FABRICATION AND CHARACTERIZATION OF POLYACRYLONITRILE ELECTROSPUN NANOFIBERS WITH CONDUCTIVE PARTICLES

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In fulfillment of the requirements for the degree of
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DECLARATION

I declare that this project report entitled "Fabrication and Characterization of Polyacrylonitrile Electrospun Nanofibers with Conductive Particles" is the result of my own work except as cited in the references

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Name : Mhd Alif Bin Mhd Sharif
Date : .....

APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the degree of Bachelor of Mechanical Engineering.

Signature :……

Supervisor Name : Dr. Nurfaizey Bin Abdul Hamid

Date :……..

ABSTRAK

Kajian ini adalah mengenai penghasilan dan pencirian polyacrylonitrile (PAN) dengan zarah konduktif. Kebanyakan kajian tentang pemintalan elektrik nanoserat ini menggunakan asas polimer terkenal seperti pendahulunya PAN untuk menghasilkan nanoserat. Walaubagaimanapun, penambahan zarah konduktif sebagai pengisi dalam polimer boleh meningkatkan sifat-sifat nanoserat untuk membentuk bahan komposit. Dalam kes ini, terdapat dua objektif yang perlu dicapai dalam kajian ini iaitu menghasilkan nanoserat PAN dengan zarah konduktif yang merupakan nanotube karbon berbilang dinding (MWCNT) dan untuk mengkaji ciri-ciri nanoserat yang telah melalui pemintalan elektrik. Tiga ciri utama nanoserat PAN/CNT yang telah disiasat dalam kajian ini adalah sifat-sifat kimia, kekonduksian dan morfologi nanoserat. Pembuatan nanoserat dilakukan dengan menggunakan mesin pemintalan elektrik dengan nilai voltan yang tetap, jarak antara jet jarum dan pengumpul yang tetap, dan kadar aliran yang tetap. Sementara itu, kepekatan MWCNT dalam larutan PAN/CNT mempunyai pelbagai nilai seperti 0.00wt%, 0.03wt% , 0.05wt%, 0.07wt% dan 0.10wt%. Ciri-ciri nanoserat disiasat dengan menggunakan FTIR, empat titik probe dan mesin pemeriksaan mikroskop elektron (SEM). Keputusan menunjukkan bahawa kehadiran partikel konduktif (MWCNT) telah meningkatkan struktur rantaian molekul nanoserat PAN/CNT dalam sifat-sifat kimia. Oleh itu, ia juga telah meningkatkan kekonduksian nanoserat dengan peningkatan kepekatan MWCNT dalam larutan PAN/CNT. Di samping itu, diameter serat PAN/CNT juga meningkat apabila kepekatan MWCNT bertambah manakala diameter serat PAN/CNT menjadi lebih kecil selepas menjalani rawatan haba dalam proses penstabilan dan proses karbonisasi.

ABSTRACT

This study is about the fabrication and characterization of polyacrylonitrile (PAN) with conductive particles. Most of the research about the electrospinning of nanofibers were using basic well-known polymer such as PAN precursor to fabricate nanofibers. In fact, the addition of conductive particles as filler in the polymer may enhance the properties of the electrospun nanofibers to form composite fibers. In this case, there were two objectives needed to be achieved in this study which are to fabricate the electrospun nanofibers of PAN with conductive particle which was multi-walled carbon nanotube (MWCNT) and to investigate the characteristics of the electrospun nanofibers. The three main characteristics of the PAN/CNT electrospun nanofibers that have been investigated in this study were the chemical characterization, the conductivity and the morphology of the nanofibers. The fabrication of the nanofibers were done by utilizing electrospinning machine with the constant value of applied voltage, distance between needle jet and collector, and flow rate while the concentration of MWCNT in PAN/CNT solution was varied which were 0.00wt%, 0.03wt%, 0.05wt%,0.07wt% and 0.10wt%. The characteristics of the nanofibers were investigated by using FTIR, four point probe and scanning electron microscope (SEM) machine. The results showed that the presence of conductive particles (MWCNT) had improved the molecule chain structure of PAN/CNT nanofibers in chemical characterization. Hence, it also had enhanced the conductivity of nanofibers with the increased in the concentration of MWCNT in PAN/CNT. Furthermore, the fiber diameter of PAN/CNT nanofibers was increased as the concentration of MWCNT increased while the fiber diameter of PAN/CNT became smaller as undergo heat treatment in stabilization and carbonization process.

DEDICATION

To my beloved father,

Mhd Sharif Bin Omar,

My beloved mother,

Hayati Bt Mat.

ACKNOWLEDGEMENTS

In the name of ALLAH, the most gracious, the most merciful, with the highest praise have given me the opportunity to complete this final year project successfully without any difficulties.

I am deeply indebted to my supervisor, Dr. Nurfaizey Bin Abdul Hamid for his kind supervision, great advice, meaningful guidance and helpful support as well as exposing me with valuable experiences throughout this entire final year project.

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Finally, special thanks to all the continuous support, consideration, understanding and moral support from my father, my mother, siblings and my friends in completing this degree. Lastly, thank you to everyone who has helped me directly and indirectly in carrying out my final year project and completing of this report. Thank you.

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LIST OF ABBREVIATIONS

AMCHALS	Advance Material Characterization Laboratory Center
CNF	Carbon nanofiber
CNT	Carbon nanotube
DMF	N,N-Dimethylformamide
DNA	Deoxyribonucleic acid
ECM	Extracellular matrix
HEPA	High efficiency particular air
MW	Molecular weight
MWCNT	Multi-walled carbon nanotube
PAN	Polyacrylonitrile
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
SNF	Stabilized nanofiber
UTeM	Universiti Teknikal Malaysia Melaka
3D	Three-dimensional

LIST OF SYMBOLS

Ω/sq	=	Resistance per square
wt%	=	Weight percentage
σ	=	Conductivity
°C	=	Celsius
A	=	Ampere
cm	=	centimeter
nm	=	nanometer
µm	=	micrometer
g	=	gram

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Nanotechnology is the formation of useful materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at the length scale. Last few decades, the evolution of nanofibers has attracted significant interest due to its extraordinary properties especially on their highly surface area-to-volume ratio (Peresin *et al.*, 2010). Consequently, this characteristic of nanofibers has widely use applications in pharmaceutical, medical, catalysis field, biosensors lithium ion batteries and many more. A nanofiber is a fiber with a diameter of 100 nanometers or less as shown in Figure 1.1.

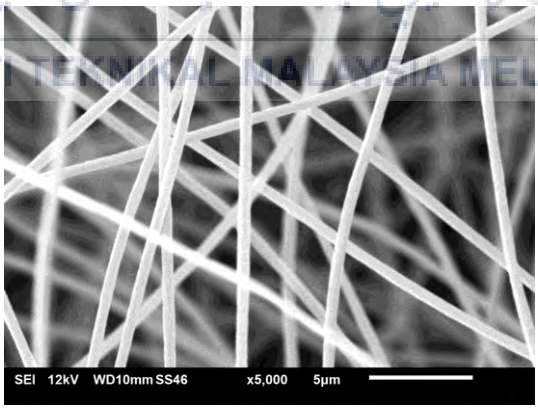


Figure 1.1: SEM Image of electrospun nanofibers

. Electrospun nanofibers of polymer polyacrylonitrile (PAN) are a new material of polymer that can be used for applications consists of filtration, medical, personal care, barrier, composites and energy storage. Electrospun nanofibers of PAN have characteristic of surface

free energy which based on its special properties that has bigger surface area per unit mass (Wu *et al.*, 2002). The special characteristic of PAN nanofibers make it suitable for various applications such as in aerospace, drug delivery system, information technology and many more (Lau and Hui, 2002; Hsiao, Alms and Advani, 2003).

Composites nanofibers can be formed by using many kinds of additives and filler in electrospinning of nanofibers (Heikkilä and Harlin, 2009). Heikkila & Harlin stated that by using nano-size fillers in electrospinning nanofibers, the properties of electrospinning fibers can be modified. Well-known filler that are widely used in electrospinning of nanofibers is carbon nanotubes (CNTs) (Qin, 2008). CNT act as a reinforcement component in electrospinning of nanofibers and it also used in modification of electrical properties of electrospun nanofibers (Jeong *et al.*, 2006; Heikkilä and Harlin, 2009).

