thermal and chemical resistance.

The fourth type of composites based on matrix is carbon-carbon composites, also known as carbon fiber reinforced carbon (CFRC) composites. This type of composite systems are composed of carbonaceous matrix and carbon fibers as reinforcement (Oku, 2003). Since they possess very good performance properties, they are used in various industrial applications or parts such as aircraft brakes or rocket nozzles (Windhorst & Blount, 1997).

2.2.3. Bio-composites

Bio composites, also referred as green composites, have become popular owing to some advantages which make them suitable substitutes to their traditional counterparts in manufacturing industries. While conventional materials are produced with synthesized fibers, such as carbon and glass, and synthesized resins, such as epoxy and polyamide, bio-composite systems are manufactured using natural resins or fibers. These natural substitutes are obtained from plants or animals (Yıldızhan, Çalık, Ozcanli, & Serin, 2018). Besides being economically-friendly, sustainable and renewable, bio-composites offer a number of advantages such as ease of disposal, high performance in mechanical properties, low cost, light weight, availability and recyclability (Roy, Shit, Gupta, & Shukla, 2014).

2.2.4. Classification of Composites Based on Nano-scale

In this class of composite systems, composites are composed of a matrix and nano-scale reinforcement. This type of composite material is also referred to as *nanomaterial*. Nanomaterials will be investigated in further chapters.

2.3. Thermoset and Thermoplastic Polymers

Thermosets, also known as thermosetting plastics or thermosetting polymers, strengthen upon heating and remain in a permanent solid state after cooling. During the heating process, thermoset polymers cross-link and perform an unbreakable, irreversible bond. As a result, even under extremely high temperatures, thermosets cannot be remolded or heated after taking their initial form. The most popular thermosets are epoxy, silicone, polyurethane and phenolic. Moreover, some polymers such as polyester can be considered to be thermoset as well as thermoplastic.

Unlike thermosets, thermoplastic can be reheated, remolded, and cooled many times often without the presence of any chemical changes. Therefore, they are known for their versatility and recyclability. Thermoplastics are highly preferred due to a variety of advantages such as high strength, shrink-resistance, impact resistance, corrosion resistance, flexibility, easy machinability and so on. Most popular

thermoplastic polymers include polyethylene, poly (vinyl chloride), and polyamide. Today, many thermoplastics are reinforced with fibers, particularly glass fibers, to improve or modify the mechanical, thermal, chemical properties of the composites.

Main differences between thermosets and thermoplastics, provided from Nordin et al. (Nordin, Kasolang, Salleh, & Ahmad, 2013) and Nijssen et al. (Nijssen, 2015), are shown in Table 2.1.

Table 2. 1. Differences between thermosets and thermoplastics

Thermoplastics	**Thermosets**
Made from polymers without cross-linking between their chains	Made from a lot of cross-linking between different polymer chains
No chemical bonding occurs during the process	Permanent chemical bonds occur during the process
Ductile	Hard and brittle
Soften upon heating	No softening upon heating
Low chemical resistance	High chemical resistance
Recyclable	Not recyclable via standard techniques
High process temperature	Lower process temperature
Short curing(chemical reaction) time	Long curing time
Prone to creep	Low creep/shrink
Examples: Polyamide, polypropylene, polyethylene, polyvinylchloride, polystyrene	Examples: Epoxy, Thermoset Polyester, Polyurethane, Polyimide

2.4. Polyamide 66

Polyamide 66, also known as Nylon 66) is a semi-crystalline engineering thermoplastic with amide link (–NH–C double bond O) in the polymer chain. Like

all other polyamides, Polyamide 66 is also a condensation polymer synthesized by the reactions between acids and amines. Figure 2.8 represents the formation of Polyamide 66 by means of polycondensation reaction of hexamethylenediamine and adipic acid. The *66* terminology in Polyamide 66 represents the quantity of methyl carbons located between the carbonyls and amine functions.

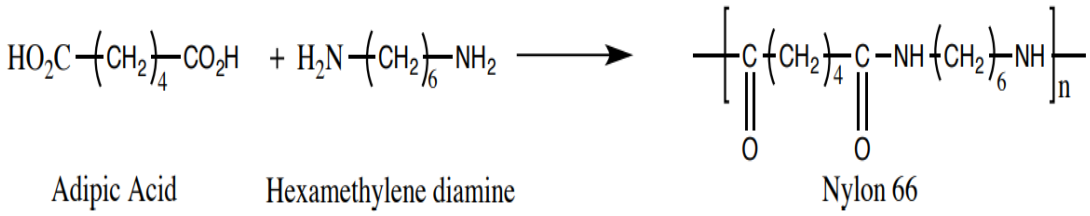

Figure 2. 8. Formation and chemical structure of PA 66 (Zaidy, 2016).

The manufacturing process of PA 66 is shown in Figure 2.9. Equal amounts of hexamethylenediamine and adipic acid come together within an aqueous solution in a reactor, with the pH adjusted at 7.8 in order to obtain PA 66 salt. Afterwards, the PA 66 salt is concentrated under vacuum and then transferred to an autoclave in which the water is removed. The temperature of the autoclave is risen up to 280ºC so that the polymerization is accomplished and the water remained from the condensation is removed. The resulting product is extruded as ribbons onto chilling rolls and transferred to a chipper that produces small PA 66 granules. According to the technical data provided from Eurotec® Tecamid® PA 66 datasheets, the density of unfilled PA 66 is about 1.14 g/cm^3, melting point is 262°C, and processing temperatures is 270-290°C.

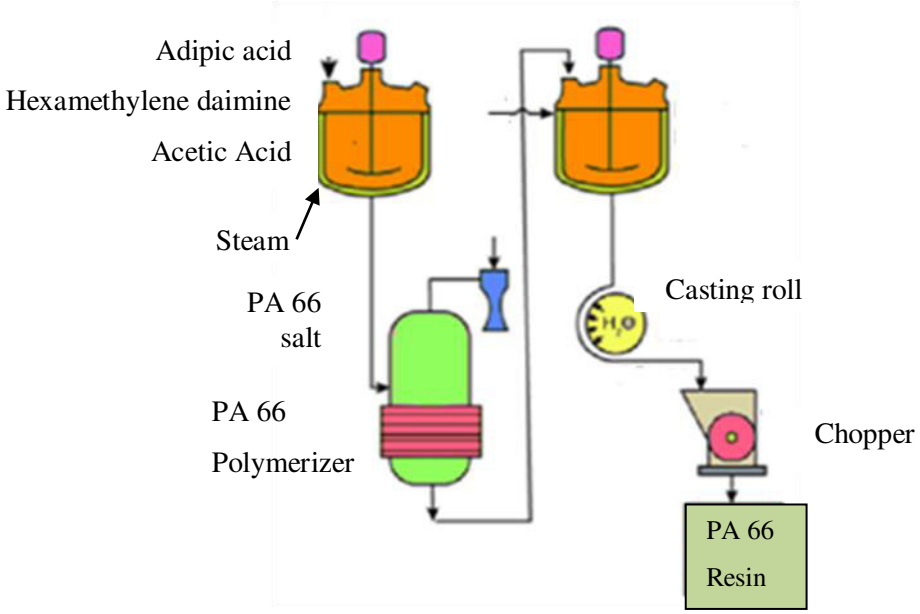

Figure 2. 9. Manufacturing process of PA 66

Since it is a suitable substitute to metallic materials, PA 66 has been one of the most popular engineering thermoplastics so far. PA 66 owes this popularity to a number of advantages such as high abrasion resistance, good thermal resistance, good fatigue resistance, high machineability, outstanding dimensional stability, high tensile strength, high rigidity, light weight, anti-friction and oil resistance. On the other hand, despite these advantageous properties, PA 66 is highly prone to absorbing moisture in the air due to the large number of acid groups it contains, which adversely affects the mechanical performance. Therefore, a drying process might be necessary during the manufacturing process.

PA 66 is being commonly used in various fields covering transportation, medicine, electronics, daily necessities, sporting goods and so forth. Therefore, it has been of great importance for researchers and engineers to know and improve the properties of PA 66. Using glass fibers in the reinforcement phase is a common way to upgrade the performance of PA 66 by incorporation of glass fibers. When PA 66 is filled with glass fiber, its flexural strength, tensile strength, and notched impact strength are significantly enhanced.

2.5. Glass Fibers

Glass fiber, shown in Figure 2.10, is one of the most preferred filler or reinforcement material used in composite systems. It offers beneficial qualifications such as high strength, hardness, transparence, resistance to chemical substances and stability. (F. Wallenberger, 2000).

Figure 2. 10. Glass fibers

GFs can be molded into various complex shapes; therefore, they are often used in aircrafts, boats, roofing, bathtubs and other applications. There are many types of GFs in the world-market according to the raw constituents used and their proportions to make glass fibers. The main types of glass fibers run as (Frederick Wallenberger, 2010):

A-glass: A-glass, also known as alkali glass, is very similar to window glass depending on its composition or proportion of its ingredients. It is also known for being resistant to chemicals.

C-glass: C-glass, also known as chemical glass, is famous for being resistant against chemical substances.

E-glass: E-glass, known as electrical glass, is famous for its ability of insulating electricity.

S glass: S-glass, also known as structural glass, is famous for its good mechanical performance.

Actually, among all types, e-glass is the most popular type and commercially referred to as *glass fiber*. Other types of glass fibers are considered to be special types.

In the manufacturing process of glass fibers, firstly, the required minerals are mixed depending on the recipe. Subsequently, the ingredients or minerals are melted down into a molten glass in the furniture at 1550 °C (for E-glass). When the mixture is molten, the liquid and homogeneous glass flows towards the bushing made of a platinum and rhodium alloy. Bushings are basically blocks pierced with hundreds of holes. The liquid glass flows through these small holes; and then it is rapidly cooled taking solid filament form while being drawn by a cylinder at high speed. Thus, several hundred filaments can be produced. Additionally, at this stage, namely forming stage, the individual filaments receive a coating of size, right after leaving the bushing. The aim of this step is to give the glass strand certain structural properties required for the final application. Figure 2.11 represents the manufacturing process of glass fibers.

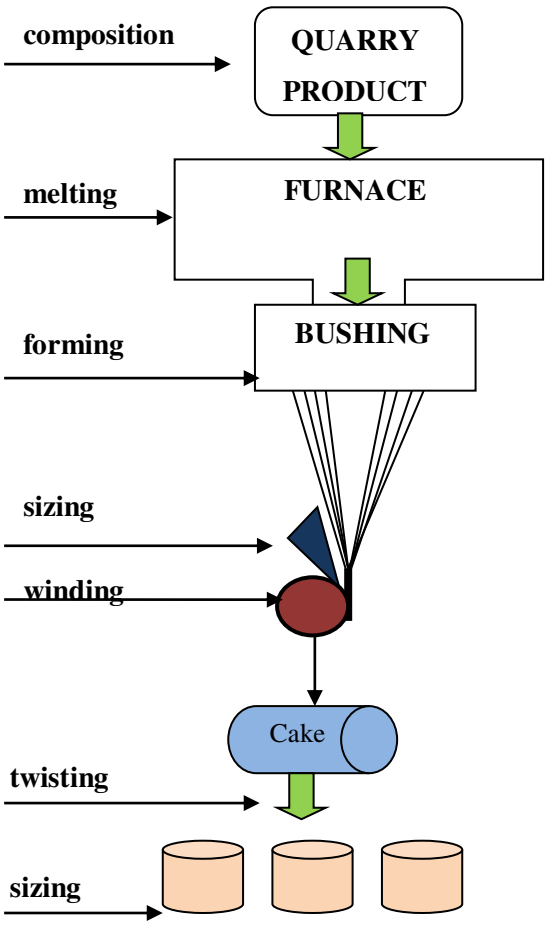

Figure 2. 11. Manufacturing process of glass fibers

2.6. Glass Fiber Reinforced PA 66

In recent years, fiber filled polymers have been commonly employed in many areas including aviation, automotive, construction and railway industry as well as sporting and consumer goods and so on (Bansal, Monsalve Cano, Muñoz, & Paulotto, 2010). As the technology is advancing, the need and demand for high-performance and light-weight materials is also increasing. Therefore, engineers and scientists have been focusing on designing new-brand materials to meet the increasing demands. The reason why GF reinforced polymers are so popular is that they offer various advantageous properties over their metallic counterparts. Since they possess good high mechanical strength and e-modulus, low density, high stiffness, very good fatigue resistance resistance, they are able to meet the demands of developing modern technology (Nuruzzaman et al., 2016).

Being a thermoplastic polymer, PA 66 is one of the toughest engineering plastics. It exhibits good resistance against corrosion and chemicals; however, its application is limited because of its relatively low strength, low rigidity, dimensional instability and tendency to absorb moisture. One of the easiest and cost-effective ways for improving the mechanical performance of PA 66 is GF reinforcement. Since GF exhibits high mechanical strength and e-modulus, the resulting composite (PA 66/GF) exhibit better performance properties (Srivastava & Lal, 1991).

CHAPTER 3

NANOTECHNOLOGY AND NANOSCIENCE

3.1. Definition

According to the description made by National Nanotechnology Initiative, nanotechnology is a branch of technology focusing on manipulating the properties of matter which posseses nano-scale dimension or dimensions sized between 1 and 100 nanometers. Although the person who first used the term *nanometer* was Richard Zsigmondy, 1925 Nobel Prize winner in chemistry, it was physics Nobel Laureate Richard Feynman who is considered to be idea father of modern nanotechnology, mainly because of his speech entitled *There's Plenty of Room at the Bottom* at Caltech in 1959. By this speech he put forward the idea of altering the qualifications of matter at atomic-scale. And since then, nanoscience and nanotechnology have drawn a great deal of attention besides urging and inspring scientists and engineers to design new materials and applications.

The word *nano* is originated from Greek word *dwarf* or *extremely short person*. Today, it is used as a prefix for any unit in order to refer to the billionth (10^{-9}) of that unit. Therefore, as the name suggests, the term *Nanoscience* describes the study, manipulation or engineering of the matters at nano-scale. Characteristics of materials are directly dependant on how its molecules and atoms assemble on the nanoscale. However, it should be noted that the properties of the matter on micro or macro scale is often different from the properties on nanoscale and this difference is mainly due to the quantum effect. Nanotechnology, on the other hand, is the application of nanoscience. Together with nanoscience, it makes it possible to manipulate the characteristics of a matter and makes a great contribution to the relevant fields to design new materials and products with new improved properties.

Nanoscience and nanotechnology disciplines are in touch with many other disciplines such as physics, chemistry, biology, material science, medicine, agriculture, informatics, electronics etc (Schummer, 2004). Therefore, in recent times, the term *nanotechnology* has been shifted to the plural form *nanotechnologies*

as well as *nanoscale technologies* in order to refer to the broad range of disciplines it is in touch with.

As aforementioned, one nanometer (nm) refers to an extremely small value equal to one billionth of a meter (i.e. 10^{-9}). For instance, the size of a water molecule is nearly 0.1 nm, a typicall paper sheet has approximately 100.000 nm thickness, the width of a hair strand is between 80.000 and 100.000 nm, the helix of human DNA is nearly 2 nm in diameter, the minimum size which is able to be seen by a human is 10,000 nm. Figure 3.1 represents a size comparison of nanoparticles with micro- and macro-sized materials.

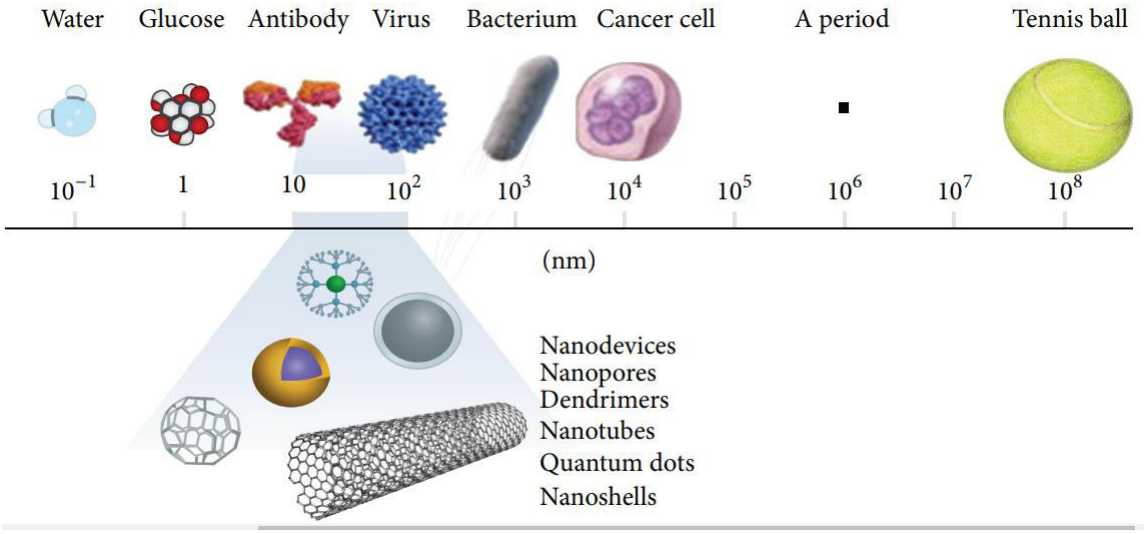

Figure 3. 1. Size comparison of nanomaterials with micro-sized and macro-sized materials (Amin, Alazba, & Manzoor, 2014).

To understand the potential of nanotechnology, it should be mentioned that, at the nanoscale (below about 100 nanometers), some properties of the materials could significantly change and the material may exhibit new properties such as different color, higher chemical reactivity, electrical conductivity, elasticity, mechanical strength and so on. This change in the properties is called “quantum effect” or “quantum size effect”. For instance, carbon in the form of graphite is soft and weak whereas it can be stiffer and stronger than steel at the nanoscale. Moreover, being an opaque substance, copper becomes transparent; being an inert material, platinum becomes a catalyst; being a solid material, gold turns into a liquid at room temperature; and being insulator, silicon becomes conductor at the nanoscale. The

reason of these significant changes is directly related to the complicated universe of quantum physics. While overall characteristics of materials are determined by classical physics, properties of the same materials at the nanoscale are dominated by modern physics, namely quantum physics.

3.2. Nanomaterial

A nanomaterials is defined as a substance whose at least one the 3 external dimension is 1-100 nm. As well as being able to occur naturally, they can also be produced via engineering on purpose so as to carry out a specific function. Nanomaterials may exhibit different physical, chemical, electrical and optical properties than that of their own micro scaled or macro scaled counterparts. This is due to the quantum effect as well as their relatively larger surface/volume ratio. Larger surface/volume ratio could make materials more chemically reactive or it can alter the properties such as strength or conductivity. To understand this concept, one can imagine a cube having 3 cm length of each side; in this case, the surface area would be 54 cm^2. If this cube was rendered into 27 identical cubes, then the side length and the surface area of each small cube would be 1 cm and 6 cm^2, respectively. Moreover, the total surface area would be 162 cm^2. Briefly, at first, the surface area of the cube was 54 cm^2; however, after being rendered into 27 pieces, the total surface area of the same cube became 162 cm^2, which means that the surface area tripled.

3.3. Classification of nanomaterials

Nanomaterials are often divided into four classes depending on their dimensionality: 0-Dimension, 1-Dimension, 2-Dimension, and 3-Dimension (see Figure 3.2).

0-D (Zero dimensional) nanomaterials: In this class, three dimensions of the nanomaterial are at nanoscale. They can be in cubic, spherical or polygonal shape with size ranging between 1 and 50nm. Nanoparticles and quantum dots are the examples of this category. They are also referred to as artificial atoms.

1-D (One dimensional) nanomaterials: In this class, two dimensions of the nanomaterial are at nanoscale. Their length is usually at microscale while their

diameter is merely a few nanometers. Some of the members of this class are nanotubes, nanofibers, nanowires nanorods and whiskers of metals or oxides.

2-D (Two dimensional) nanomaterials: In this class, one dimension of the nanomaterial is at nanoscale. Examples include graphene, nanolayers, nanoclays, nanosheets, nanoflakes, or nanoplatelets and silicate nanoplatelets.

3-D (Three dimensional) nanomaterials: In this class, in fact, no dimension of the material is at nanoscale. They are a combination of individual nanomaterials and therefore known as bulk nanomaterials. This class of nanomaterials includes bulk powders, bundles of nanowires and dispersion of nanoparticals.

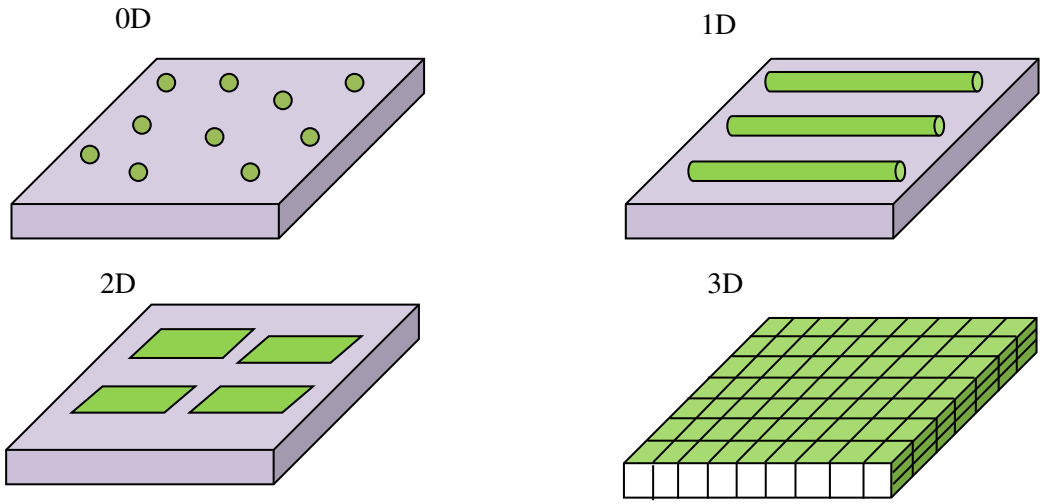

Figure 3. 2. Types of nanomaterials based on their dimensions (Dolez, 2015).

3.4. Carbon nanotubes

The word “carbon” is originated from Latin “carbo” which means coal. Being represented with the symbol “C”, carbon is considered to be the most sophisticated element in the periodic table as it can form various elements depending on type, strength and number of bonds. Properties of C highly depend on the configuration of e^- around the nucleus. It is non-metallic and tetravalent, which means that its four electrons are ready to form covalent bonds. This bonding mechanism can occur in various ways so that various allotropes of carbon emerge. Each carbon allotrope exhibits different physical properties; for instance, whereas graphite is opaque and black and malleable, diamond is rather transparent and extremely hard, in fact it is the hardest material known so far.

Being an allotrope of carbon, *buckminsterfullerene,* a molecule made up of 60C atoms in sp^2 hybridized bonds formed into a perfectly symmetric structure, discovered by some researchers at Rice University in 1985. This surprising discovery brought the Nobel Prize to its inventors, Richard Smalley, Robert Curl, and Harry Kroto; and it laid the foundations of modern carbon technology.

In 1991, Sumio Iijima discovered another allotrope of carbon, known as MWCNTs (Iijima, 1991); and after a few years, Iijima et al. and Bethune et al. simultaneously discovered SWCNTs (Iijima & Ichihashi, 1993). The first observed MWCNT is shown in Figure 3.3.

A CNT can simply be imagined as a graphene layer, which is a honeycomb-like lattice made of carbon atoms, rolled up and taken a tubular form. This tubular C molecules exhibit very high length/diameter ratio, since its length is at microscale while the diameter is at nanoscale. SWCNTs can have a diameter less than 1 nm whereas MWCNTs can consist of several interlinked nanotubes, with diameters reaching more than 100 nm. On the other hand, the value of their lengths may reach up to a few millimeters or micrometers.

MWCNTs have aroused a great deal of interest owing to the ultra-high performance properties they possess: Their tensile strength is 11-63 GPa (M. F. Yu et al., 2000) and e-modulus is nearly 1 TPa (Salvetat et al., 1999; M. F. Yu et al., 2000), which means that they are 100 times stronger than steel. Therefore, they have become promising materials for composite industry as they may increase the mechanical performance of polymers, ceramics and metals. However, among all types of composite systems, CNT/polymer-matrix systems have drawn more attention owing to their light weight, easy machinability and production costs (Du et al., 2007; Sahoo et al., 2010; Shankar & Rhim, 2016; Song et al., 2013).

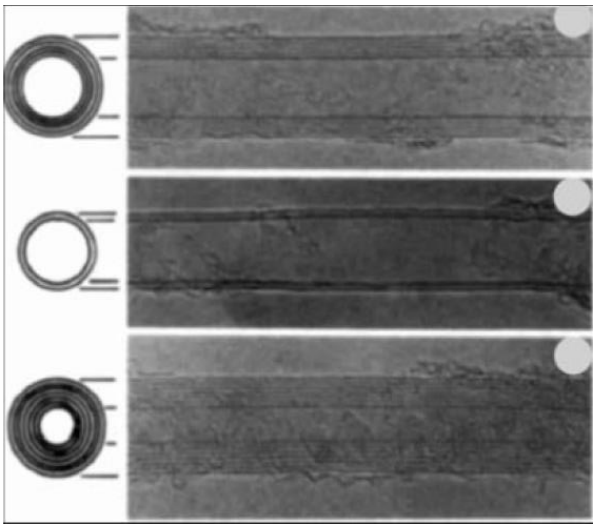

Figure 3. 3.Transmission electron micrographs of the first monitored MWCNTs introduced by Iijima in 1991 (Iijima, 1991)

Based on the number of their walls, CNTs are simply categorized as single-walled and multi-walled CNTs, as represented in Figure 3.4.

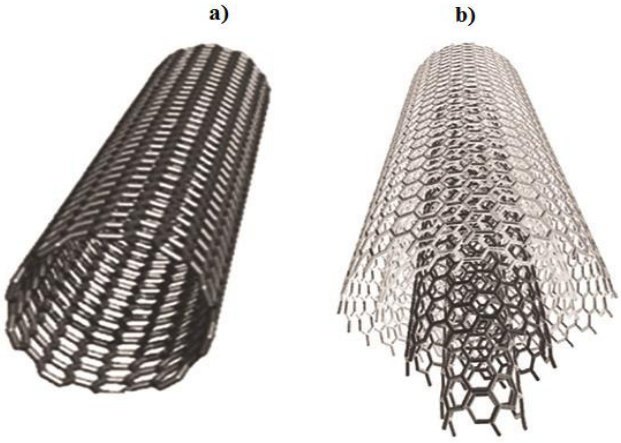

Figure 3. 4. Illustration of; (a) SWCNT and (b) MWCNT (Choudhary & Gupta, 2011).

SWCNTs can be classified into 3 main subclasses, which are identified by chiral vector (n, m) and these 3 types of SWCNTs are called armchair, zigzag, and chiral carbon nanotubes. Figure 3.5 reperents the formation and types of CNTs. “n” and “m” represents the integers of vector equation R = na1+ma2 and the arrows represent rolling direction of graphene layer.

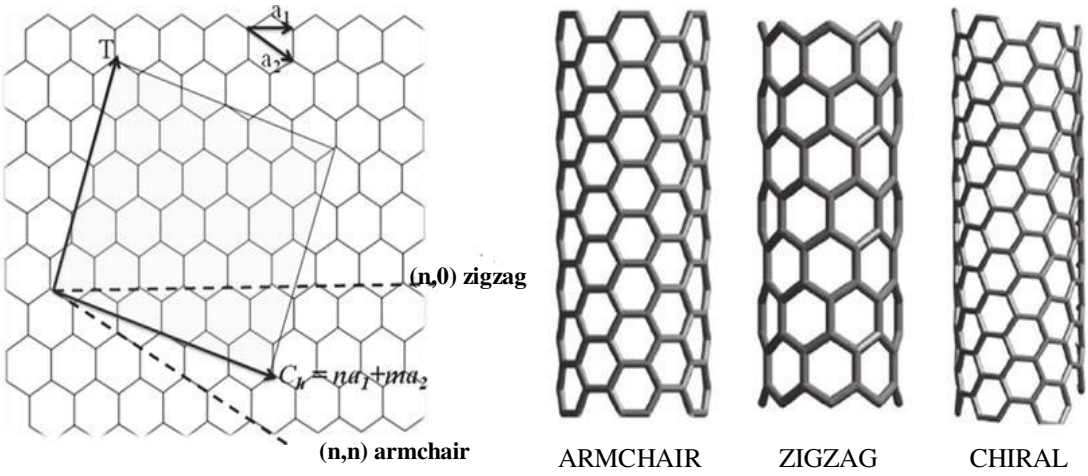

Figure 3. 5. Illustration of (a) formation of SWCNTs and (b) types of SWCNTs based on chirality (Choudhary & Gupta, 2011).

3.5. Mechanical Properties of Carbon nanotubes

3.5.1. Young's Modulus of Carbon nanotubes

Young's modulus (E) is considered to be one of the crucial parameters defining tensile properties of a material. Young's modulus, also known as e-modulus, characterizes mechanical behaviour of materials under tension or compression. E-modulus of a material is strongly dependent on chemical composition of the atoms as well as the cohesion of the solid.

Thanks to strong sp^2 C-C bonds, CNTs exhibit superior tensile and flexural properties. Moreover, their density could even reach down to 1.3g/cm^3, which is 1/6 of stainless steel. Young's modulus of CNT is greater than 1 TPa and the highest tensile strength measured so far can reach up to 63 GPa (Yu, Files, Arepalli, & Ruoff, 2000; M. F. Yu et al., 2000).

Being the first researchers having measured the Young's modulus of MWCNTs, (Treacy, Ebbesen, & Gibson, 1996) analyzed 11 MWCNTs and noted that the mean value of Young's modulus was 1.8TPa; moreover, they suggested that the MWCNTs with smaller tube diameters exhibit higher elastic moduli. On the other hand, (Salvetat et al., 1999) stated that Young's modulus of arc-grown CNT is 810±410 GPa.

(Wong, Sheehan, & Lieber, 1997) noted that the mean value of six individual MWNTs, with diameters between 26 and 76nm, is 1.28±0.59TPa. Similarly, (Kulik, Kis, Lukic, Lee, & Forró, 2007) noted that Young's modulus of MWCNT is virtually 1 TPa.

3.5.2. Strength of Carbon nanotubes

Measuring mechanical strength of materials is more complicated than Young's modulus as this measurement can be adversely dominated by certain parameters such as pressure, temperature, humidity, measuring system etc. (Wong et al., 1997) reported that flexural strength of MWNTs with large diameter is about 14.2± 0.8 GPa. Yu et al. (M. F. Yu et al., 2000) studied mechanical performance of MWCNTs by scanning electron microscopy. The authors revealed that tensile strength of MWNT layer varies within 11-63GPa and that the Young's modulus varies within 270-950GPa. Similarly, according to direct measurements of (Li, Cheng, Bai, Su, & Dresselhaus, 2000), tensile strength of a SWNT rope is approximately 3.6 ±0.4GPa.

Considering the excellent mechanical qualifications of CNTs, we can conclude that CNTs have an enormous potential for the applications which requires mechanical performance.

3.6. CNT Synthesis Methods

Since the discovery of MWCNTs by Iijima, CNTs have been commonly used in various applications, such as solar cells, supercapacitors, conductive films, fuel cells, sensors, purification systems, separation membranes and filters, displays, textiles and so on, owing to the splendid physical, mechanical, thermo-mechanical, optical and electrical properties they possess (Prasek et al., 2011). These properties are often dependant on the structural properties of CNT, such as the quantity of walls, length and diameter of the tube, or chiral angle of the graphene sheet. The first CNTs synthesis occurred unintentionally by Iijima via arc-discharge technique; however today, there are various methods to produce CNTs. These methods may be categorized with several classes according to the properties of CNTs to be produced, mechanism, time, temperature, heat source, precursor, atmosphere of reactions and so on (Rajesh Jesudoss Hynes et al., 2019). Today, there are various methods for

synthesizing CNTs, as shown in Figure 3.6.; however, three of them, namely arc-discharge, laser ablation and chemical vapor deposition(CVD) (Ando, Zhao, Sugai, & Kumar, 2004) are considered to be the major ones.

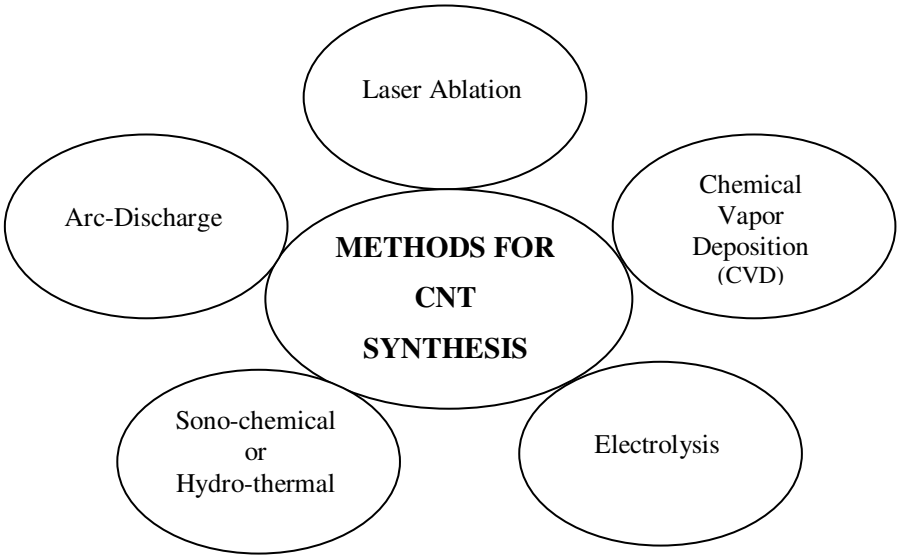

Figure 3. 6. Methods used for CNTs synthesis (Prasek et al., 2011).