1.2 PROBLEM STATEMENT

Most of the research about the electrospinning of nanofibers were using basic well-known polymer such as PAN, PVA and many more polymer solution to fabricate nanofibers. PAN precursor has been widely used for the fabrication of nanofiber as it exhibit high conductivity for carbon nanofiber (CNF) especially in electronic applications. However, the addition of conductive filler can enhance the characteristics of electrospun nanofibers. The use of conductive particles as filler in the polymer solution may result in different properties of the solution such as it can be a charge carrier. Charge carrier or conductive filler particles in the solution can improve the conductivity of the solution and the charge density of the jet. The increase of the solution conductivity and the net charge density can enhance the instability of the jet that can lead to the formation of bead-free electrospun nanofibers and nanofibers with smaller diameter. Heikkilä & Harlin, 2009; Jeong et al., 2006 stated that basically, conductive particles such as carbon nanotubes (CNTs) as filler in polymer solution can serve as a reinforcement component and also used as a modification in the electrical properties of the electrospun nanofibers.

1.3 OBJECTIVE

The objectives of this study are:

1.3.1 To fabricate a new electrospun nanofibers by combining polyacrylonitrile (PAN) and conductive particles with various concentrations.

1.3.2 To investigate the characteristics of the electrospun nanofibers.

1.4 SCOPE OF PROJECT

The scopes of this project are concerns on fabricating electrospun nanofibers by using a mixture of polymer between polyacrylonitrile (PAN) with conductive particles. Multi-Wall Carbon nanotube (MWCNT) is the conductive particle that has been chosen as filler. The concentration of MWCNT will be varied while the process parameter such as applied voltage, distance between needle tip to the collector and flow rate will be fixed. This is due to examine the characteristics of PAN/CNT with different concentrations of MWCNT.

1.5 REPORT OVERVIEW

The structure of this report is outlined as follow:

Chapter 2 presents about the literature review that covers the historical of electrospinning process along with the system of electrospinning machine. Moreover, the effect of parameter toward the electrospun nanofibers also will be discussed, the application of electrospun nanofibers and lastly about the current development of electrospun nanofibers.

Chapter 3 gives a review of the experiment methodology consisting of preparation of the polymer solution, fabrication of electrospun nanofibers, process of thermal treatment and characterization of the electrospun nanofibers.

Chapter 4 presents the description on the result that have been obtained and discussions about the results.

Chapter 5 presents the conclusions along with the recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 History of Electrospinning Process

Electrospinning is a unique technique that uses electrostatic force to produce fibers from a polymer solution. The history of electrospinning process started from William Gilbert who was the first observed the electrostatic attraction of liquid in 1600.

In 1934, Anton Formhals had managed to use the electric charge to spin small diameter of synthetic fiber. However, some improvements was needed on Formhals works due to the distance between the collector and the polymer solution was close that may causes the polymer solution not fully evaporate when the fiber stick to the collector. Then, Formhals had works on the second patent which the distance between the polymer solution and the collector was more greater (Sill & von Recum, 2008). Figure 2.1 shows some of Formhal's drawings that he inserted in his patent.

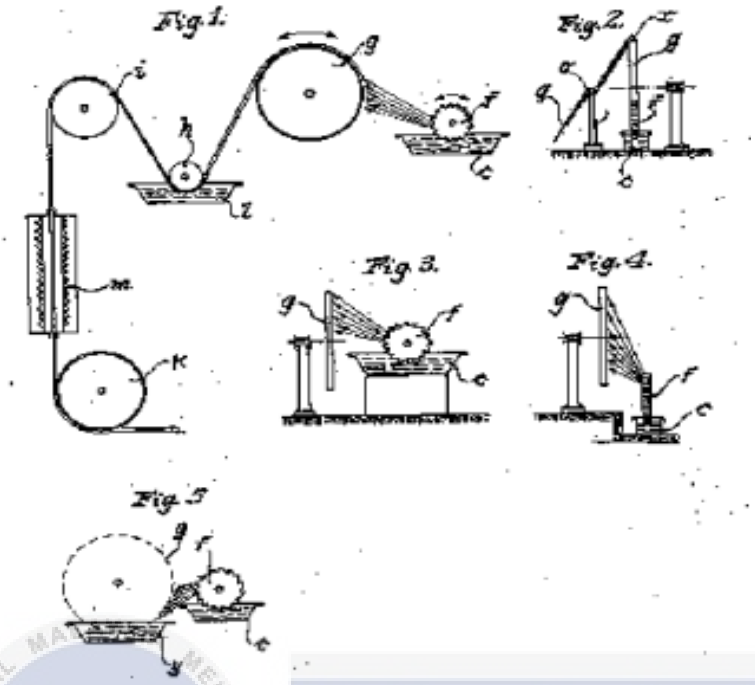


Figure 2.1: Some of schematic drawings by Formhals in his patent (Source: Vrieze & Clerck, 2009)

The electrospinning of nanofibers technology appears to be inactive after the revolution of Formhals until Simons design an apparatus that prove the feasibility of fabrication nanofiber. Simon shows that by using electrospinning process, ultrafine fiber will be produced. He also shows that lower viscous solution will produce shorter fiber but has a finer fiber while higher viscous solution will produce longer fiber but the fiber is thicker (Hwan, 2014).

There was another person has developed Formhals work on electrospinning at the same time as Simon. It was Taylor who had done the research about the jet forming process. In 1964, Taylor recommended that under an electric field at semi-vertical angle of 49.3° the equilibrium charged conducting fluid can exist in the form of cone (Nurfaizey *et al.*, 2014). This phenomenon of cone later became known as the Taylor Cone. Taylor also found out that when the fiber jet is ejected from the tip of the cone, it can produce fiber with smaller diameter (Sill & von Recum, 2008) as shown in Figure 2.2.

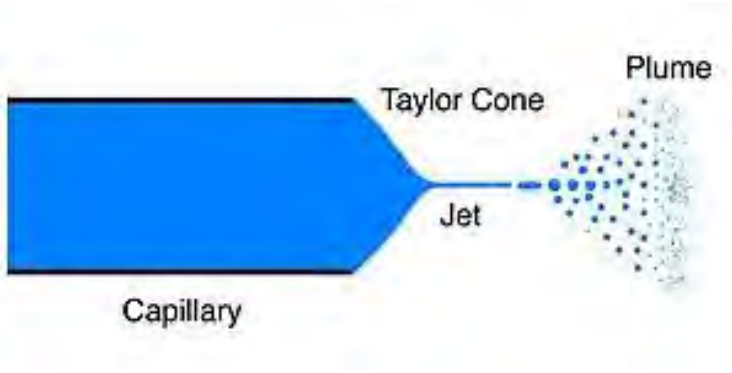


Figure 2.2: Taylor Cone formation at the tip of the needle (Source: en.wikipedia.org)

The research of electrospinning was continuing after Taylor and Simon by Baumgarten in 1971. Baumgarten had made substantial evidence about the effect of voltage applied to the solution as the fluid stream will be form instead of droplets (Hwan, 2014) as shown in Figure 2.3.

Figure 2.3: Formation from droplet to fluid stream (Source: Hwan, 2014)

Since then, many researches paper and patent have been done about the fabrication of electrospun nanofibers with various kind of polymer solution. The nanotechnology of fabricating nanofibers has grown widely from year to years.

2.2 Electrospinning Machine

Electrospinning machine is an effectual technology machine to produce fibrous membrane with nanometers unit of fiber diameter. Electrospinning machine is a fairly direct process to be setup. Han, Boyce and Steckl (2011) stated that there are three advantages of electrospinning machine system. An electrospinning machine has the ability to control:

1) Micrometer of fiber diameter to a nanometer dimensions.

2) Various fiber compositions.

3) Multiple fibers with the spatial alignment.

2.2.1 Basic component of electrospinning machine

The electrospinning machine consists of four crucial components which is source of electric field, syringe with a nozzle, collector and a pump. The polymer solution that will be electrospun is applied to the system via the nozzle of the syringe. Then, it is pushed by the pump. Next, a high electrical voltage present between the nozzle and the counter electrode will be subjected to the polymer. The source generates the high electrical voltage that causes a cone-shaped deformation of the drop of polymer solution. On its way to the collector, the solvent in the solution will evaporates.

2.2.2 Type of electrospinning machine

There are three types of electrospinning machines which are shaft type, converse type and horizontal type. Shaft type and converse type are included in the category of vertical type of electrospinning machine. The differences between these three types are based on its geometrical arrangement of ejecting capillary polymer solution and the collector. The ejecting capillary for the shaft type will be on the top while the collector will be on the bottom as shown in Figure 2.4. For the converse type, the ejecting capillary position will be on the bottom and facing the top while its collector position will be on the top as shown in Figure 2.5. Next, the horizontal type is more different from the other two types which are converse and shaft type. For the horizontal type the ejecting capillary will be horizontally parallel same position as the collector as shown in Figure 2.6.