It should also be mentioned that it is not economically convenient to produce large amounts of CNTs through laser ablation or arc discharge methods (Moses, Gangrade, & Mandal, 2019). Therefore, chemical vapor disposition method has been surpassing others in terms of the ability of producing bulk quantities of CNT. This is mainly due to the fact that arc-discharge and laser ablation are carried out in high-temperature conditions, wherein controlling the purity, orientation, length, diameter, and density of CNTs is quite challenging. Chemical vapor deposition, on the other hand, is relatively easier as it can be carried out at lower temperatures (< 800°C) (Ganesh, 2013).

3.6.1. Arc-discharge Method

Arc-discharge was the initial technique used for synthesizing CNTs. CNT production apparatus is illustrated in Figure 3.7. First of all, the enclosed chamber is evacuated by means of a vacuum pump and a suitable noble gas, such as He or Ar, is

introduced to the setup at a certain pressure (50-700 mbar) ; afterwards, a dc arc-voltage(12-25V) is applied between the graphite rods (Journet et al., 1997). These graphite rods, which have different potentials, function as electrodes and they are moved towards each so as to produce the arc. During the entire process (approximately 1 minute), electrodes are kept at the distance of 1mm.

In this method, if purified graphite rods are utilized, the anode moves away in order to produce fullerenes and the obtained fullerenes are accumulated in the form of carbon black inside the setup. However, a little amount of anode remains on the cathode surface including MWCNTs. On the other hand, if the anode is a graphite rod incorporating metal catalyst and the cathode is pure graphite, in this case, SWCNTs are produced in the form of carbon black (Ando et al., 2004).

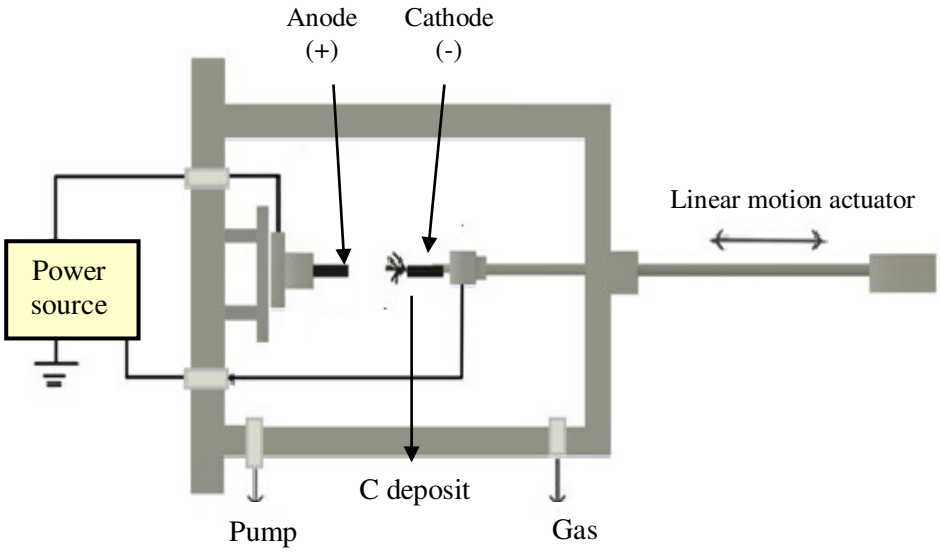

Figure 3. 7. Illustration of CNT synthesis setup via arc-discharge method (Rastogi et al., 2014)

3.6.2. Laser Ablation

This is a similar technique to arc-discharge in terms of precess principles. However, in this method, a laser is used instead of electrical discharge. Powerful laser rays are sent through the window of the setup and these rays are aimed at the target at the centre of the heating unit which is heated up to 1200°C. In the mean time, SWCNTs are grown on the trap and a noble gas collects them flowing through the chamber. This method, whose setup is illustrated in Figure 3.8, offers some advantages such as diameter control, temperature control and high-quality of SWCNT production. Moreover, since the critical parameters can be finely

controlled, this method enables tuning the CNTs and production of brand-new materials.

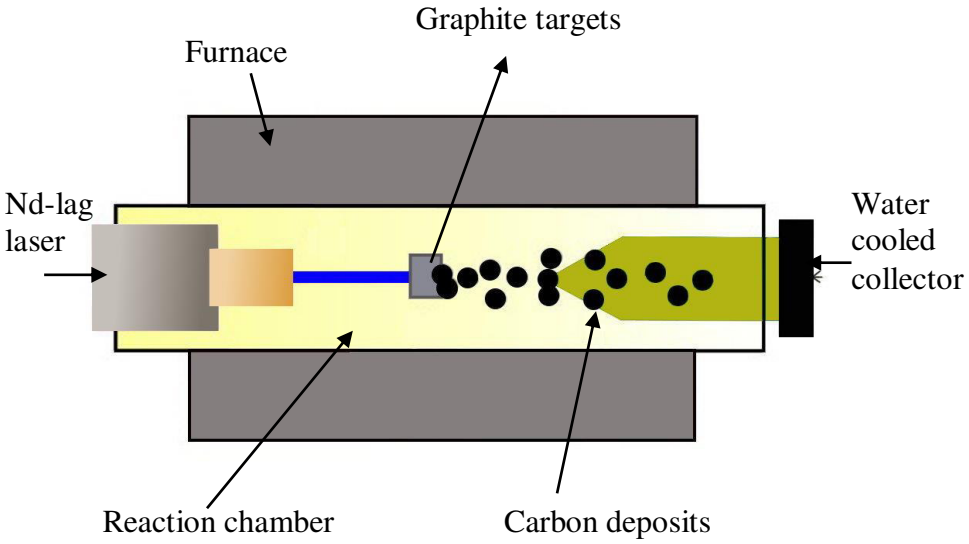

Figure 3. 8. Illustration of CNT synthesis setup via laser ablation method (Rastogi et al., 2014).

3.6.3. Chemical Vapor Deposition

Nowadays, CVD is among the most useful and easiest techniques of producing CNTs (Kumar & Ando, 2010). This technique is also referred to as thermal or catalytic CVD, since a hydrocarbon vapour is thermally degrades in the presence of a metal catalyst during this technique. Figure 3.9 represents the setup of CNT growth by CVD. In this technique, a substrate, whose surface is covered with a metal catalyst, is located inside a tubular heating chamber. Temperature of catalyst material is adjusted at 600-1200°C. The hydrocarbon vapor, such as acetylene, ethylene etc, passes through this tube for 15-60 minutes to decompose the hydrocarbon. The carbon atoms dissociate from the gas molecules and rearrange on the catalyst so as to form the carbon nanotubes. When the temperature of system falls down to nearly 25°C, the CNTs emerged over the catalyst are gathered.

In this method, there are three crucial parameters for carbon nanotube growth: i) the hydrocarbon, ii) catalyst, and iii) growth temperature. MWCNTs can be grown at low temperatures (600-900°C) whereas SWCNTs need higher temperatures (900-1200°C) to grow, which means that higher energy is required to obtain SWCNTs (Ando et al., 2004).

Unlike arc-discharge and laser ablation, CVD offers a continuous CNT growth, which enables mass production of carbon nanotubes. Moreover, it allows better control over growth parameters and hence enables the formation of CNTs in various forms.

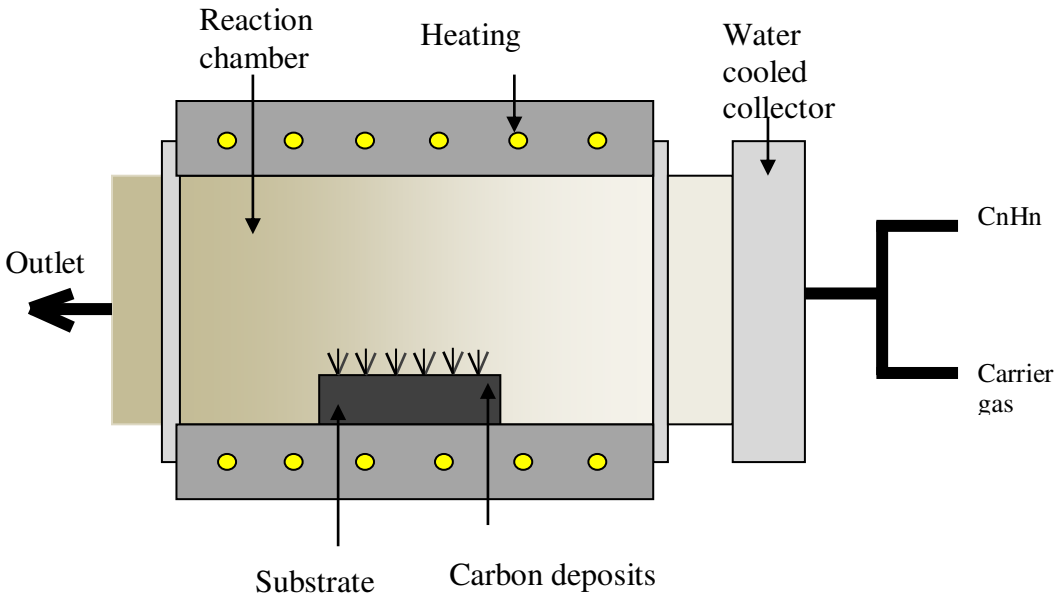

Figure 3. 9. Illustration of CNT synthesis setup via CVD (Rastogi et al., 2014).

Table 2.2 summarized and compares these three major methods.

Table 2.2. Summary and comparison of three most common CNT synthesis (Eatemadi et al., 2014)

Method	**Arc-discharge**	**Laser ablation**	**CVD**
Yield rate	More than 75%	More than 75%	More than 75%
SWCNT or MWCNT	Both of them can be synthesized	Both of them can be synthesized	Both of them can be synthesized
Advantage	High-quality CNTs, simple, inexpensive	Synthesis at room temperature, high purity	Synthesis at low temperature, simple, production at larger scale, high purity, aligned growth facility
Disadvantage	Synthesis at higher temeprature, relatively less pure, tangled CNTs	Production amount is limited to the labscale, purification is necessary	More suitable for the synthesis of MWCNTs, defects

3.7. Application Areas of Carbon nanotubes

Having superior and unique mechanical and electrical qualifications, CNTs are one of the most outstanding materials to be utilized in various industrial and daily applications. Since they have ultra high mechanical strength, they can be used in reinforcement phase for composite systems. Moreover, their high surface/volume ratio and high conductivity allows them to be utilized in the applications in which conductivity is necessary. Thanks to the advancements and innovations in synthesis techniques, potential use of CNTs has been expanding year by year. Today, there are plenty of potential applications and fields where CNTs can be used, such as electrodes, capacitors, solar cells, strong composites, storage, drug delivery, diagnostics, thin films and so on (Schnorr & Swager, 2011).

CHAPTER 4

NANOCOMPOSITES

4.1. Definition

A nanocomposite is a material which is composed of multiphases where at least one of the phases has nano-scale (less than 100 nm) dimensions. Nanocomposites offer a lot of solutions and innovations for the difficulties in various fields covering medical industry, pharmaceutical industry, electronics, energy industry and food packaging. Nanocomposites are divided into two main classes according to dimensions of nanomaterials and to matrix material. The first class includes four types of nanocomposites incorporating 0-dimensional (such as nanospheres or nanoparticles), 1-dimensional (such as nanotubes, nanorods or nanowhiskers), 2-dimensional (such as nanosheets or nanoplatelets) and 3-dimensional (such as graphite) fillers. All nanomaterials used as filler are important since they contribute to the mechanical strength of the matrix phase. Similar to other conventional composites, characteristics of nanocomposites are determined by constituent properties, structure, composition and nanofiller-matrix interaction.

Other classification of nanocomposites includes three subclasses following as: i) ceramic matrix nanocomposites (CMNC), ii) metal matrix nanocomposites (MMNC) and ii) polymer matrix nanocomposites (PMNC). It should also be noted that the most popular classification is the one dividing the nanocomposites based on the matrix material. Figure 4.1. represents the classification of nanocomposites.

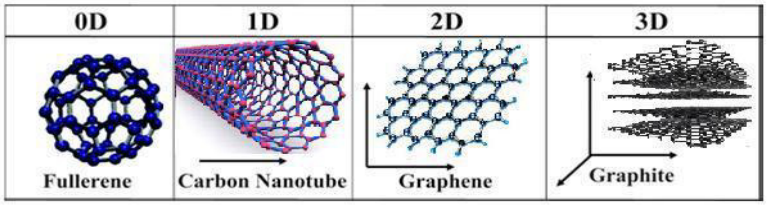

Figure 4. 1. Classification of nanocomposites according to their dimensions (Machado, Fagan, Zanella da Silva, & Andrade, 2015)

4.2. Polymer Matrix Nanocomposite

A polymer nanocomposite is a composite which incorporates nano-scale fillers embedded in a polymeric matrix. This polymer may be either thermoset or thermoplastic. The purpose of filling polymers with nanomaterials is to improve certain properties of the bulk material. It is known that nowadays, in advanced and advancing technologies, low-weight materials are more preferable as they generally decrease the energy consumption of the designed application. With the inclusion of a small amount of nanomaterial, performance properties of the bulk material can significantly enhance while the weight slightly changes. Therefore, combining nanomaterials with polymers has been investigated by scientists and engineers in order to design thinner and lighter structures with high performance.

It is known that nanomaterials are capable of bettering the mechanical performance of polymers. This desired effect is mainly owing to the splendid mechanical qualifications of nanomaterials in addition to their high surface/volume ratiowhich allows more facial interaction with the matrix compared to micro-scale fillers. In order to achieve an effective reinforcement, the external load introduced to the matrix is expected to be evenly shared with filler network. If external load is adequately conveyed to the reinforcing fillers, mechanical strength of the composite can increase. However, to obtain such an enhancement, the fillers or nanofillers should be compatible with the polymer chosen as matrix.

Another reason why nanomaterials leads to increment in mechanical properties of polymers is that they are capable of improving toughness by deflecting or bridging across the microcracks during the fracture. By deflecting, they can change to direction of the crack; and by bridging or stretching, they can prevent the crack opening and propagation. However, achieving a homogenous dispersion of nanomaterials may be quite challenging as they are prone to form agglomerates in the polymer matrix. In that case, they may act like defects and adversely affect the mechanical properties.

Polymer matrix nanocomposites are being used in several fields such as food packaging, sports accessories, energy storage systems, optical glass and membranes, electronics and automobile sectors, coatings and so on (Omanović-Mikličanin, Badnjević, Kazlagić, & Hajlovac, 2019).

4.3. Polymer/CNT Nanocomposites

CNTs are one of the most outstanding nanomaterials offering improved performance properties for polymer, which is mainly owing to their high volume/surface ratio, stiffness, extraordinary mechanical qualifications, unique electrical, magnetic and thermal qualifications (Elksnite, Bitenieks, Zicans, & Bledzki, 2009). CNTs enhance the mechanical strength of polymers deflecting or bridging the cracks during the fracture, as shown in Figure 4.2. In other words, while a crack is opening, nanotube is stretched absorbing the fracture energy transferred from the matrix or changes the direction of the crack, which leads to an enhancement in mechanical performance of the polymer resim. However, like many nanomaterials, CNTs are prone to gathering and forming entangled agglomerates or bundles due to their very high length/diameter ratio, relatively longer length, polarizability and Van der Waals forces (Banerjee & Dutta, 2019; Wernik, Cornwell-Mott, & Meguid, 2012). In the presence of these agglomerates, the external stress is unevenly distributed along the matrix and CNTs may act like defects; therefore, the mechanical strength may exhibit a decreasing trend.

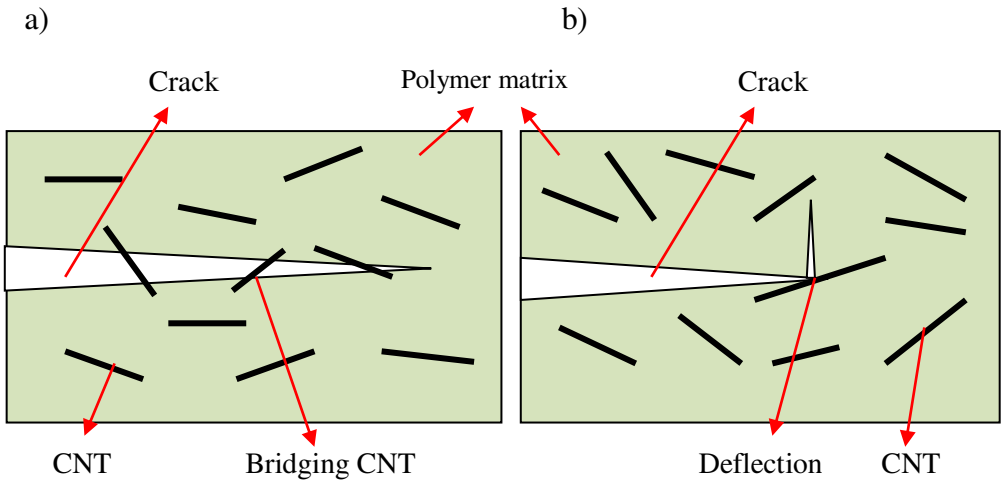

Figure 4. 2. (a) crack bridging and (b) crack deflection mechanisms of CNTs in polymer matrices.

For an effective reinforcement, a proper bonding or good facial polymer-CNT interaction should be achieved. To obtain a desired reinforcement effect in CNT/polymer composites, there are three critical parameters needed to be addressed. The first parameter is uniform dispersion of CNTs within polymeric resin; the

second is alignment of CNTs within polymer resin; and third is good interfacial bonding between CNTs and polymer resin.

4.3.1. Dispersion of CNTs in Polymer Matrix

In order to escalate the benefits of CNT within a polymer matrix, agglomeration tendency and slippage of CNTs should be prevented. Providing that agglomeration occurs, CNTs easily slip against each other since they are less adhered to the polymer when an external load is applied. Consequently, mechanical properties of the composite system exhibit a decreasing trend. To prevent this failure, CNTs should be as well-dispersed as possible, as illustrated in Figure 4.3. There are some useful methods to obtain an improved CNT dispersion within polymer matrices: Chemical functionalization, sonication, shear mixing, surfactant assisted processing and in-situ polymerization are among these methods (Sharma, 2018).

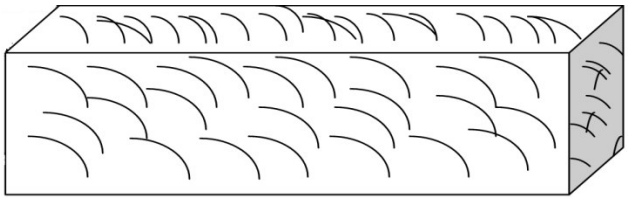

Figure 4. 3. Illustration of MWCNTs dispersed in polymer matrix

4.3.2. Alignment of CNTs in Polymer Matrix

Another critical parameter for providing effective reinforcement in CNT/polymer composite systems is to achive a sufficient level alignment of CNT inside continuous phase. CNTs exhibit highly anisotropic properties due to their high length/diameter ratio. To utilize their load carrying capacity effectively, CNTs should be well aligned along the axial direction within the polymer matrix. Aligning CNTs in the matrix allows us to control the strength, stiffness, thermal and electrical characteristics of composite system. Alignment process of CNTs within polymer is carried out during composite casting. There are several methods for aligning CNTs in polymer matrices. For horizontal alignment; electric field, magnetic field, shear force, mechanical stretching, electrospinning and infiltration; for vertical alignment, infiltration, in-situ polymerization and external field methods can be used Among

these methods, electrical alignment and magnetic alignment are the major ones (Goh, Ismail, & Ng, 2014). Figure 4.4 represents the alignment of CNTs within polymer resin.

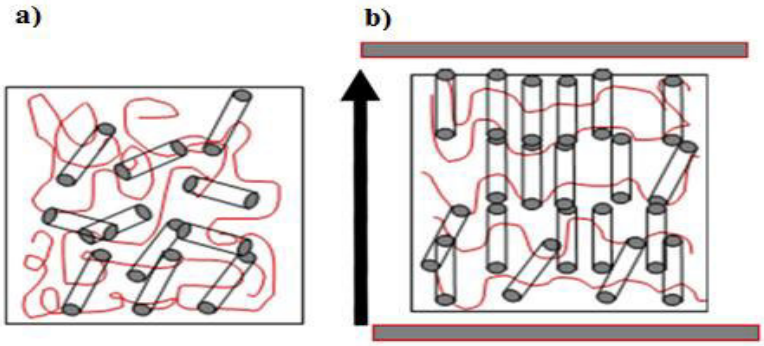

Figure 4. 4. Illustration of (a) randomly oriented CNTs and (b) well-aligned CNTs within polymer matrix (Sharma, 2018)

4.3.3. Interfacial Bonding between CNTs and Polymer Matrix

Bonding or interaction between CNTs and polymer surfaces plays a dominant role on mechanical properteies of the CNT/polymer composite systems. The term "interphase or interface" can be described as the surroundings of the filler where it is physically or chemically adhered to the matrix (Kashfipour, Mehra, & Zhu, 2018).Figure 4.5 represents the interface of CNTs in polymer matrix. Good interfacial bonding has a great influence on the polymer chain mobility and provides an even load transfer to the reinforcement phase. However, since this bonding is aromatic in nature, C atoms on CNT walls are chemically stable, which indicates that CNT-matrix facial interaction depends on Van der Waals interactions (Wernik et al., 2012). In other words, because of low chemical reactivity of CNTs, achieving desired interfacial CNT-polymer bonding or adhesion is quite challenging. To overcome this difficulty, CNT surface can be chemically or physically modified. The most popular way to attain this purpose is chemical functionalization by which new functional groups are chemically adhered to CNT surface. An appropriate functionalization can improve the interfacial bonding and thereby improve mechanical, thermal and electrical properties of CNT/polymer composite systems (Avilés, Cauich-Rodríguez, Toro-Estay, Yazdani-Pedram, & Aguilar-Bolados, 2018).

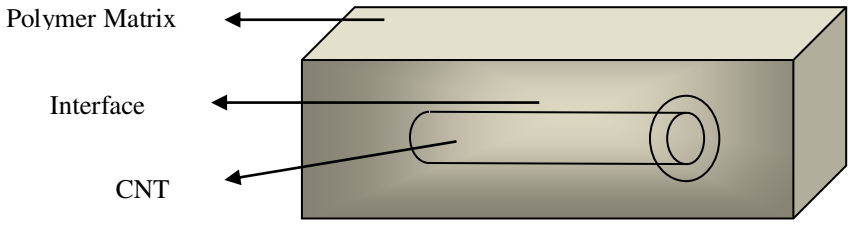

Figure 4. 5. Illustration of the CNT interface in a polymer composite (Arash et al., 2014).

4.4. Processing Methods of Polymer/CNT Nanocomposites

As aforementioned, CNTs are highly prone to forming agglometarions or bundles since the possess very high surface/volume ratio. Consequently, it is essential to use the most appropriate processing method for dispersing CNTs sufficiently within the polymeric matrix and to avoid presence of agglomerates. Major methods which are proven to have achieved this goal are solution processing, melt mixing and in-situ polymerization (Choudhary & Gupta, 2011).

In solution processing, as shown in Figure 4.6., first of all, CNTs are dispersed inside an appropriate solution and then intensely blended with the polymer resin by mechanical mixing, magnetic mixing or ultasonication at room temperature or elevated temperature. After the desired dispersion is achieved, the mixture is poured in to the film cast and the solvent is allowed to evaporate.

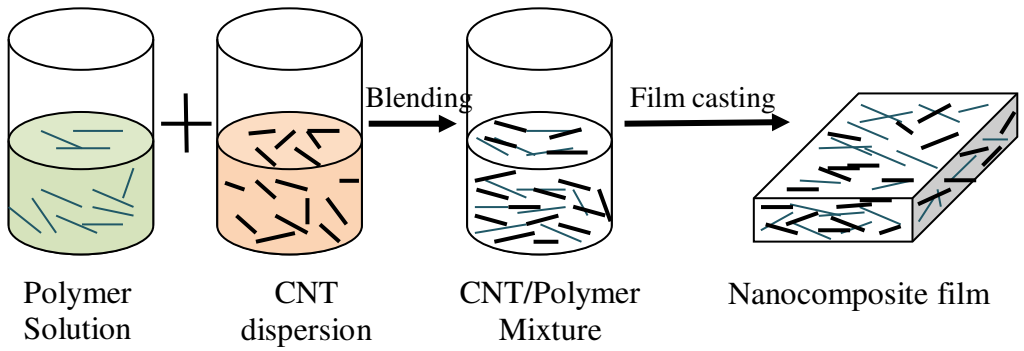

Figure 4. 6. Illustration of solution processing of CNT/polymer nanocomposites (W. Khan, Sharma, & Saini, 2016b).

In melt mixing method, as shown in Figure 4.7, polymer granules and CNTs, which are loaded in separated funnels, are transferred to the heating zones of an extruder by rotating screws. Once they reach the heating zone, they are gradually

melt-mixed and then reach the homogenization zone. Afterwards, the melt phase is sprayed into a mold where it takes its final shape or it is sprayed out as semisolid strands and then chopped into granules in order to be used as raw material of another product. This method is more suitable than solution processing in terms of producing large amount of CNT/polymer nanocomposites.

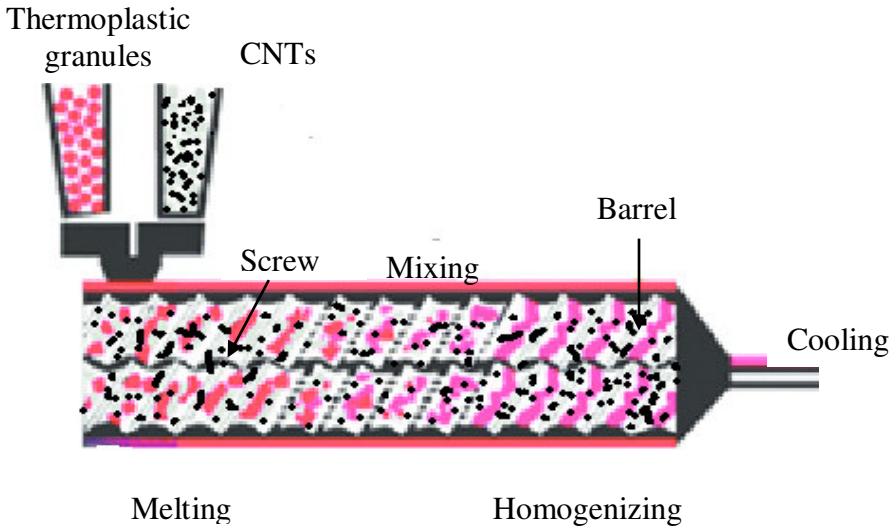

Figure 4. 7. Illustration of melt-mixing of CNT/polymer nanocomposites (W. Khan et al., 2016b).

In-situ polymerization, shown in Figure 4.8, is among the most popular methods for processing CNT/polymer composite systems. In this method, CNTs are introduced to liquid monomers. Once a homogeneous phase is achieved, polymerization reaction starts by the incorporation of a suitable starter. When the polymerization process is over, CNT/polymer takes its final shape.

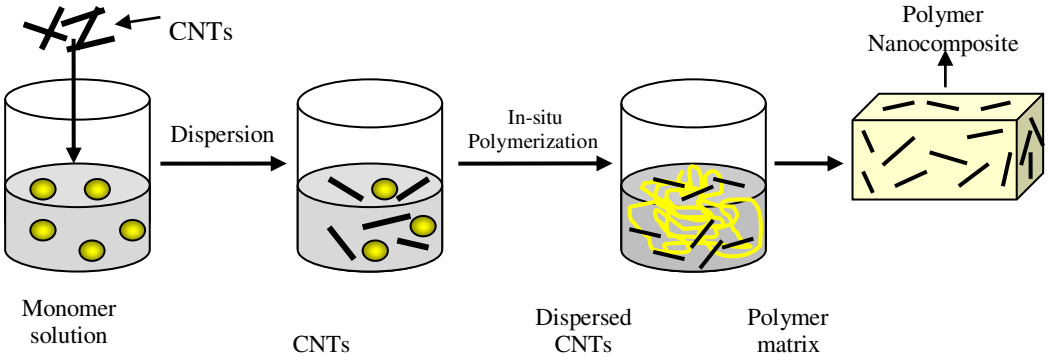

Figure 4. 8. Illustration of in-situ polymerization of CNT/polymer (Oliveira & Beatrice, 2019).

CHAPTER 5

EXPERIMENTAL STUDY OF THE INTEGRATION OF MWCNTS WITH PA 66/GLASS FIBER COMPOSITES

5.1. Aim of the Study

Being a semicrystalline thermoplastic, PA 66 is one of the most outstanding engineering plastics which has been widely employed in several areas fields including textile, electronics, construction, marine, automotive and so on, owing to its mechanical properties, chemical resistance, abrasion resistance, good wear resistance, thermal stability, easy processability and relatively low production expenditure (Chow & Mohd Ishak, 2015). On the other hand, PA 66 possesses several disadvantages such as absorbtion of moisture in the air, which cause inferior dimensional stability and limit the potential use and benefits of it. To improve the thermo-mechanical performance of PA 66, SGF are known to be efficient fillers. It is known that incorporation of glass fibers to PA 66 causes a considerable enhancement in the mechanical, chemical and thermal properties (Autay et al., 2019). Recently nanomaterials have also been used as reinforcing material; and one of the most outstanding one among them are certainly CNTs. The use of CNTs as reinforcement is due to their extraordinary mechanical properties.

In literature, a great number of studies are available regarding high-performance CNT/polymer composites. However, there are merely a few studies focused on mechanical behavious of polymeric composites systems incorporating more than one filler type. In the present study, we investigated the mechanical behaviour of MWCNT-integrated PA66/SGF composites to reveal the potential use of MWCNT-SGF hybrid reinforcement in a polymeric resin. We expect that the obtained results make a contribution to designing brand-new products offering superior advantages.

5.2. Materials and Methods

5.2.1. Composite Constituents

Neat PA66, 15 wt.% short glass fibres filled PA66 (PA66/15SGF) and 30wt.% short fibre filled P 66 (PA66/30SGF) granules were obtained from Mat Polymer, Istanbul/Turkey. MWCNTs were purchased from Ege Nanotek Kimya Sanayi, Izmir/Turkey. Figure 5.1. (a) and (b) represent the poylmer granules and MWCNTs that are used in this study.

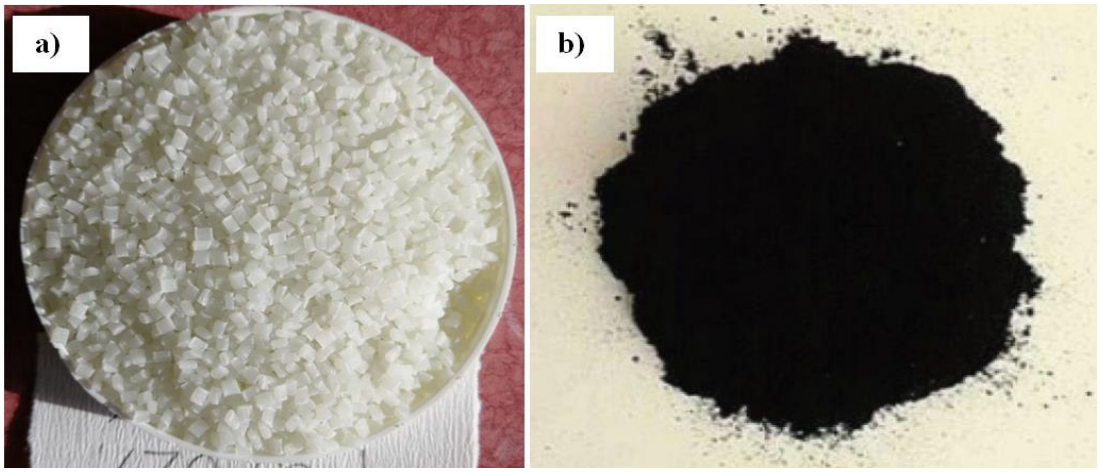

Figure 5. 1. (a) Polymer granules, (b) MWCNTs.

5.2.2. Preparation of the PA 66/30SGF/MWCNT Granules

Figure 5.2. (a) to (f) represent the preparation process of the PA 66/30SGF/MWCNTs composite. Firstly, MWCNTs and PA 66/30SGF granules were weighed on a sensitive scale to achieve the desired constituent ratio in the composite system. Subsequently, PA66/30SGF granules were blended with MWCNTs in ethanol by means of a magnetic stirrer. When homogeneity was achieved, PA 66/30SGF/MWCNT mixture was kept in a clean place at room temperature for several days in order to allow the ethanol to evaporate. After ethanol evaporated, 0.4 wt. % MWCNTs integrated PA66/ 30SGF granules were obtained. Afterwards, neat PA66, PA66/ 15SGF, PA66/ 30SGF and PA66/ 30SGF/ MWCNTs granules which had just been obtained were conditioned in an oven at 100^{o}C during 2 hours so as to avoid the moisture they incorporate; and these four types of granules

were transferred to the plastic injection moulding machine by which the test specimens were produced.