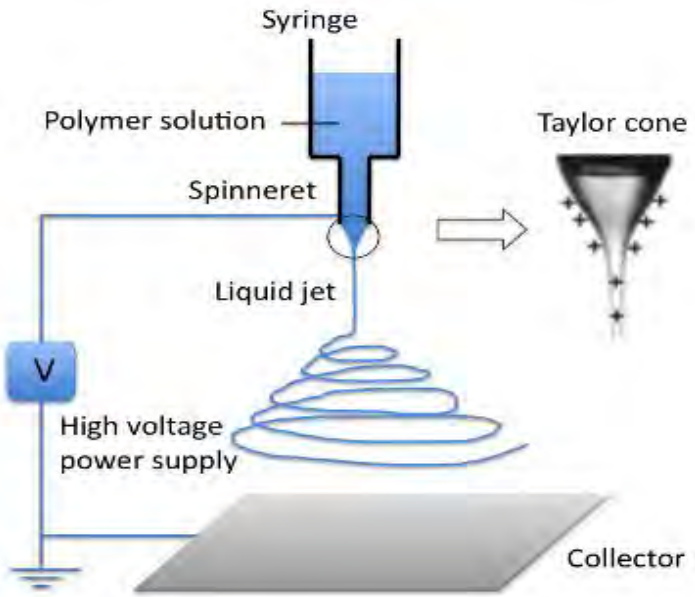


Figure 2.4: Illustration of electrospinning system of shaft type (Source: Athira, Sanpui, & Chatterjee, 2014)

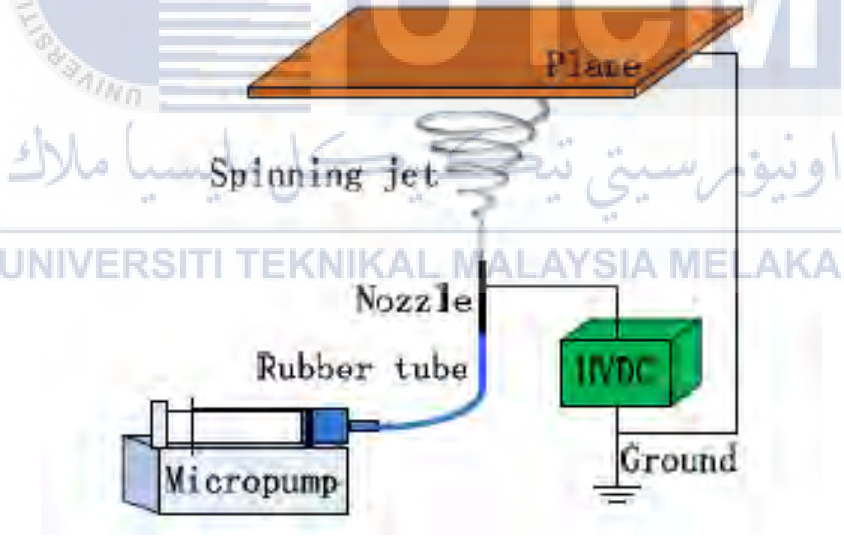


Figure 2.5: Illustration of electrospinning system of converse type (Source: C. Yang et al., 2009)

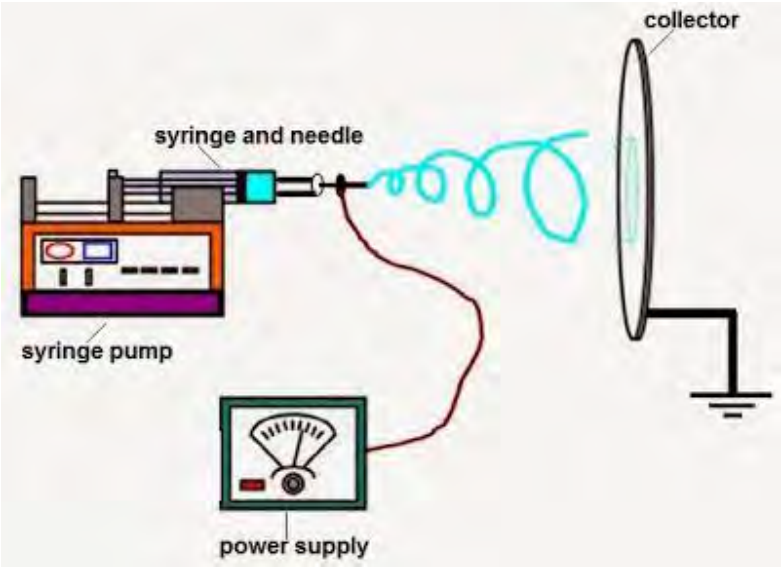


Figure 2.6: Illustration of electrospinning system of horizontal type (Source: Kiron, 2013)

All of these three types of electrospinning machine system will produce the differences in experimental phenomena, fiber diameter and fiber size distribution. In early 2009, Yang et al studied about the differentiations of fibers properties between horizontal and vertical type of electrospinning system at voltages forces of 10kV, 12.5kV, 15kV, 17.5kV and 20kV for 15cm distance from the needle tip to the center of the collector and 1.0 ml/h of feed rate (Yang *et al.*, 2009). The result from the studied show that the drops and fibers position were differences for all of the three types of electrospinning machine system. There were a lots of drops deposited on the center of the fibers mat and few fibers on the center of collector for the shaft type of electrospinning machine. Moreover, for the converse type of electrospinning machine, the drops deposited on the center of collector and fibers were around with the drops on the center of collector. Next, for the horizontal type of electrospinning machine, the drops and fibers mat deposited on the center of the collector but the fibers mat was mostly on side of the drops. All of these results showed that the gravity and electric field forced on fibers were differences according to its type of electrospinning system. The shaft type system influenced by the same orientations of gravity and electric forced on fibers while the converse type system influenced by the opposite orientations of gravity and electric field forced on fibers. Besides, the horizontal type system influenced by the perpendicular orientations of gravity and electric field forced on fibers.

Different type of electrospinning systems also influence on the fiber diameter as shown in Figure 2.7. Result studied by Yang et al. showed that the shaft type of electrospining system could produce the thinnest diameter of fiber while the converse type could produce the thickest diameter of fibers. Meanwhile, the horizontal type of electrospinning system could produce the average diameter of fiber between the shaft and converse type. These results were proved by explanation as for the shaft type system, the gravity strengthen the effect of electric field. This phenomenon makes the fiber to extend adequately. For the converse type system, the gravity weaken the electric field that make the extending effect of fiber would be weakened. Besides, for the horizontal type system the gravity had slightly effects on the electric field that make the extending effect of the fiber will be average between the shaft and the converse type of electrospinning machine.

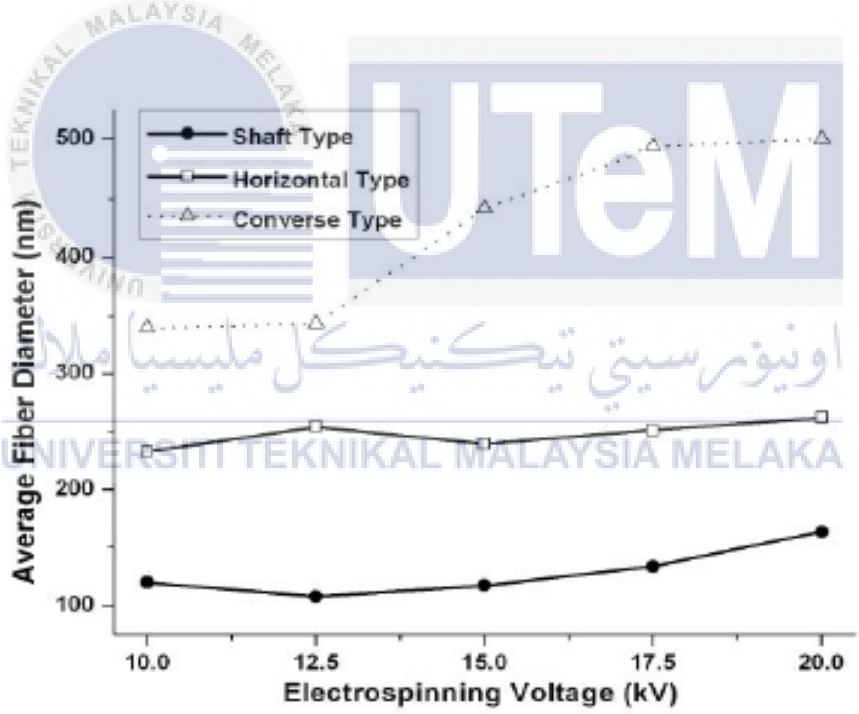


Figure 2.7: The average diameter of fiber in different voltages (Source: Athira, Sanpui, & Chatterjee, 2014)

The variability of fiber diameters can be measured by the standard deviation. The fiber diameter that are very near to the average fiber diameter has the lower standard deviation while the fiber diameter that are spread out over a large range of average fiber diameter has the higher standard deviation. However, to show the consistency of fiber size distribution it is compulsory to find its relative standard deviation which is the percentage of the standard deviation divided by the average fiber diameter. Based on the experiment by Yang et. al, it showed that the fiber size distribution of the shaft type system was the broadest as it had the highest relative standard deviation while the fiber size distribution of the converse type system was the narrowest as it had the lowest relative standard deviation. Besides, the fiber size distribution for the horizontal type system was in the middle between the shaft and the converse type.