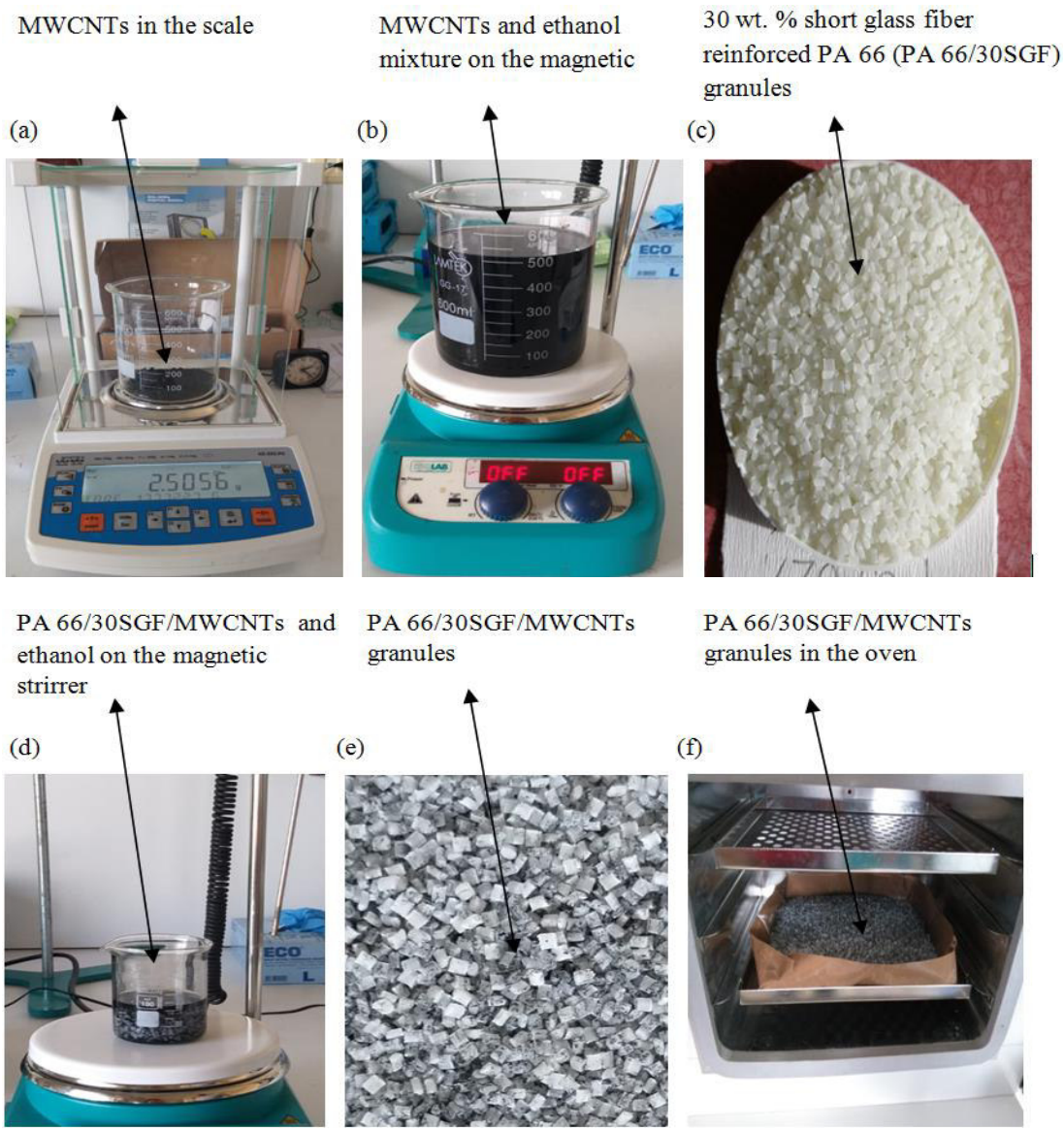

Figure 5. 2. Preparation process of PA 66/30SGF/MWCNT granules for the specimen production

5.2.3. Production of the Specimens

To produce PA 66/glass fiber composite, plastic injection molding is one of the easiest and cost-effective polymer processing methods. In this method, granule formed raw material is transferred to the machine through a funnel. As soon as the granules touch the cylinder, they are pushed forward into the hot resistances by a rotating screw. Inside these hot zones, the granules begin to melt as they are being

conveyed towards the nozzle. When a certain volume of melt polymer arrives at the nozzle, the screw stops rotating and pushes the melt polymer towards the empty mould which is kept in a clamping unit. During the melt polymer is being injected, the clamps are kept closed. While the mold is being filled with the polymer, the screw remains at the forward position to keep the stability of the pressure. In the meanwhile, the polymer starts to cool down and solidifies taking the shape of the mould. When the cooling ends, the clamps open and release the final product (Singh & Verma, 2017).

In the present study, all granules (neat PA 66, PA 66/ 15SGF, PA66/ 30SGF and PA66/30 SGF/MWCNT) were conveyed to the injection molding machine, shown in Figure 5.3 (a) and (b), to produce composite specimens. Since the shape of the mold is intentionally designed for tensile and flexural tests, composite specimens, shown in Figure 5.4 (a) and (b), were produced in accordance with ISO 527-2 type-1A and ISO 178 standards.

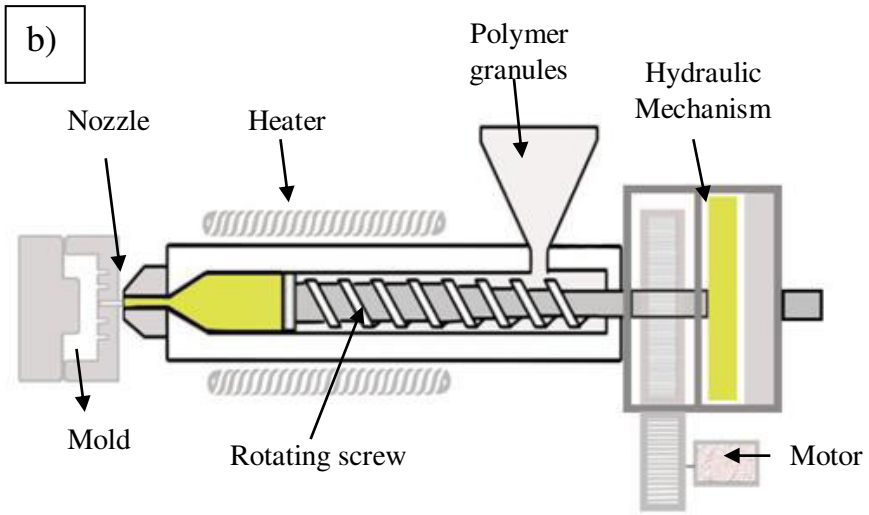

Figure 5. 3. (a) Plastic injection molding machine, (b) illustration of injection molding process setup

Figure 5. 4. Composite specimens in accordance with (a) ISO 527-2 type-1A and (b) ISO 178

5.3. Characterization

Four types of specimens in accordance with ISO 527-2 type-1A and ISO 178 standards were produced by plastic injection moulding machine. Tensile and flexural behaviours of the specimens were characterized using Instron 5982 100 KN (USA) test machine with a crosshead speed of 5mm/ min at nearly 25 ^{o}C. Mechanical tests and all specimens are shown in Figure 5.5 (a) to (d). Surface morphologies of the specimens were characterized by means of JSM-7001 F analytical field-emission SEM (Japan) and optical microscope in Central Laboratory (KİTAM), Ondokuz Mayıs University.

Figure 5. 5. Mechanical tests and specimens: (a) tensile test; (b) tensile test specimens in accordance with ISO 527-2 type-1A standard; (c) 3-point flexural test; (d) flexural test specimens in accordance with ISO 178 standard.

Tensile testing is one of the fundamentals for characterizing the mechanical behaviour of a material, such e-modulus, elongation at break or tensile strength.

In the present study, mechanical behaviour of the specimens, whose dimensions are shown in Figure 5.6., were directly measured via the tensile test mechine. Tensile strength and e-modulus of the specimens were calculated from the stress-strain curves using the equations below (Zweben, Smith, & Wardle, 1979).

$$E = \frac{\sigma(\varepsilon)}{\varepsilon} = \frac{F/A}{\Delta L/L_0} = \frac{FL_0}{A\Delta L}$$

E =Young's modulus or elastic modulus (MPa)

σ (ε) = stress (N/mm2)

ε = engineering extentional strain

F = applied force (N)

A=cross sectional area of the object (mm2)

L_0 =initial length

ΔL = the change in length

Flexural strength and flexural modulus of the specimens were calculated according to the equations below (Zweben et al., 1979);

$$\sigma_f = \frac{3FL}{2bd^2}$$

$$E_f = \frac{L^3 m}{4bd^3}$$

σ_f =flexural stress (MPa)

E_f =flexural Modulus (MPa)

F =load at a given point on the load deflection curve (N)

L =support span (mm)

b =width of the specimen (mm)

d =depth or thickness of the specimen

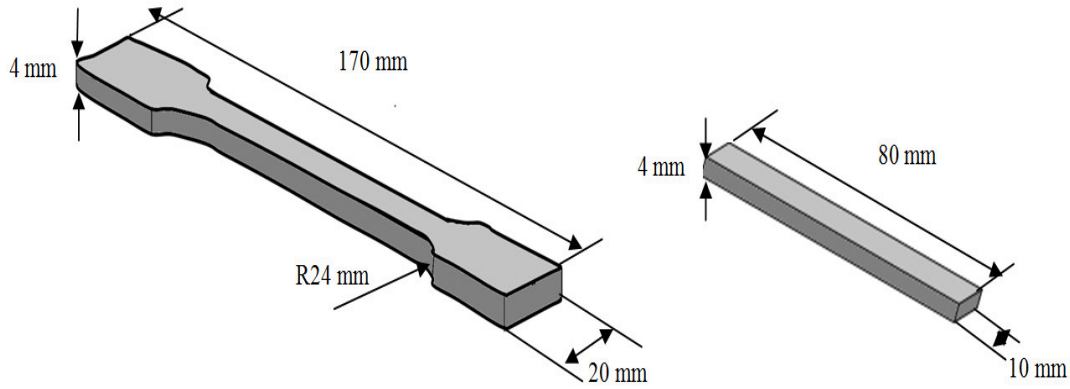

Figure 5. 6. Specimen dimensions in accordance with (a) ISO 527-2 type-1A and (b) ISO 178 (Akande, Dalgarno, Munguia, & Pallari, 2016)

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Surface Characteristics of PA 66/30SGF/MWCNT Composites

Surface morphologies of the fractured specimens were characterized by the SEM in Central Laboratory, OMU. Figure 6.1 (a) to (c) represents the SEM micrographs of PA 66/30SGF/MWCNT composite specimen. Figure 6.1 (a) shows the SEM micrograph of an individual glass fibre covered with MWCNTs whereas Figure 6.1 (b) and (c) represents higher-magnification SEM micrographs of the same specimen.

Well-dispersion of reinforcing materials or fillers and their strong facial interaction with the matrix are dominant parameters to achieve an effective reinforcement mechanism. To obtain improved mechanical qualifications, the load introduced to continuous phase must be evenly transferred to dispersed phase. As for the CNT/polymer composites, CNTs are expected to stretch and to bridge across the cracks formed inside the matrix during the fracture. Thus, CNTs can prevent crack opening and propagation and hence upgrade the mechanical performance of composite systems. Furthermore, if incorporated together with glass fibers, CNTs can modify the surface of GF and thereby ease the GF-polymer adhesion.

The SEM micrographs in Figure 6.1 (a) to (c) reveal that some individual MWCNTs function as bridges between the surface of GF and PA 66 resin. This bridging phenomenon contributes to the stress transfer by allowing CNTs to absorb the fracture energy and hence improves the toughness of composite system. Similar results were obtained in a number of studies. (Qian, Dickey, Andrews, & Rantell, 2000) monitored the nanotubes bridging across the cracks in polystyrene matrix using TEM and reported that the e-modulus of the composite specimens improved by virtually 25% after the inclusion of 1 wt. % CNT content.

(J. Jin, Zhang, Chen, & Li, 2013) obtained clear SEM images of CNTs and MWCNTs bridging across the cracks inside the PA 66/GF composites. They also reported that MWCNTs which coat the glass fibres notably better the facial

interaction and adhesion of polymer-CNT couple. (Puch & Hopmann, 2014) too monitored the fractured surface morphology of PA 6/SCF/MWCNT composites by SEM and obtained clear images of CNTs stretching across the cracks occurred in PA 6 resin.

(Liu et al., 2004) analyzed the SEM micrographs of fractured surface of PA6/ MWCNT composites which incorporate 0.5 wt % MWNTs content and monitored microcracks linked by bridged or stretched MWCNTs and their agglomerates within the PA 6 matrix. The authors also reported a notable enhancement in the mechanical performance, which was explained by the uniform dispersion of MWCNTs throughout PA 6 resin and an efficient interaction between MWCNTs and PA6.

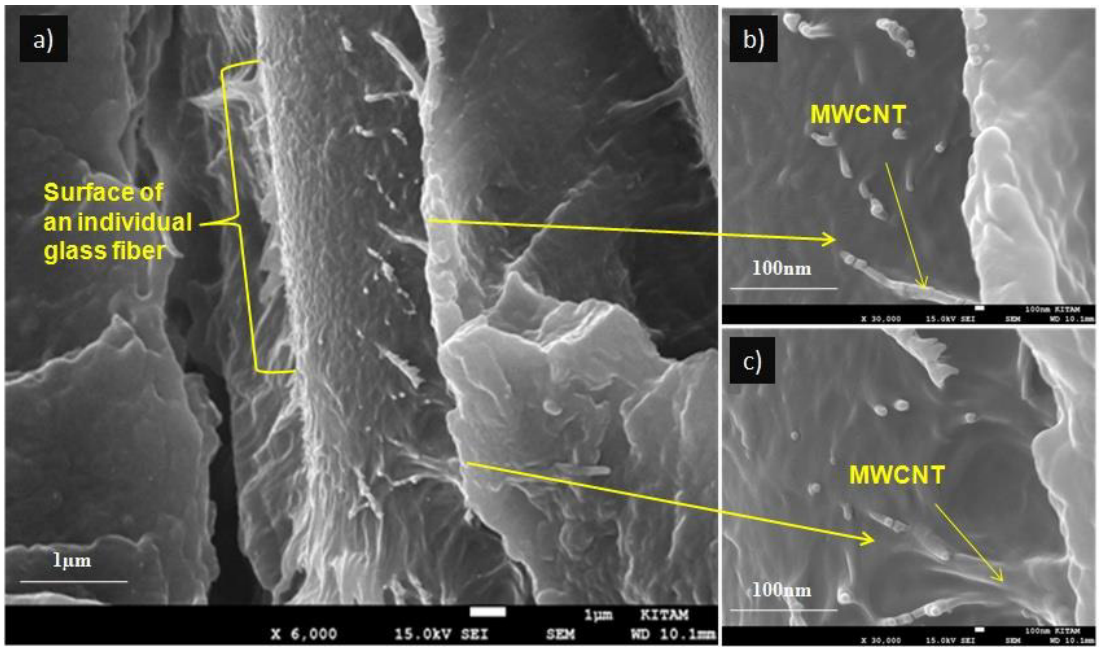

Figure 6. 1. SEM images of MWCNTs integrated PA 66/30SGF specimen

Figure 6.2 (a) and (b) represents MWCNT pull-out, which is probably because of the fracture and weak facial interaction. During the crack opening, MWCNT is stretched absorbing the fracture energy. This bridging phenomenon results in an increasing trend in mechanical performance of the CNT integrated composites. Once the fracture stops, the crack somewhat closes and MWCNT loosens getting a worm-like form, which can be explained by the relaxation after fracture or uneven crack propagation (Liu et al., 2004).

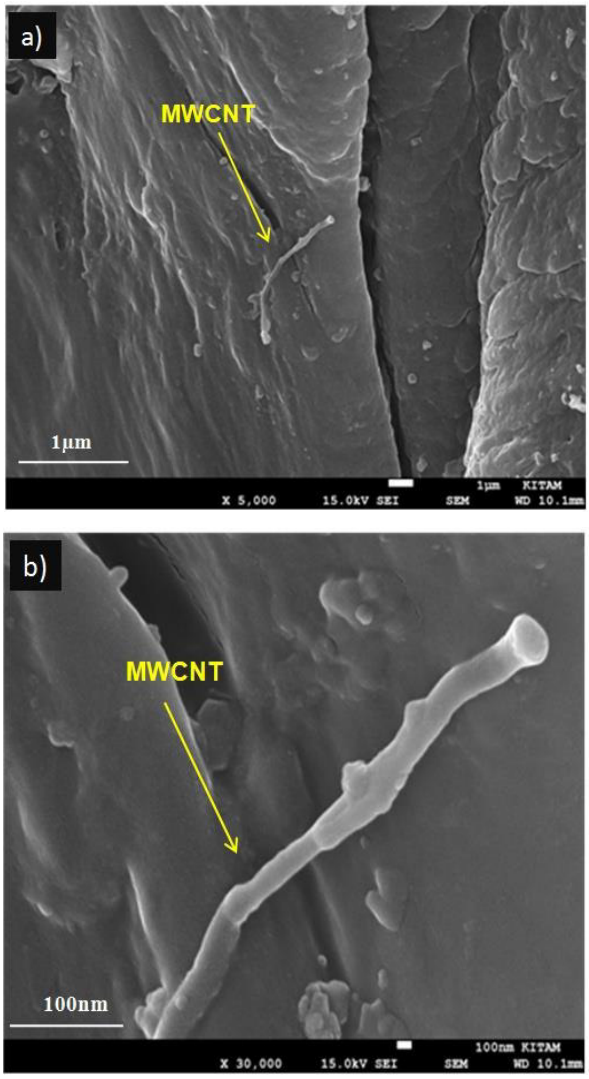

Figure 6. 2. SEM images of an individual MWCNT pull-out in PA 66/30SGF matrix

Figure 6.3 (a) and (b) represents the MWCNTs embedded within PA 66 matrix, which indicates the presence of good MWCNT-PA 66 interaction. Nevertheless, entangled MWCNT agglomerates, shown in Figure 6.3 (c), were also monitored. Unfortunately, these agglomerates restrict the dispersion and lead to failure in mechanical performance as they may act like defects and lead to uneven stress transfer throughout the PA 66 matrix. It is a fact that CNTs tend to agglomerate since they possess very high surface/volume ratio. At first, agglomeration tendency of CNTs was attributed to the Van der Waals forces; however, it was discovered that the long length and high polarizability of the CNTs could also be highly responsible for the presence of agglomerates as they increase the energy required for dispersion of nanotubes (Banerjee & Dutta, 2019).

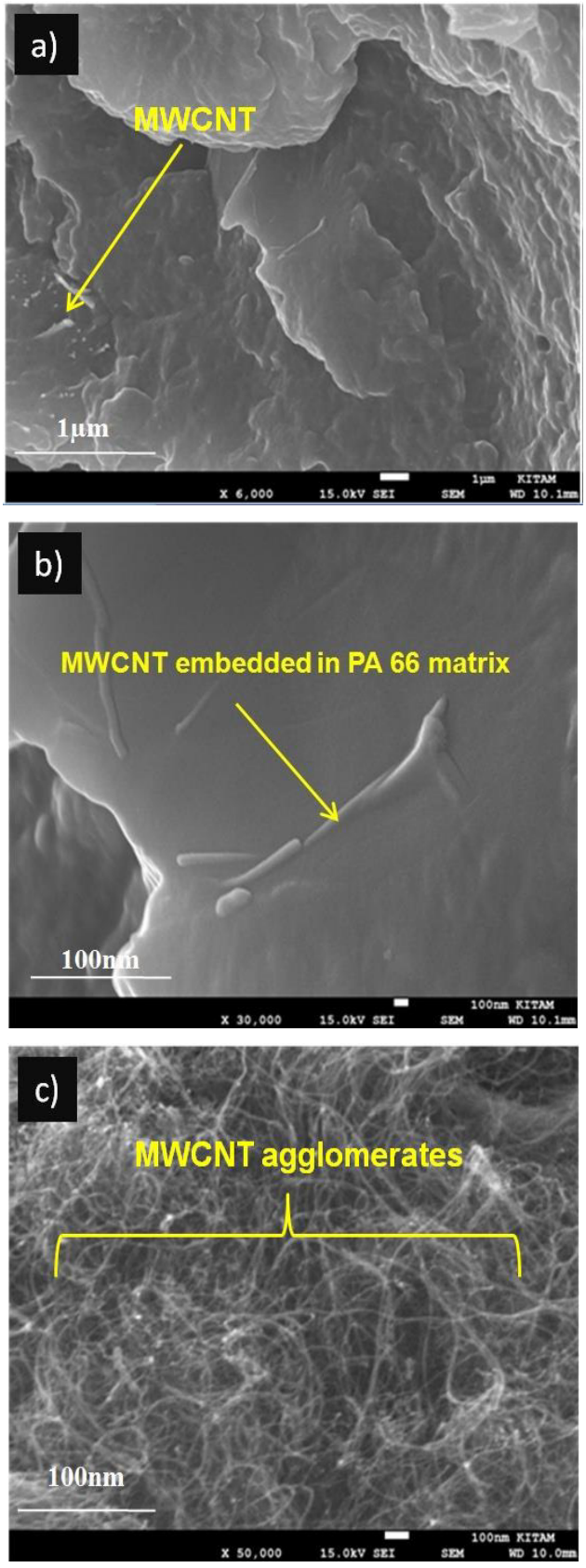

Figure 6. 3. SEM images of (a) MWCNTs embedded in PA 66/30SGF; (b) (higher-magnification) MWCNT embedded in PA 66/30SGF; (c) agglomerated MWCNTs

6.2. Tensile Test Results

Figure 6.4 represents the graphs of stress-strain curves which were obtained from the tensile tests. There is a linear dependency between tensile stress and strain until a certain point, which is obvious in the graphs of each specimen. However, when a certain strain value is reached, the tensile stress suddenly decreases and thereby the tensile properties of the specimens are obtained.

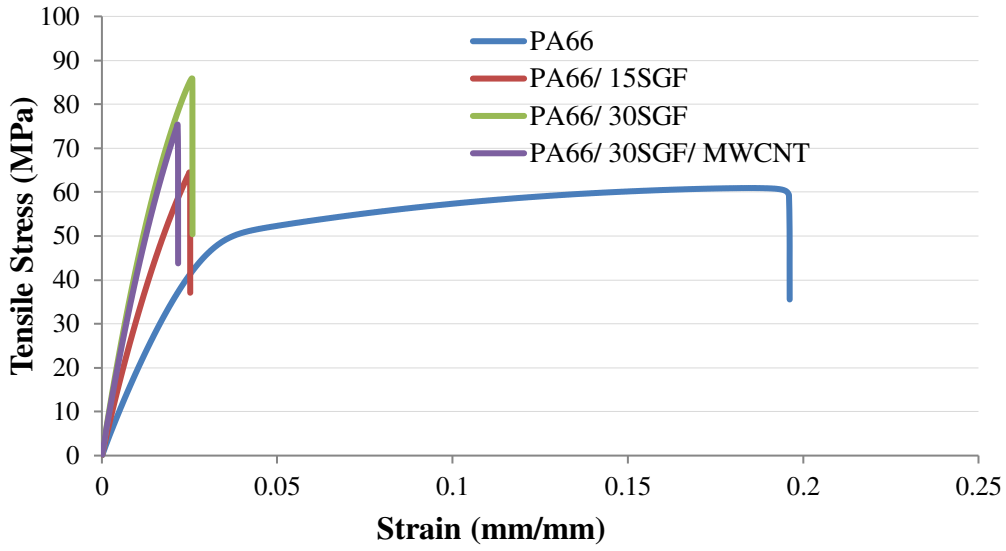

Figure 6. 4. Stress - strain curves from the tensile tests of the composite specimens

Figure 6.5 shows the graph of tensile strength and elastic moduli of the tested specimens. The graph shows that PA 66/30SGF composite exhibits the highest tensile strength (87.05 MPa) whereas PA 66/30SGF/MWCNT composite exhibits the highest e-modulus (4.69 GPa). It is also obvious that the increasing GF content leads to an increasing trend in tensile properties of PA 66. Similar results were obtained by several studies in literature (Autay et al., 2019; Çuvalci et al., 2014; Lingesh et al., 2014; Nuruzzaman et al., 2016).

The graphs also show that the presence of MWCNTs content rises the elastic modulus of PA 66/30SGF by 4.7 %. Similarly, (J. Jin et al., 2013) noted a slight increase in e -modulus of PA 66/GF composite with the inclusion of CNTs and MWCNTs. The authors explained this by the interconnecting effect between the glass fibres and the PA 66 as a result of MWCNT coating. Moreover, (Koilraj & Kalaichelvan, 2015) studied the affect of CNTs on mechanical performance of PA66 and noted that the addition of 2.5 wt.% CNT rises the Young's modulus of PA 66 by

nearly 60%. They attributed this improvement to high Young's modulus of CNT as well as their uniform dispersion within PA 66.

(Mahmood, Islam, Hameed, Saeed, & Khan, 2013) studied the tensile properties of PA 66/CNT composites and reported that incorporating 0.5 wt.% CNT content leads to an increment of e-modulus by 23%. The authors attributed this improvement to high interfacial strength and uniform dispersion of CNTs in the continuous phase. (Qiu, Chen, Yang, Xu, & Liu, 2013) studied the mechanical properties of PA 66/MWCNT composite and noted that the inclusion of 1.0 wt. % MWCNTs content improves e- modulus of PA 66 by 3.14%. (W. Zhang, Shen, Phang, & Liu, 2004) studied tensile behaviour of PA6/ MWCNT and noted that e-modulus and tensile strength of the composite improves by approximately 115% and 120%, respectively, when only 1 wt.% MWCNT content was incorporated.

(Puch & Hopmann, 2014) investigated the tensile properties of SGF reinforced Polyamide 6/MWCNTs hybrid composites and revealed that Young's modulus of PA 6/MWCNTs system improves wherase the tensile strength remain nearly the same with the incorporation of increasing MWCNTs-content. The authors explained this decrease in tensile strength by agglomeration tendency and random orientation of the nanotubes in PA 6 matrix.

In this study it is noted that tensile strength of PA 66/30SGF exhibit a decreasing trend by 14% when 0.4 wt. % MWCNTs content is incorporated. This undesired behaviour might be explained by the poor-dispersion of MWCNTs as well as the presence of MWCNT agglomerates in the PA 66 resin.

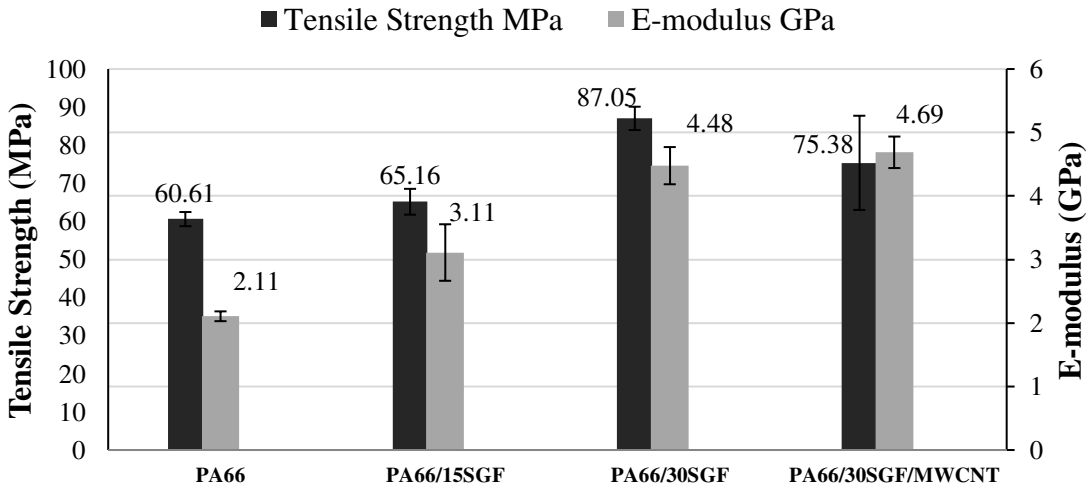

Figure 6. 5. Tensile properties of the composite specimens

6.3. Flexural Test Results

The stress-strain curves acquired from 3-point flexural tests performed on the composite specimens are shown in Figure 6.6. The relation between the flexural stress and strain exhibits linear dependency until a certain point, where flexural stress begins to decrease. Using the values at this certain point, the flexural strength and modulus of the specimens are obtained.

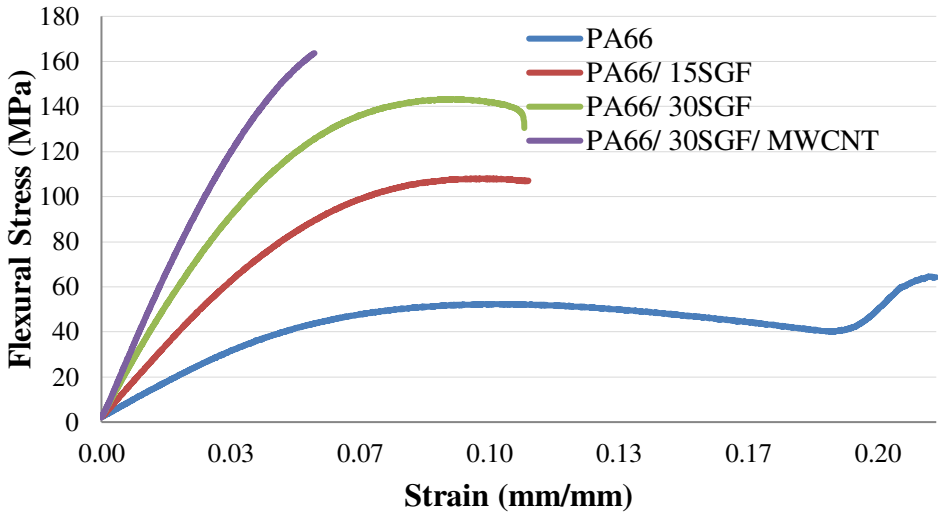

Figure 6. 6. Stress-strain curves from the 3-point flexural test of the composite specimens

Figure 6.7 represents the flexural tests results of each type of specimen. According to the obtained results, PA 66/30SGF/MWCNTs composite exhibits the highest flexural strength (145.11 MPa) and flexural modulus (3.69 GPa) whereas neat PA 66 exhibits the lowest strength (65.33 MPa) and e-modulus (1.07 GPa). The results also revealed that flexural performance of the specimens exhibit an enhancing trend with the increasing amount of SGFs. This positive behaviour can be explained high mechanical performance of GFs and their sufficient dispersion and homogeneous distribution in PA 66. Moreover, it was noted that flexural strength and modulus of PA 66/30SGF rose by approximately 1 % and 12 %, respectively, after the inclusion of MWCNTs, which can be explained by the good PA 66-MWCNT interaction as well as the improvement of glass fibre surface by MWCNTs coating.

The obtained results aforementioned conform with the relevant studies in literature. (Autay et al., 2019) studied flexural properties of PA 66/ SGF and reported that the addition of GF leads to enhancement in the flexural strength by

virtually 36.3% for PA 66/10GF and 47.2% for PA 66/30GF in comparison to neat PA 66. (Koilraj & Kalaichelvan, 2015) produced injection moulded PA 66/MWCNT composite specimens and reported that incorporation of 0.5 wt.% CNT content enhances the flexural modulus by 5.8%. (Goriparthi, Naveen, Ravi Sankar, & Ghosh, 2019) noted that flexural modulus and strength of polyoxymethylene/CNTs increase by approximately 6% and 3%, respectively, after the addition of 0.5 wt.% purified CNT content. The study of (Ibn Ali, Mohamed, & Osman, 2020) revealed that tensile modulus and flexural modulus of PA 11 improve by 20% and 34.8%, respectively, after the addition of 0.5 wt.% CNT content. Similarly, (Salmoria, Paggi, Lago, & Beal, 2011) reported that the inclusion of 0.5 wt.% MWCNTs within PA 12 matrix leads to a 10% increase in flexural strength.

(Panchagnula & Kuppan, 2019) prepared Epoxy/GF/CNT hybrid composites and reported that the flexural strength exhibits an increasing trend by nearly 39.41 % with the addition of 0.3 wt. % CNT content. Similarly, (Yip, Lin, & Wu, 2011) prepared MWCNT integrated epoxy/GF hybrid composite and noted that the flexural strength rises by approximately 9.2%, when 0.75 wt.% MWCNT content is incorporated.

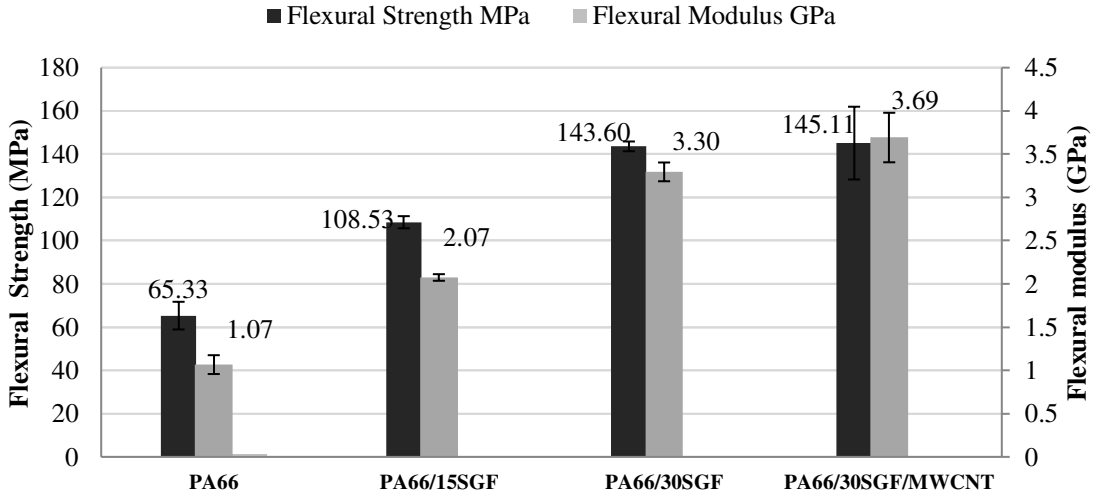

Figure 6. 7. Flexural properties of the composite specimens

After three-point bending tests, optical micrographs (see Figure 6.8 (a) and (b)) of the fractured specimens were obtained. It is clear that the crack of PA 66/30SGF along the direction of the tension is longer than that of MWCNT

integrated PA 66/30SGF. This might be due to: i) well-dispersion of the MWCNTs, which enables efficient stress transfer from matrix to the filler network; ii) good facial interaction between matrix and MWCNTs, which eases the absorption of the fracture energy by MWCNTs; iii) bridging or deflection phenomenon of MWCNTs, which prevents crack opening and propagation; iv) interlocking effect of MWCNTs, which improves the surface of glass fibers and hence allows them to adhere to PA 66 matrix. As a result, we can state that the optical micrographs approve the flexural test results and that an efficient reinforcement was obtained for PA 66/SGF composites by the integration of MWCNTs.