2.3 Electrospinning Parameter

Electrospinning parameter is divided into two, which is independent parameter and dependent parameter (Jirsak and Petrik, 2012). Independent parameters consist of material parameter, process parameter and ambient parameter, while dependent parameters consist of process parameter and material parameter. All of these parameters would affect the morphologies of the fabricated electrospun nanofibers according to each parameter. By proper controlling of those parameters, a desired morphologies and diameters of the electrospun nanofibers will be produced (Bhardwaj and Kundu, 2010).

2.3.1 Voltage applied

Source of electric field that produces high voltage is one of important component in order to fabricate nanofiber. Voltage applied is one of the process parameter that has to be considered before fabricate nanofiber. Applied voltage is one of the electrospinning variables that can changed the shape of the initiating droplet at the tip of needle (Zong *et al.*, 2002). Applied voltage on the droplet of polymer solution at the tip of needle will make the liquid of polymer solution to be charged. The liquid of the polymer solution will be charged via the motion of electric field ions through the liquid that can overcome the surface tension of the liquid. Hence, by increasing the voltage of the electrospinning machine can changes the shape

of the initial droplet at the tip of the needle that ensuring the changed of fiber morphology from a cylindrical shape to a beaded structure.

2.3.2 Concentration of solution

Concentrations of polymer solution are also one of the important parameter that needs to be considered during the electrospinning process. It is one of the important roles in the process of the fiber formation. In 2013, Li and Wang stated that there are four critical concentration of the polymer solution should be noted from low to high (Li and Wang, 2013):

1. The nano particles will be formed as the concentration of the polymer solution is very low.

2. A little higher concentration of the polymer solution produced a mixture of beads and fibers.

3. Smooth nanofibers will be produced as the concentration of the polymer solution is suitable.

4. Helix-shaped micro-ribbons will be produced as the concentration of the polymer is very high.

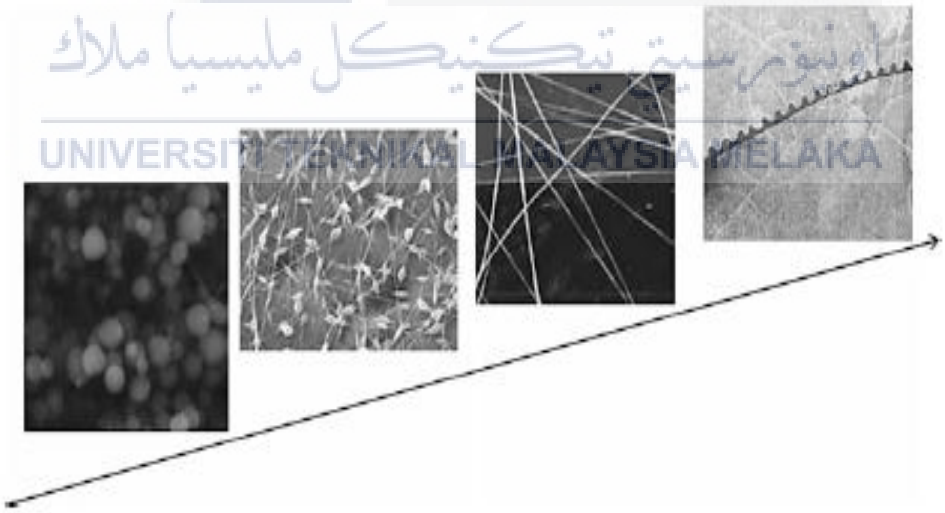


Figure 2.8: SEM images of the sequences of fiber formation from low to high concentrations (Source: Li & Wang, 2013)

Figure 2.8 shows that the sequences of the image of fiber formation with different critical concentrations of polymer solution from low to high concentration. Basically, it can prove that the diameter of the electrospun nanofiber will increase as the concentration of the polymer solution is increasing if the concentration of the polymer is suitable for electrospinning process.

2.3.3 Distance between needle tips to collector

Distance between needle tips and the collector also play an vital role to control the fiber diameter and morphology (Bhardwaj and Kundu, 2010). Even with a constant voltage supplied, the lower distance may increase the dripping tendency in horizontal structure of electrospinning machine (Heikkilä and Harlin, 2009). Athira, Sanpui and Chatterjee (2014) stated that distance from 10 cm to 15 cm is the optimum distance that produced fiber mat with no beads. Optimum distance between the needle jet and the collector resulting in sufficient time for the solvent to be fully evaporate or dry (Han, Boyce and Steckl, 2011; Athira, Sanpui and Chatterjee, 2014).

2.3.4 Flow rate

Another crucial parameter during the process of electropinning is the flow rate of the polymer solution within the syringe. Flow rate of the polymer solution in the syringe affect the fiber diameter distribution, initial shape of the droplet at the needle tip and its size, jet trajectory, Taylor cone maintenance and morphology of nanofiber (Zargham *et al.*, 2012). Zargham et al. stated that:

1) A small amount of polymer solution will be ejected from the needle tip at the lower flow rate which leads to the small droplet size.

2) A greater amount of polymer solution will be ejected from the needle tip at the higher flow rate which caused the jet of solution to be electrosprayed without sufficient stretching.

3) But with higher flow rate at a constant voltage, the stretching of the ejected polymer solution was not capable with the electric field strength due to insufficient amount of charged ions.

Hence, it was noticed that flow rate can affects the droplet size distribution and the average droplet size.

2.4 Application of Nanofiber

Nowadays nanofibers are the new nanotechnology that can be used in various applications in different sectors, example Figure 2.9. The various in systemic and process parameters in many cases can lead themselves to invention and modification, hence providing them to fabricate nanofibers for specific uses in future (Vasita and Katti, 2006). The applications of electrospun nanofibers are wide and varied. They have been studied in biomedical field consists of tissue engineering, wound dressing and many more (Lu *et al.*, 2006) as shown in Figure 2.10.

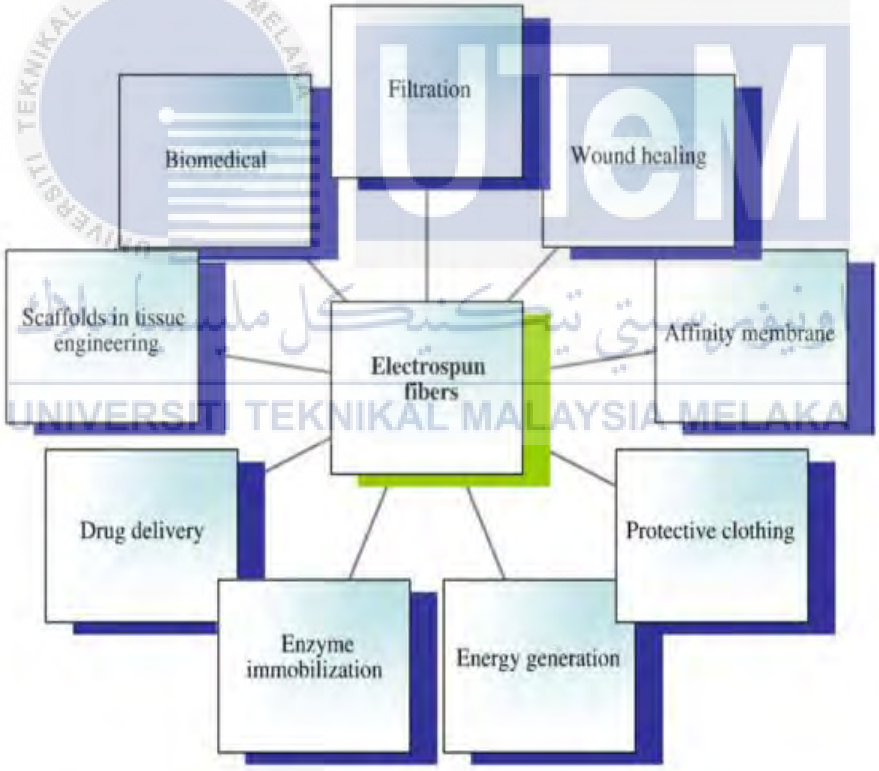


Figure 2.9: Application of nanofibers in various sectors

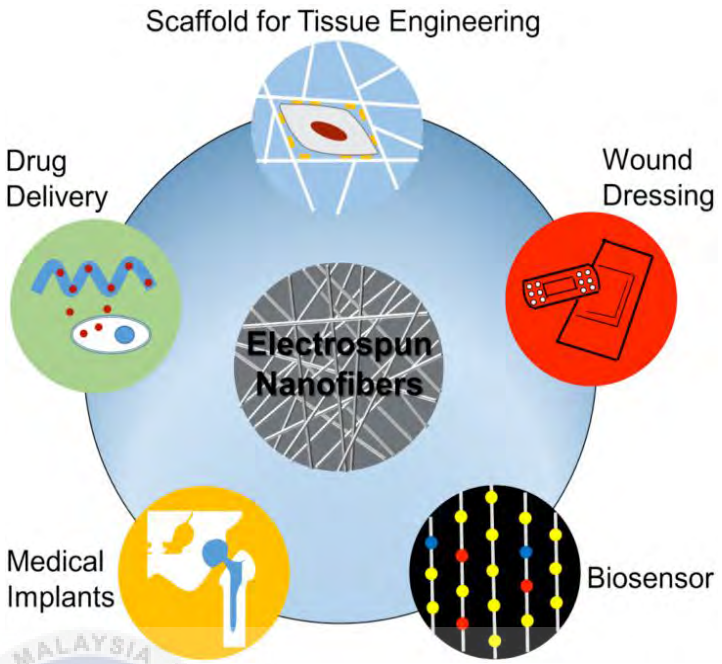


Figure 2.10: Some application of nanofibers in biomedical field (Source: Weng & Xie, 2015)

2.4.1 Drug delivery system

In this few decades, many developments in the technology of pharmaceutical were advancing and many researches had been done to find the most efficient ways for human systems to accept drugs. According to Ping Chen et al. (2010), there are many groups of researches have been done to reinforce more efficient release system, improve selective toxicities and decrease side effects against cancer cell. There are also some researchers that investigating about the controlled release of various drugs for repairing wound or broken tissue. Research shows that a appropriate controlled release system is crucial to enhance safety and efficacy of cancer chemotherapy (Chen *et al.*, 2010). Consequently, drug delivery system and controlled release is a crucial thing to maintain the safety and ensuring the efficiency of drug transport.

Electrospinning process is a flexible method that can produce nanofibers for drug delivery system by selecting suitable materials. The materials is either biodegradable or non-degradable that can be used to control the drug delivery. Antibiotics, anticancer drugs, proteins and DNA are the examples of the drugs that can be delivered by this technique. Coatings,

embedded drug and encapsulated drug are some of the drug loading method that can be produced by various of electrospinning method (Sill & von Recum, 2008).

In wound dressings, controlled release is an efficient process for drug delivery system. Sill & von Recum (2008) stated that it is a recommendable to design a drug delivery device that gives controlled release agent (Sill & von Recum, 2008). Controlled release can improve patient convenience, minimize the toxicity and balance the delivery kinetics (McCann, Marquez and Xia, 2006; Kenawy *et al.*, 2009). The active substance is loaded into a carrier or device is the first step in controlled release system. Then, when applied by injected or non-injected, it is then releases at a predictable rate in vivo. Electrospun nanofibers have many advantages in drug delivery carrier. In electrospinning process, the drug loading is very easy to implant and the high voltage applied may had some influence on the drug activity. Furthermore, the electrospun nanofibers drug system have higher overall release rate than the bulk material as it has the high specific surface area and short diffusion passage length.

2.4.2 Filtration

Filtration is the most common application of electrospun nanofibers. What makes the electrospun nanofibers as the best filtration is because of its properties. According to Jirsak and Petrik, 2012, the morphology of nanofibers on its small diameter, bigger surface area and controllable pore size are the characteristics of the electrospun nanofibers that make it as the best filtration. By using electrospun nanofibers as filtration, tiny particles with size below than 0.5 mm can be simply trapped. Consequently, application of electrospun nanofibers in the manufacture of filtration can improves the efficiency of filtration.

According to Tsai, Schreuder-Gibson and Gibson (2002), by assimilating the spinning and charging of solution polymer can improve the efficiency of filtration without increase the pressure drop. This situation is due to the modification of electrostatic attraction ability of particles by electrostatically charged the polymer nanofibers. One of the most crucial filter performances is based on the filter efficiency and its efficiency is related to the fiber fineness. In 2006, Ahn et al. had investigated the efficiency and pressure drop of filtration of Nylon 6 nanofilters using nanofibers in diameter of 80-200 nm (Ahn *et al.*, 2006). At the face velocity

of 5 cm/s and $0.3x10^{-7}$ test particles, they had founded that the filtration efficiency of Nylon 6 nanofilter is 99.993% superior to the commercialized HEPA filter.

2.4.3 Tissue engineering

Tissue engineering is one of the most famous researches today, and there has been exponential growth of research publications in recent years in this area. It includes the use of living cells, manipulated through their extracellular environment or genetically to enhance biological substitutes for implantation into the body and to encourage remodeling of tissues in some activity manners.

Electrospun nanofiber mat is very identical to human native extracellular matrix (ECM) in morphology (Yang *et al.*, 2005). Hence, it could be a promising scaffolding material in application of tissue engineering and cell culture. It is possible to fabricate nanofiber scaffolds with complex, seamless and three-dimensional (3D) by electrospinning process that supports diverse types of cells to grow in the artificial tissues. Electrospun nanofibers fabricated from various polymers such natural polymers, synthetic polymers, biodegradable polymers and non-biodegradable polymers. The cell culture has been conducted for potentially different engineering tissues such as muscles, skins, neural tissues, blood vessels, and many others.

2.5 Current Development

The development in fabricating nanofibers is always has been researched from year 1600 until now. There are still many new researches that related to the process itself and its application of electrospun nanofibers although it is a traditional process. The world of nanomaterials comprises a variation of materials with outstanding chemical and physical properties such as nanotubes, nanofibers, one-dimensional nanowires and many more (Kenry and Lim, 2017).

In 2009, Heikkilä & Harlin investigated on the impact of conductive additive and filler in the process of electrospinning polyacrylonitrile (PAN) solution. Carbon nanotubes (CNTs) and salt have been utilized as the conductive filler to investigate the diameter of nanofiber and

its solution conductivity. The experiment was conducted with the different nozzle sizes, voltage applied and various distance from needle tip to collector. The results showed that PAN/Salt fibers had a larger diameter than PAN/CNT fibers and the conductivity of PAN/Salt solution was higher than PAN/CNT solution.

In 2014, Rubia et al. investigated on morphology, conductivity and thermal stability study of the electrospun PAN nanofiber reinforced with mixture CNT-CNF (I. *et al.*, 2014). The experiment was conducted by using 10wt% of PAN slurry to a mixture of CNT: CNF with ratios 5:3, 5:5 and 3:5. The result showed that CNT-CNF 5:3 had diameter of 0.68 micrometer which was the smallest and CNT-CNF 5:5 had diameter of 0.83 micrometer which was the biggest diameter. CNT-CNF 3:5 fiber had diameter of 0.76 micrometer between the ratios CNT-CNF 5:3 and 5:5. Hence, this show that CNF is 10 times bigger than CNT in size. Based on Figure 2.11, it shows the result of experiment that has been done by Rubia et al. consist of fiber diameter, thermal stability, electric resistivity and conductivity. ATF represents PAN/CNT-CNF with ratio 5:3, AFT represents PAN/CNT-CNF with ratio 3:5 and ATT represents PAN/CNT-CNF with ratio 5:5.