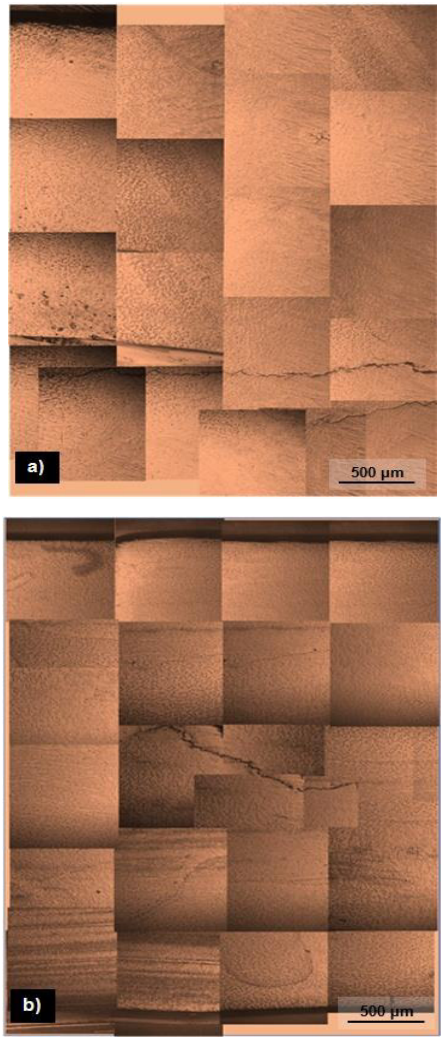

Figure 6. 8. Optical micrographs of (a) PA 66/30SGF and (b) 0.4 wt. % MWCNT integrated PA 66/30SGF specimens monitored after 3-point bending tests

CHAPTER 7

CONCLUSION

In the present study mechanical properties and surface characteristics of neat PA66, PA66/ 15SGF, PA66/ 30SGF and 0.4 wt. % MWCNT integrated PA 66/30SGF were investigated. The mechanical test results revealed that presence of GFs improves mechanical properties of PA 66 and this improvement exhibit linear dependency with the GFs content. This positive effect is mainly due to the high mechanical performance of GFs as well as their efficient interaction with PA 66 matrix.

Regarding PA 66/30SGF/MWCNT composites, mechanical characterization revealed that the presence of MWCNTs increases e-modulus (by 4.7%), flexural strength (by 1%) and flexural modulus (by 12%). This enhancement might be explained by the superior mechanical performance of MWCNTs and their bridging and deflecting behaviour which prevents crack opening and propagation during the fracture. Shorter cracks observed by optical microscopy approved this explanation. Moreover, considering the SEM images of MWCNT coated GFs, we can conclude that MWCNTs improve the surface of GFs and create interlocking effect which eases the adhesion between GF and PA 66 and thus increase the mechanical performance. However, despite the increasing trend of e-modulus and flexural properties, a decrease in the tensile strength was observed. This failure might be associated with the presence of entangled MWCNT bundles or agglomerations acting like defects in the matrix.

Considering the mechanical test results indicating enhancement of e-modulus, flexural modulus and strength, we can conclude that even a small mass fraction of MWCNT is able to improve the mechanical performance of PA 66/SGF. Moreover, since it was observed that MWCNTs modify the surface of GFs and improve their adhesion to PA 66, we can also conclude that MWCNTs and GFs are rather compatible with each other and their hybrid use as reinforcement is very promising for designing new high-performance thermoplastic composites.

REFERENCES

Ajayan, P. M., Schadler, L., Giannaris, C., & Rubio, A. (2000). Single-walled carbon nanotube-polymer COMPOSITES: Strength and weakness. *Advanced Materials, 12*, 750-+. doi:10.1002/(SICI)1521-4095(200005)12:103.0.CO;2-6

Akande, S. O., Dalgarno, K. W., Munguia, J., & Pallari, J. (2016). Assessment of tests for use in process and quality control systems for selective laser sintering of polyamide powders. *Journal of Materials Processing Technology, 229*, 549-561. doi:https://doi.org/10.1016/j.jmatprotec.2015.10.010

Amin, M., Alazba, P., & Manzoor, U. (2014). A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials. *Advances in Materials Science and Engineering, 2014*, 1-24. doi:10.1155/2014/825910

Ando, Y., Zhao, X., Sugai, T., & Kumar, M. (2004). Growing carbon nanotubes. *Materials Today, 7*(10), 22-29. doi:10.1016/s1369-7021(04)00446-8

Arao, Y., Yumitori, S., Suzuki, H., Tanaka, T., Tanaka, K., & Katayama, T. (2013). Mechanical properties of injection-molded carbon fiber/polypropylene composites hybridized with nanofillers. *Composites Part A: Applied Science and Manufacturing, 55*, 19-26. doi:https://doi.org/10.1016/j.compositesa.2013.08.002

Arash, B., Wang, Q., & Varadan, V. K. (2014). Mechanical properties of carbon nanotube/polymer composites. *Sci Rep, 4*, 6479. doi:10.1038/srep06479

Autay, R., Mars, J., & Fakhreddine, D. (2019). Mechanical and tribological study of short glass fiber-reinforced PA 66. *Polymers and Polymer Composites, 27*. doi:10.1177/0967391119853956

Avilés, F., Cauich-Rodríguez, J. V., Toro-Estay, P., Yazdani-Pedram, M., & Aguilar-Bolados, H. (2018). 5 - Improving Carbon Nanotube/Polymer Interactions in Nanocomposites. In R. Rafiee (Ed.), *Carbon Nanotube-Reinforced Polymers* (pp. 83-115): Elsevier.

Banerjee, J., & Dutta, K. (2019). Melt-mixed carbon nanotubes/polymer nanocomposites. *Polymer Composites, 40*(12), 4473-4488. doi:10.1002/pc.25334

Bansal, A., Monsalve Cano, J., Muñoz, B., & Paulotto, C. (2010). Examples of Applications of Fibre Reinforced Plastic Materials in Infrastructure in Spain. *Structural Engineering International, 20*, 414-417. doi:10.2749/101686610793557726

Baughman, R., Zakhidov, A., & Heer, W. (2002). Carbon Nanotubes-The Route Toward Applications. *Science (New York, N.Y.), 297*, 787-792. doi:10.1126/science.1060928

Bernasconi, A., & Cosmi, F. (2011). Analysis of the dependence of the tensile behaviour of a short fibre reinforced polyamide upon fibre volume fraction, length and orientation. *Procedia Engineering, 10*, 2129-2134. doi:10.1016/j.proeng.2011.04.352

Callister, W. D., & Rethwisch, D. G. (2011). *Materials science and engineering* (Vol. 5): John wiley & sons NY.

Chawla, K. (2012). Ceramic Matrix Composites. In (pp. 249-292).

Chen, T., Liu, H., Wang, X., Zhang, H., & Zhang, X. (2018). Properties and Fabrication of PA66/Surface-Modified Multi-Walled Nanotubes Composite Fibers by Ball Milling and Melt-Spinning. *Polymers (Basel), 10*(5). doi:10.3390/polym10050547

Chopra, S., Deshmukh, K. A., Deshmukh, A. D., & Peshwe, D. R. (2018). Functionalization and Melt-compounding of MWCNTs in PA-6 for Tribological Applications. *IOP*

Conference Series: Materials Science and Engineering, 346. doi:10.1088/1757-899x/346/1/012005

Choudhary, V., & Gupta, A. (2011). Polymer/Carbon Nanotube Nanocomposites. In.

Chow, W. S., & Mohd Ishak, Z. A. (2015). Polyamide blend-based nanocomposites: A review. *Express Polymer Letters, 9*(3), 211-232. doi:10.3144/expresspolymlett.2015.22

Coleman, J. N., Khan, U., Blau, W. J., & Gun'ko, Y. K. (2006). Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites. *Carbon, 44*(9), 1624-1652. doi:10.1016/j.carbon.2006.02.038

Coleman, J. N., Khan, U., & Gun'ko, Y. K. (2006). Mechanical Reinforcement of Polymers Using Carbon Nanotubes. *Advanced Materials, 18*(6), 689-706. doi:10.1002/adma.200501851

Çuvalci, H., Erbay, K., & İpek, H. (2014). Investigation of the Effect of Glass Fiber Content on the Mechanical Properties of Cast Polyamide. *Arabian Journal for Science and Engineering, 39*(12), 9049-9056. doi:10.1007/s13369-014-1409-8

Dolez, P. I. (2015). Chapter 1.1 - Nanomaterials Definitions, Classifications, and Applications. In P. I. Dolez (Ed.), *Nanoengineering* (pp. 3-40). Amsterdam: Elsevier.

Du, J. H., Bai, J., & Cheng, H. M. (2007). The present status and key problems of carbon nanotube based polymer composites. *Express Polymer Letters, 1*(5), 253-273. doi:10.3144/expresspolymlett.2007.39

Dynisco. (2018). Why Thermoplastic Materials are Important. Retrieved from https://www.azom.com/article.aspx?ArticleID=13568

Eatemadi, A., Daraee, H., Karimkhanloo, H., Kouhi, M., Zarghami, N., Akbarzadeh, A., . . . Joo, S. (2014). Carbon nanotubes: properties, synthesis, purification, and medical applications. *Nanoscale Research Letters, 9*(1). doi:10.1186/1556-276x-9-393

Egbo, M. (2020). A fundamental review on composite materials and some of their applications in biomedical engineering. *Journal of King Saud University - Engineering Sciences*. doi:10.1016/j.jksues.2020.07.007

Egbo, M. K. (2020). A fundamental review on composite materials and some of their applications in biomedical engineering. *Journal of King Saud University - Engineering Sciences*. doi:https://doi.org/10.1016/j.jksues.2020.07.007

Europe, P. (2019). Plastics-the Facts 2019 An analysis of European plastics production, demand and waste data. Retrieved from https://www.plasticseurope.org

Ferreira, T., Paiva, M. C., & Pontes, A. J. (2013). Dispersion of carbon nanotubes in polyamide 6 for microinjection moulding. *Journal of Polymer Research, 20*(11). doi:10.1007/s10965-013-0301-7

Fu, S.-Y., & Lauke, B. (1996). Effects of fiber length and fiber orientation distributions on the tensile strength of short-fiber-reinforced polymers. *Composites Science and Technology, 56*(10), 1179-1190. doi:https://doi.org/10.1016/S0266-3538(96)00072-3

Ganesh, D. E. N. (2013). *Single Walled and Multi Walled Carbon Nanotube Structure, Synthesis and Applications*.

Gilbert, M. (2017). Chapter 1 - Plastics Materials: Introduction and Historical Development. In M. Gilbert (Ed.), *Brydson's Plastics Materials (Eighth Edition)* (pp. 1-18): Butterworth-Heinemann.

Goh, P. S., Ismail, A. F., & Ng, B. C. (2014). Directional alignment of carbon nanotubes in polymer matrices: Contemporary approaches and future advances. *Composites Part A: Applied Science and Manufacturing, 56*, 103-126. doi:https://doi.org/10.1016/j.compositesa.2013.10.001

Gorga, R. E., Lau, K. K. S., Gleason, K. K., & Cohen, R. E. (2006). The importance of interfacial design at the carbon nanotube/polymer composite interface. *Journal of Applied Polymer Science, 102*(2), 1413-1418. doi:10.1002/app.24272

Goriparthi, B. K., Naveen, P. N. E., Ravi Sankar, H., & Ghosh, S. (2019). Effect of functionalization and concentration of carbon nanotubes on mechanical, wear and fatigue behaviours of polyoxymethylene/carbon nanotube nanocomposites. *Bulletin of Materials Science, 42*(3). doi:10.1007/s12034-019-1746-z

Gupta, A. K., & Harsha, S. P. (2014). Effect of crack and determination of fracture energy of carbon nanotube–reinforced polymer composites. *Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems, 229*(3), 110-116. doi:10.1177/1740349914531758

Güllü, A., Özdemir, A., & Özdemir, E. (2006). Experimental investigation of the effect of glass fibres on the mechanical properties of polypropylene (PP) and polyamide 6 (PA6) plastics. *Materials & Design, 27*(4), 316-323. doi:10.1016/j.matdes.2004.10.013

Hassani, A. J., Mohd Ishak, Z. A., & Mohamed, A. R. (2014). Preparation and characterization of polyamide 6 nanocomposites using MWCNTs based on bimetallic Co-Mo/MgO catalyst. *Express Polymer Letters, 8*(3), 177-186. doi:10.3144/expresspolymlett.2014.21

Hsiung, H., Ren, H., Ning, W., & Chi, K. (2016). *Study on Tensile Properties of Nylon 66 Reinforced Composites*.

Hv, D. (2016). Processing Techniques of polymer matrix composites-A review. *International Journal Of Engineering Research and General Science, Volume 4*.

Ibn Ali, M., Mohamed, A., & Osman, T. (2020). Enhanced mechanical and tribological properties of polyamide using carbon nanotube. *The International Journal of Advanced Manufacturing Technology, 106*. doi:10.1007/s00170-019-04643-9

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature, 354*(6348), 56-58. doi:10.1038/354056a0

Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature, 363*(6430), 603-605. doi:10.1038/363603a0

Javangula, S., Ghorashi, B., & Draucker, C. C. (1999). Mixing of glass fibers with nylon 6,6. *Journal of Materials Science, 34*(20), 5143-5151. doi:10.1023/A:1004777520458

Jin, F.-L., & Park, S.-J. (2011). A review of the preparation and properties of carbon nanotubes-reinforced polymer compositess. *Carbon letters, 12*(2), 57-69. doi:10.5714/cl.2011.12.2.057

Jin, J., Zhang, L., Chen, W., & Li, C.-Z. (2013). Synthesis of glass fiber-multiwall carbon nanotube hybrid structures for high-performance conductive composites. *Polymer Composites, 34*(8), 1313-1320. doi:10.1002/pc.22544

Jogi, B. F., Sawant, M., Kulkarni, M., & Brahmankar, P. K. (2012). Dispersion and Performance Properties of Carbon Nanotubes (CNTs) Based Polymer Composites: A Review. *Journal of Encapsulation and Adsorption Sciences, 02*(04), 69-78. doi:10.4236/jeas.2012.24010

Journet, C., Maser, W., Bernier, P., Loiseau, A., Chapelle, M., Lefrant, S., . . . Fischer, J. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature, 388*. doi:10.1038/41972

Kartel, M., Sementsov, Y., Mahno, S., Trachevskiy, V., & Bo, W. (2016). Polymer Composites Filled with Multiwall Carbon Nanotubes. *Universal Journal of Materials Science, 4*(2), 23-31. doi:10.13189/ujms.2016.040202

Kashfipour, M. A., Mehra, N., & Zhu, J. (2018). A review on the role of interface in mechanical, thermal, and electrical properties of polymer composites. *Advanced Composites and Hybrid Materials, 1*(3), 415-439. doi:10.1007/s42114-018-0022-9

Khan, M., & Srivastava, S. (2018). Development, Characterization and Application Potential of Bio-composites: A Review. *IOP Conference Series: Materials Science and Engineering, 404*, 012028. doi:10.1088/1757-899X/404/1/012028

Khan, W., Sharma, R., & Saini, P. (2016a). Carbon Nanotube-Based Polymer Composites: Synthesis, Properties and Applications. In *Carbon Nanotubes - Current Progress of their Polymer Composites*.

Khan, W., Sharma, R., & Saini, P. (2016b). Carbon Nanotube-Based Polymer Composites: Synthesis, Properties and Applications. In.