Sample	Average Fiber Diameter (micrometer)	Thermal Stability (%)	Electric Resistivity (Ω cm^{-1})	Conductivity (Scm^{-1})
PAN	0.59	45.9	2.49 x 10^{5}	1.6 x 10^{-7}
ATF	0.68	60.0	857.4	4.6 x 10^{-4}
AFT	0.76	56.0	1179.0	3.3 x 10^{-4}
ATT	0.83	65.0	817.2	4.8 x 10^{-4}

Figure 2.11: Result of experiment done by Rubia et al. (Source: I. et al., 2014)

CHAPTER 3

METHODOLOGY

3.1 Introduction

One set of solutions which is PAN/CNT with five different concentrations of MWCNT were electrospun. PAN precursor used as a control. The five concentrations of MWCNT used in the polymer solution are 0.00wt%, 0.03wt%, 0.05wt%, 0.07wt% and 0.10wt%. The 0.00wt% concentration of MWCNT in the PAN/CNT used as a reference to compare between polymer with conductive particle and polymer without conductive particle. Electrospinning parameters such as: flow rate, applied voltage and distance from the needle tip to the collector were kept constant as to prohibit them from having a consequence effect on the fiber morphology.

3.2 General Experimental Setup

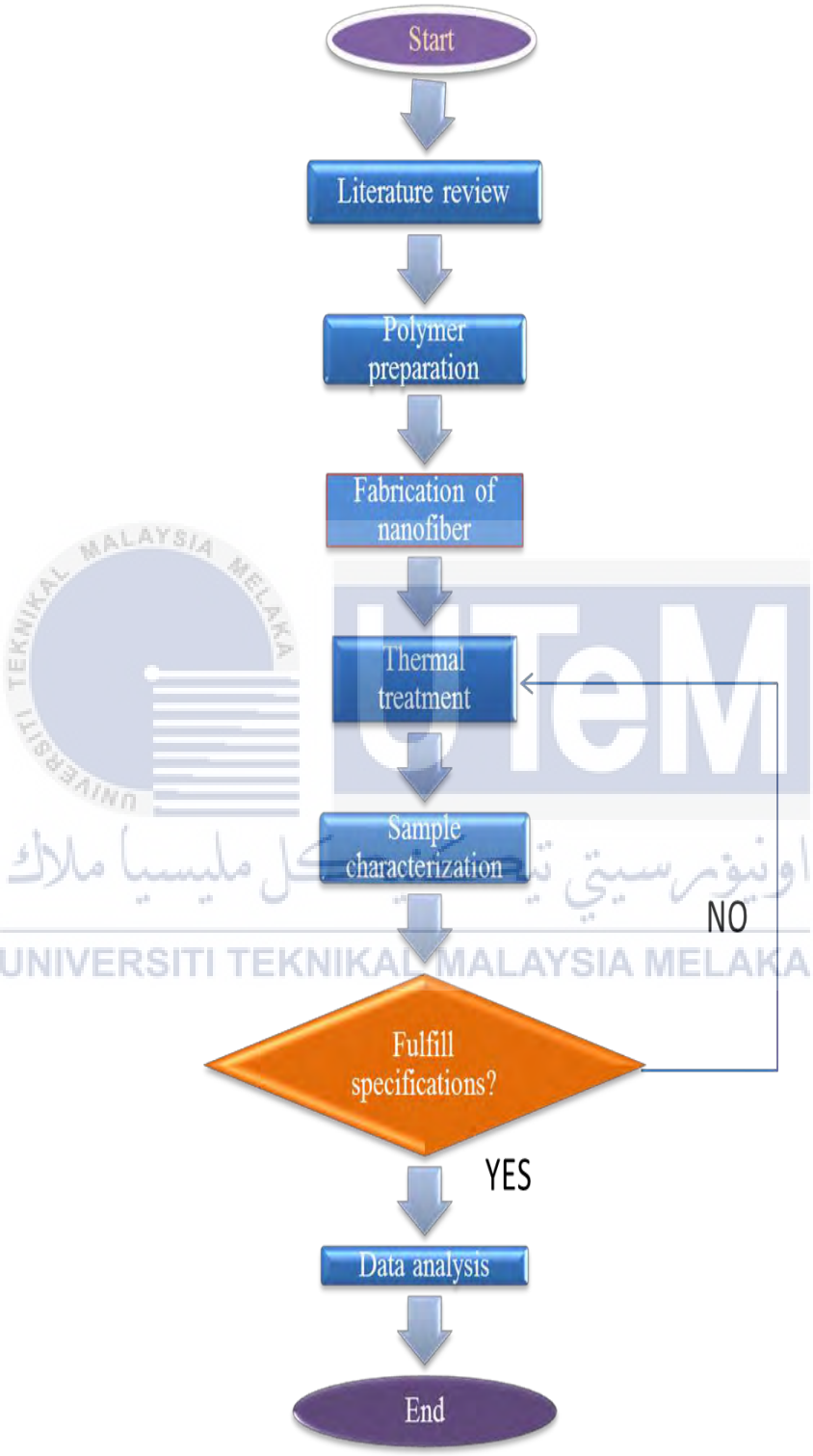


Figure 3.1: Flow chart of general methodology

Table 3.1: Table of Gantt Chart for Final Year Project

GANTT CHART FOR FINAL YEAR PROJECT														
No.	**Tasks**	**Weeks**												
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1.	**Introduction for PSM tittle**														
2.	**Literature review**														
3.	**Progress report**														
4.	**Preparation of polymers**														
	Fabrication of nanofibers														
	Carbonisation process														
5.	**Characterisation of nanofibers**														

3.2.1 Materials

Polyacronitrile (PAN) with MW 150,000 from Sigma-Aldrich and multi-walled carbon nanotube (MWCNT) were supplied by the AMCHAL Laboratory, UTeM. N,N-dimethylformamide solvent (DMF) was supplied form the Chemistry Laboratory, UTeM.

3.2.2 Preparation of PAN/CNT Solution

PAN polymer, DMF solvent, and MWCNT were measured by using the AL204 analytical balance, Figure 3.2. The total solution needed for each polymer is 15 ml. Hence, each of the polymers needs to be calculated before weigh on the analytical balance. The sample calculation is:

PAN concentration: 10wt%

Total volume target: 15mL

Hence, $\frac{10wt\%}{100}$ x 15mL = 1.5g (3.1)

Table 3.2: Table of amount of PAN, MWCNT, and DMF needed to be weighed

	PAN	MWCNT	DMF
1	10wt%	0.00wt%	90.00wt%
	1.5g	0.000g	13.50g
2	10wt%	0.03wt%	89.97wt%
	1.5g	0.0045g	13.495g
3	10wt%	0.05wt%	89.95wt%
	1.5g	0.0075g	13.497g
4	10wt%	0.07wt%	89.93wt%
	1.5g	0.0105g	13.4895g
5	10wt%	0.10wt%	89.90wt%
	1.5g	0.0150g	13.485g

MWCNT particle was dispersed in the N,N-dimethylformamide solvent for PAN/CNT solution. The mixtures then need to be sonicate process for 60 minutes in the B8510 ultrasonic bath from Branson as shown in Figure 3.3.

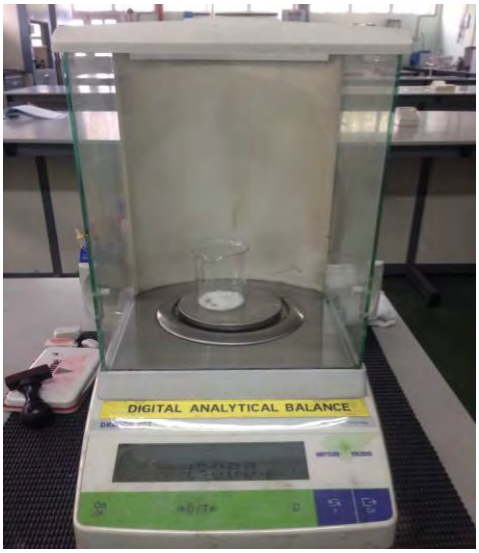


Figure 3.2: AL204 Analytical Balance

Figure 3.3: Sonication process in ultrasonic bath

Then, PAN polymer with molecular weight 150,000 g mol^{-1} (Sigma-Aldrich) was dissolved in the N,N-dimethylformamide solvent and MWCNT. The solution then was stirred vigorously for 24 hours at room temperature at the speed of 1000 RPM by using CMAG HS 7 Magnetic Stirrer, refer Figure 3.4.