Kim, J.-W., Kim, H.-S., & Lee, D.-G. (2012). Tensile Strength of Glass Fiber-Reinforced Plastic by Fiber Orientation and Fiber Content Variations. *International Journal of Modern Physics: Conference Series, 06*, 640-645. doi:10.1142/s201019451200390x

Koilraj, T. T., & Kalaichelvan, K. (2015). Experimental Study on Mechanical Properties of PA66 Blended with MWNTs. *Applied Mechanics and Materials, 766-767*, 383-388. doi:10.4028/www.scientific.net/AMM.766-767.383

Kulik, A. J., Kis, A., Lukic, B., Lee, K., & Forró, L. (2007). Mechanical Properties of Carbon Nanotubes. In *Fundamentals of Friction and Wear* (pp. 583-600).

Kuronuma, Y., Shindo, Y., Takeda, T., & Narita, F. (2010). Fracture behaviour of cracked carbon nanotube-based polymer composites: Experiments and finite element simulations. *Fatigue & Fracture of Engineering Materials & Structures, 33*(2), 87-93. doi:10.1111/j.1460-2695.2009.01419.x

Kuronuma, Y., Shindo, Y., Takeda, T., & Narita, F. (2011). Crack growth characteristics of carbon nanotube-based polymer composites subjected to cyclic loading. *Engineering Fracture Mechanics, 78*(17), 3102-3110. doi:10.1016/j.engfracmech.2011.09.006

Li, F., Cheng, H. M., Bai, S., Su, G., & Dresselhaus, M. S. (2000). Tensile strength of single-walled carbon nanotubes directly measured from their macroscopic ropes. *Applied Physics Letters, 77*(20), 3161-3163. doi:10.1063/1.1324984

Lingesh, B. V., Rudresh, B. M., & Ravikumar, B. N. (2014). Effect of Short Glass Fibers on Mechanical Properties of Polyamide66 and Polypropylene (PA66/PP) Thermoplastic Blend Composites. *Procedia Materials Science, 5*, 1231-1240. doi:10.1016/j.mspro.2014.07.434

Liu, T., Phang, I. Y., Shen, L., Chow, S. Y., & Zhang, W.-D. (2004). Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. *Macromolecules, 37*(19), 7214-7222.

Machado, F., Fagan, S., Zanella da Silva, I., & Andrade, M. (2015). Carbon Nanoadsorvents. In.

Mahato, K. K., Rathore, D. K., Prusty, R. K., Dutta, K., & Ray, B. C. (2017). Tensile behavior of MWCNT enhanced glass fiber reinforced polymeric composites at

various crosshead speeds. *IOP Conference Series: Materials Science and Engineering, 178*. doi:10.1088/1757-899x/178/1/012006

Mahmood, N., Islam, M., Hameed, A., Saeed, S., & Khan, A. N. (2013). Polyamide-6-based composites reinforced with pristine or functionalized multi-walled carbon nanotubes produced using melt extrusion technique. *Journal of Composite Materials, 48*(10), 1197-1207. doi:10.1177/0021998313484779

Miyagawa, H., Misra, M., & Mohanty, A. K. (2005). Mechanical properties of carbon nanotubes and their polymer nanocomposites. *J Nanosci Nanotechnol, 5*(10), 1593-1615. doi:10.1166/jnn.2005.181

Moniruzzaman, M., Chattopadhyay, J., Billups, W. E., & Winey, K. I. (2007). Tuning the mechanical properties of SWNT/nylon 6,10 composites with flexible spacers at the interface. *Nano Lett, 7*(5), 1178-1185. doi:10.1021/nl062868e

Moses, J. C., Gangrade, A., & Mandal, B. B. (2019). Carbon Nanotubes and Their Polymer Nanocomposites. In *Nanomaterials and Polymer Nanocomposites* (pp. 145-175).

Nguyen-Tran, H. D., Hoang, V. T., Do, V. T., Chun, D. M., & Yum, Y. J. (2018). Effect of Multiwalled Carbon Nanotubes on the Mechanical Properties of Carbon Fiber-Reinforced Polyamide-6/Polypropylene Composites for Lightweight Automotive Parts. *Materials (Basel), 11*(3). doi:10.3390/ma11030429

Nijssen, R. (2015). *Composite Materials: An Introduction*: Inholland University of Applied Sciences.

Nordin, N., Kasolang, S., Salleh, Z., & Ahmad, M. A. (2013). Wear Rate of Natural Fibre: Long Kenaf Composite. *Procedia Engineering, 68*. doi:10.1016/j.proeng.2013.12.160

Nuruzzaman, D. M., Iqbal, A. K. M. A., Oumer, A. N., Ismail, N. M., & Basri, S. (2016). Experimental investigation on the mechanical properties of glass fiber reinforced nylon. *IOP Conference Series: Materials Science and Engineering, 114*. doi:10.1088/1757-899x/114/1/012118

Oku, T. (2003). Chapter 33 - Carbon/Carbon Composites and Their Properties. In E.-i. Yasuda, M. Inagaki, K. Kaneko, M. Endo, A. Oya, & Y. Tanabe (Eds.), *Carbon Alloys* (pp. 523-544). Oxford: Elsevier Science.

Oliveira, A., & Beatrice, C. (2019). Polymer Nanocomposites with Different Types of Nanofiller. In (pp. 26).

Omanović-Mikličanin, E., Badnjević, A., Kazlagić, A., & Hajlovac, M. (2019). Nanocomposites: a brief review. *Health and Technology, 10*(1), 51-59. doi:10.1007/s12553-019-00380-x

Panchagnula, K. K., & Kuppan, P. (2019). Improvement in the mechanical properties of neat GFRPs with multi-walled CNTs. *Journal of Materials Research and Technology, 8*(1), 366-376. doi:https://doi.org/10.1016/j.jmrt.2018.02.009

Pötschke, P., Bhattacharyya, A. R., Janke, A., Pegel, S., Leonhardt, A., Täschner, C., . . . Cech, J. (2005). Melt Mixing as Method to Disperse Carbon Nanotubes into Thermoplastic Polymers. *Fullerenes, Nanotubes and Carbon Nanostructures, 13*(sup1), 211-224. doi:10.1081/fst-200039267

Prasek, J., Drbohlavova, J., Chomoucka, J., Hubalek, J., Jasek, O., Adam, V., & Kizek, R. (2011). Methods for carbon nanotubes synthesis—review. *Journal of Materials Chemistry, 21*(40). doi:10.1039/c1jm12254a

Puch, F., & Hopmann, C. (2014). Morphology and tensile properties of unreinforced and short carbon fibre reinforced Nylon 6/multiwalled carbon nanotube-composites. *Polymer, 55*(13), 3015-3025. doi:10.1016/j.polymer.2014.04.052

Qian, D., Dickey, E. C., Andrews, R., & Rantell, T. (2000). Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Applied Physics Letters, 76*(20), 2868-2870. doi:10.1063/1.126500

Qiu, L., Chen, Y., Yang, Y., Xu, L., & Liu, X. (2013). A Study of Surface Modifications of Carbon Nanotubes on the Properties of Polyamide 66/Multiwalled Carbon Nanotube Composites. *Journal of Nanomaterials, 2013*, 1-8. doi:10.1155/2013/252417

Rajak, D. K., Pagar, D. D., Kumar, R., & Pruncu, C. I. (2019). Recent progress of reinforcement materials: a comprehensive overview of composite materials. *Journal of Materials Research and Technology, 8*(6), 6354-6374. doi:10.1016/j.jmrt.2019.09.068

Rajesh Jesudoss Hynes, N., Sankaranarayanan, R., Kathiresan, M., Senthamaraikannan, P., Khan, A., Asiri, A. M., & Khan, I. (2019). 27 - Synthesis, properties, and characterization of carbon nanotube-reinforced metal matrix composites. In A. Khan, M. Jawaid, Inamuddin, & A. M. Asiri (Eds.), *Nanocarbon and its Composites* (pp. 805-830): Woodhead Publishing.

Rastogi, V., Yadav, P., Bhattacharya, S., Mishra, A., Verma, N., Verma, A., & Pandit, J. (2014). Carbon Nanotubes: An Emerging Drug Carrier for Targeting Cancer Cells. *Journal of drug delivery, 2014*, 670815. doi:10.1155/2014/670815

Roy, S., Shit, D. R., Gupta, D. R., & Shukla, P. (2014). A Review on Bio-Composites: Fabrication, Properties and Applications. *International Journal of Innovative Research in Science, Engineering and Technology, 03*, 16814-16824. doi:10.15680/IJIRSET.2014.0310058

Sahoo, N. G., Rana, S., Cho, J. W., Li, L., & Chan, S. H. (2010). Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in Polymer Science, 35*(7), 837-867. doi:10.1016/j.progpolymsci.2010.03.002

Salmoria, G. V., Paggi, R. A., Lago, A., & Beal, V. E. (2011). Microstructural and mechanical characterization of PA12/MWCNTs nanocomposite manufactured by selective laser sintering. *Polymer Testing, 30*(6), 611-615. doi:https://doi.org/10.1016/j.polymertesting.2011.04.007

Salvetat, J.-P., Briggs, G., Bonard, J.-M., Bacsa, R., Kulik, A., Stöckli, T., . . . Forró, L. (1999). Elastic and Shear Moduli of Single-Walled Carbon Nanotube Ropes. *Physical Review Letters, 82*(5), 944-947. doi:10.1103/PhysRevLett.82.944

Sato, N., Kurauchi, T., Sato, S., & Kamigaito, O. (1988). Reinforcing Mechanism by Small Diameter Fiber in Short Fiber Composite. *Journal of Composite Materials, 22*(9), 850-873. doi:10.1177/002199838802200905

Schnorr, J. M., & Swager, T. M. (2011). Emerging Applications of Carbon Nanotubes. *Chemistry of Materials, 23*(3), 646-657. doi:10.1021/cm102406h

Schummer, J. (2004). Interdisciplinary issues of nanoscale research.

Shankar, S., & Rhim, J.-W. (2016). Polymer Nanocomposites for Food Packaging Applications. In (pp. 29-55).

Sharma, A. (2018). Alignment of Carbon Nanotubes in Polymer Matrix. In *Carbon-Based Polymer Nanocomposites for Environmental and Energy Applications* (pp. 199-214).

Shindo, Y., Kuronuma, Y., Takeda, T., Narita, F., & Fu, S.-Y. (2012). Electrical resistance change and crack behavior in carbon nanotube/polymer composites under tensile loading. *Composites Part B: Engineering, 43*(1), 39-43. doi:10.1016/j.compositesb.2011.04.028

Singh, G., & Verma, A. (2017). A Brief Review on injection moulding manufacturing process. *Materials Today: Proceedings, 4*(2, Part A), 1423-1433. doi:https://doi.org/10.1016/j.matpr.2017.01.164

Song, K., Zhang, Y., Meng, J., Green, E., Tajaddod, N., Li, H., & Minus, M. (2013). Structural Polymer-Based Carbon Nanotube Composite Fibers: Understanding the Processing–Structure–Performance Relationship. *Materials, 6*, 2543-2577. doi:10.3390/ma6062543

Spitalsky, Z., Tasis, D., Papagelis, K., & Galiotis, C. (2010). Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science, 35*(3), 357-401. doi:10.1016/j.progpolymsci.2009.09.003

Srivastava, V. K., & Lal, S. (1991). Mechanical properties of E-glass fibre reinforced nylon 6/6 resin composites. *Journal of Materials Science, 26*(24), 6693-6698. doi:10.1007/bf02402662

Takeda, T., Shindo, Y., Naraoka, F., Kuronuma, Y., & Narita, F. (2013). Crack and Electrical Resistance Behaviors of Carbon Nanotube-Based Polymer Composites under Mixed-Mode I/II Loading. *Materials Transactions, 54*(7), 1105-1109. doi:10.2320/matertrans.M2013080

Tarfaoui, M., Lafdi, K., & El Moumen, A. (2016). Mechanical properties of carbon nanotubes based polymer composites. *Composites Part B: Engineering, 103*, 113-121. doi:10.1016/j.compositesb.2016.08.016

Thomason, J. (2006). Structure–property relationships in glass-reinforced polyamide, part 1: The effects of fiber content. *Polymer Composites, 27*, 552-562. doi:10.1002/pc.20226

Thomason, J. (2007). Structure-property relationships in glass reinforced polyamide, Part 2: The effects of average fiber diameter and diameter distribution. *Polymer Composites, 28*, 331-343. doi:10.1002/pc.20260

Treacy, M. M. J., Ebbesen, T. W., & Gibson, J. M. (1996). Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature, 381*(6584), 678-680. doi:10.1038/381678a0

Vagholkar, P. (2016). Nylon (Chemistry, Properties and Uses). *International Journal of Scientific Research, 5*, 349-351.

Vinson, J. R., & Sierakowski, R. L. (2008). Introduction To Composite Materials. In J. R. Vinson & R. L. Sierakowski (Eds.), *The Behavior Of Structures Composed Of Composite Materials* (pp. 1-38). Dordrecht: Springer Netherlands.

Wallenberger, F. (2000). Structural Silicate and Silica Glass Fibers. doi:10.1007/978-1-4419-8722-8_6

Wallenberger, F. (2010). Commercial and Experimental Glass Fibers. *Fiberglass and Glass Technology: Energy-Friendly Compositions and Applications*. doi:10.1007/978-1-4419-0736-3_1

Wang, R.-M., Zheng, S.-R., & Zheng, Y.-P. (2011). 1 - Introduction to polymer matrix composites. In R.-M. Wang, S.-R. Zheng, & Y.-P. Zheng (Eds.), *Polymer Matrix Composites and Technology* (pp. 1-548): Woodhead Publishing.

Wernik, J. M., Cornwell-Mott, B. J., & Meguid, S. A. (2012). Determination of the interfacial properties of carbon nanotube reinforced polymer composites using atomistic-based continuum model. *International Journal of Solids and Structures, 49*(13), 1852-1863. doi:10.1016/j.ijsolstr.2012.03.024

Windhorst, T., & Blount, G. (1997). Carbon-carbon composites: a summary of recent developments and applications. *Materials & Design, 18*(1), 11-15. doi:https://doi.org/10.1016/S0261-3069(97)00024-1

Wong, E., Sheehan, P., & Lieber, C. (1997). Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes. *Science, 277*, 1971–1975. doi:10.1126/science.277.5334.1971

Xanthos, M. (2010). Polymers and Polymer Composites. In *Functional Fillers for Plastics* (Second ed., pp. 1-18).

Yern Chee, C., Chuah, C. H., Ching, K. Y., Luqman Chuah, A., & Rahman, A. (2017). Applications of thermoplastic-based blends. In (pp. 111-129).

Yıldızhan, Ş., Çalık, A., Ozcanli, M., & Serin, H. (2018). Bio-composite materials: a short review of recent trends, mechanical and chemical properties, and applications. *European Mechanical Science, 2*. doi:10.26701/ems.369005

Yip, M.-C., Lin, Y.-C., & Wu, C.-L. (2011). Effect of Multi-Walled Carbon Nanotubes Addition on Mechanical Properties of Polymer Composites Laminate. *Polymers and Polymer Composites, 19*, 131-140. doi:10.1177/0967391111019002-313

Yu, M.-F., Files, B. S., Arepalli, S., & Ruoff, R. S. (2000). Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties. *Physical Review Letters, 84*(24), 5552-5555. doi:10.1103/PhysRevLett.84.5552

Yu, M. F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F., & Ruoff, R. S. (2000). Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science, 287*(5453), 637-640. doi:10.1126/science.287.5453.637

Zabegaeva, O. N., Sapozhnikov, D. A., Buzin, M. I., Krestinin, A. V., Kotelnikov, V. A., Baiminov, B. A., . . . Vygodskii, Y. S. (2016). Nylon-6 and single-walled carbon nanotubes polyamide composites. *High Performance Polymers, 29*(4), 411-421. doi:10.1177/0954008316645848

Zaidy, S. (2016). *Atmospheric Plasma Induced Coloration of Textile Fibers.*

Zainudin, E. S., Sapuan, S., & Imihezri, S. S. S. (2006). A Review of the Effect of Moulding Parameters on the Performance of Polymeric Composite Injection Moulding. *Turkish Journal of Engineering and Environmental Sciences, 30*, 23-34.

Zhang, J., Gao, X., Zhang, X., Liu, H., Zhang, H., & Zhang, X. (2019). Polyamide 66 and amino-functionalized multi-walled carbon nanotube composites and their melt-spun fibers. *Journal of Materials Science, 54*(16), 11056-11068. doi:10.1007/s10853-019-03619-0

Zhang, W., Shen, L., Phang, I., & Liu, T. (2004). Carbon Nanotubes Reinforced Nylon6 Composite Prepared by Simple Melt-Compounding. *Macromolecules, 37*, 256-259. doi:10.1021/ma035594f

Zweben, C., Smith, W. S., & Wardle, M. W. (1979). Test Methods for Fiber Tensile Strength, Composite Flexural Modulus, and Properties of Fabric-Reinforced Laminates. In S. W. Tsai (Ed.), (pp. 228-262). West Conshohocken, PA: ASTM International.