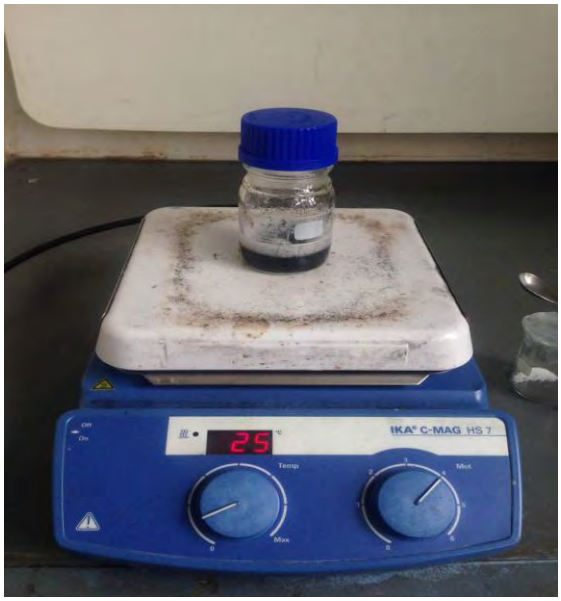


Figure 3.4: Solution was stirred by using CMAG HS 7 Magnetic Stirrer

3.2.3 Fabrication of Electrospun Nanofiber

The polymer solution that had been completed on the preparation then will fed into syringes as to undergo the electrospinning process by using electrospinning machine fabricated by UTeM student. Fixed electrospinning parameters were setting and used. These parameters are: (i) Distance from needle tip to the collector = 13 cm, (ii) voltage applied = 18.0 kV, (iii) Flow rate = 1.30 ml/h.

The electrospinning machine setup consisted syringe pump that connected with the machine that can control the flow rate of the ejected polymer solution, refer Figure 3.5. A small diameter tube was connected between the tip of the syringe and the high-voltage rod as the solution of polymer flow in the tube. The distance was adjusted between the needle tip and the collector by loosen the nut. The collector plate was made from aluminium. Hence, aluminium foil was attached as a second layer of the aluminium collector plate to offer a fast and remove technique for attaining the multiple samples, Figure 3.6. Then, the voltage at the high voltage power supply was adjusted to desire voltage and the ―start" button was pressed to run the process of electrospinning.

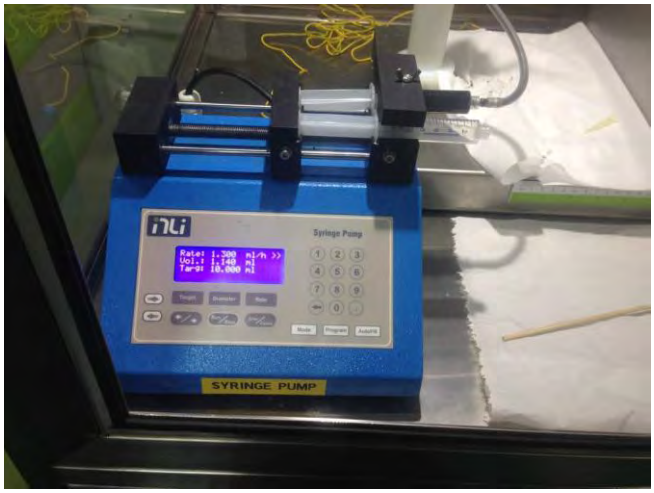


Figure 3.5: Syringe pump in electrospinning machine

Figure 3.6: Aluminium foil as a covered on the collector plate

3.2.4 Thermal Treatment

The electrospun nanofiber of PAN/CNT was further treated under thermal treatment. This heat treatment consists of two stages to remove a non-carbon element and to do pyrolysis of a long-chain carbon. The first stage is the stabilization stage. In the stabilization process, a non-carbon element will be removed after the heat treatment was done. Stabilization process was done at 240 °C with heating rates 1 °C/min at atmosphere condition. The second stage is

the carbonization stage. In the carbonization stage, it would allow the carbon to self-arrange to become a ladder structure polymer. Carbonization process was done at 1000 °C with heating rates 5 °C/min at nitrogen condition by using horizontal tube furnace from LT Furnace, refer Figure 3.7. Each process in each stage was continuing with 30 minutes of dwell time.

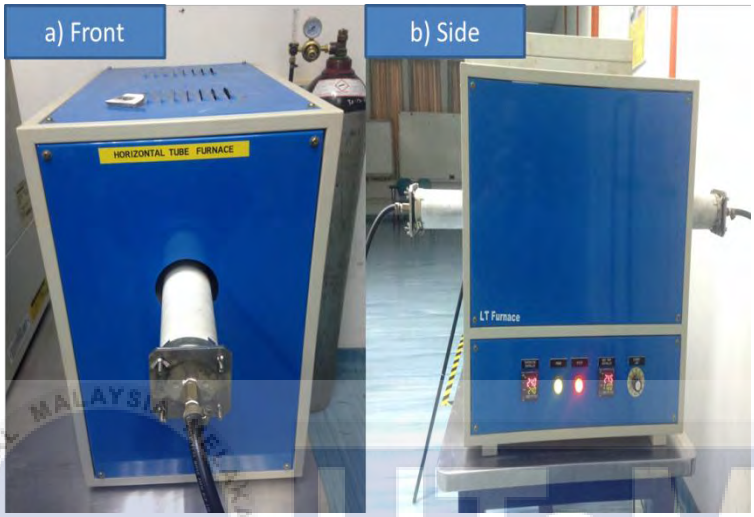


Figure 3.7: Horizontal tube furnace. (a) Front view, (b) Side view

3.2.5 Characterization

After all of the procedure in fabricating and heat treatment had been done, the process had been continued with the analysis of characteristics of the electrospun nanofiber. The characteristics of the electrospun nanofiber that had to be investigated were morphology, conductivity, and the chemical characteristic.

3.2.5.1 Morphology of Electrospun Nanofiber

The morphology of the electrospun nanofiber had been characterized by using InTouchScope SEM JSM-6010PLUS/LV, Figure 3.8. Before using the scanning electron microscope (SEM), the samples need to be coated as to clear the image of the sample, reduce thermal damage, create conductive layer and enhance the secondary electron. The machine that had been used is Auto Fine Coater model JEC-3000FC model, Figure 3.9.

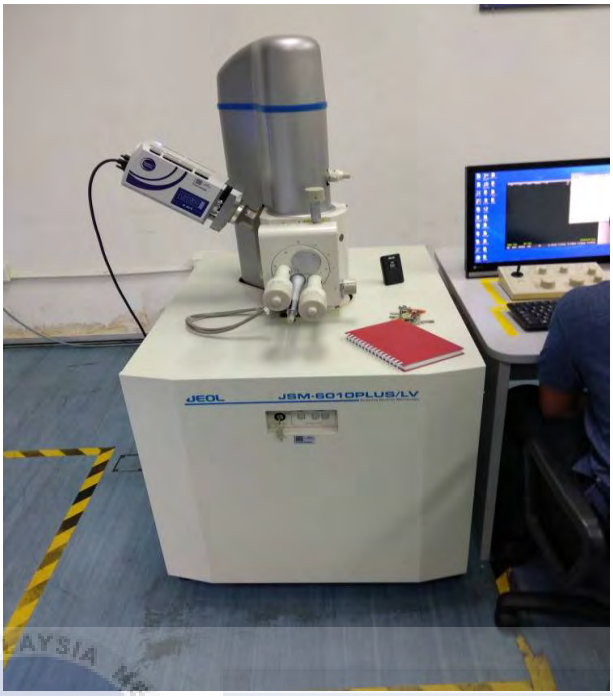


Figure 3.8: SEM JSM-6010PLUS/LV machine

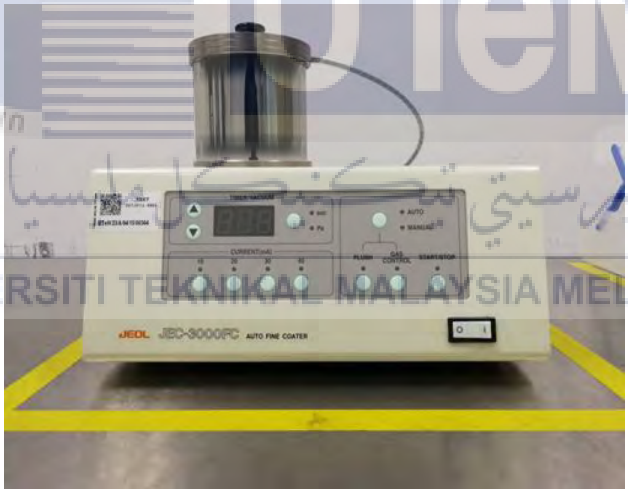


Figure 3.9: Auto Fine Coater JEC-3000FC machine

The process continued with the procedure of finding the diameter of the nanofibers. The nanofibers diameter was evaluated by using the image J software. Image J software is an open source image processing program created for specific multidimensional images. Figure 3.10 shows the procedure for findings the diameter of the nanofibers from the SEM images by using image J software.

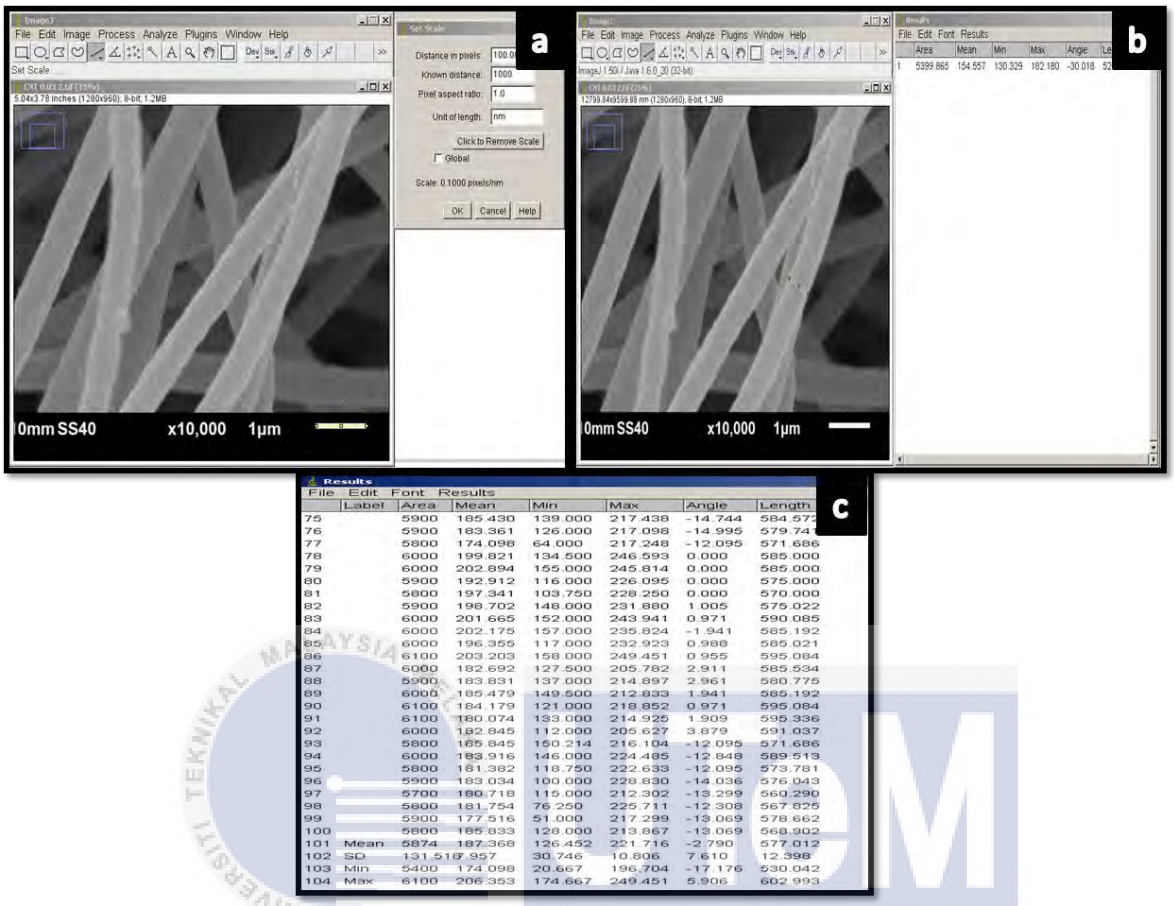


Figure 3.10: Procedure of finding the diameter of nanofibers from the SEM images by using image J software, (a) set scale in the software, (b) slot in the diameter of the nanofiber, (c) summarize the data.

The procedure for finding the diameter of nanofibers by using image J software were started by set the scale of the SEM image (Figure 3.11 (a)). 1µm is equal to 1000nm. Hence, the unit length needs to be changed to nm. Then, the procedure continued by making the straight line along the diameter of the nanofiber. Press _M' on the keyboard to slot in the diameter (Figure 3.10 (b)). The procedure was repeated until 100 diameters were slotted in the data. Finally, all the data was summarized and the average length and the standard deviation were taken as the result.

3.2.5.2 Conductivity of Carbon Nanofiber

The conductivity of the electrospun nanofiber had been characterized by using four point probe machine JANDEL RM3000+ model in AMCHALS laboratory as shown in Figure 3.11. This machine was used as to measure the resistivity of the samples. The samples that had been used in this machine were only the carbonized samples. The current was set to $1x10^{-4}$ Ampere

Figure 3.11: Four point probe machine JANDEL RM3000+ model

Based on the Figure 3.11, the sample was pressed by the four point probe tool and the reading of the resistivity will appeared on the screen of the machine. 20 readings were taken and the average of the resistivity will be count as the result for the resistivity of the sample. Then, the conductivity of the sample was calculated by using the following equation:

$$\sigma = \frac{1}{4.5324 \times Rs \times t} \text{ S/m} \quad (3.2)$$

Where:

4.5324 = correction factor

Rs = sheet resistance by four-point probe

t = thickness by digital micrometer

3.2.5.3 Chemical Characterization

The chemical characterization of the electospun nanofiber had been conducted by using Fourier Transform Infrared Spectroscopy (FTIR) machine from Perkin Elmer in AMCHALS laboratory as shown in Figure 3.12. This machine was used to examine the chemical bonding of electrospun nanofiber. This machine converts raw data into an actual spectrum transfer in the software in computer.

Figure 3.12: Fourier Transform Infrared Spectroscopy (FTIR) machine by Perkin Elmer

The procedure was started by taking a small piece of the sample and the sample was put in the pellet as shown in Figure 3.13. Initially, the sample was mixed with the potassium bromide (KBr) in the pellets as the potassium bromide can turn into plastic when subjected to the pressure and form a sheet that is transparent in the infrared region. Then, the pellet was put in the machine as shown in Figure 3.14.

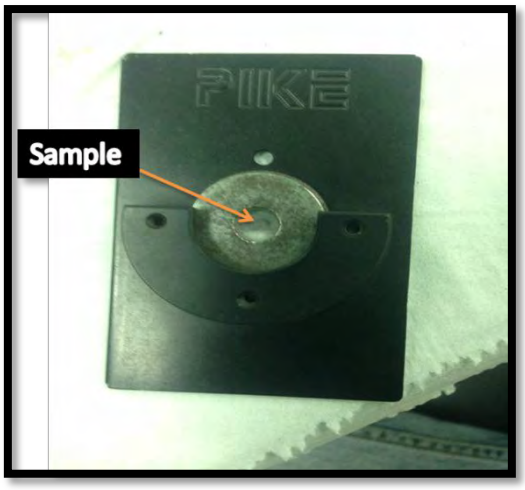


Figure 3.13: Pellet to be used in FTIR machine

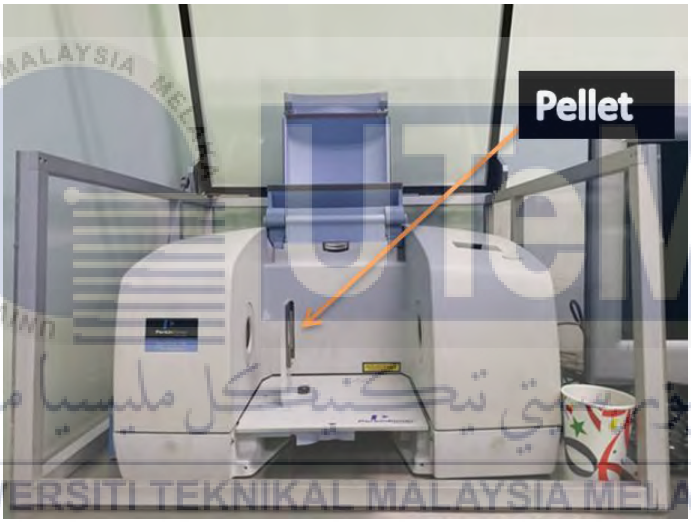


Figure 3.14: Pellet was put in the FTIR machine

Finally, the procedure was continued by using the Spekwin32-Spectroscopy software. This software can translate the molecule chain structure of the sample to the pattern of spectrum as shown in Figure 3.15. Hence, the FTIR result will be analyzed to observe the chemical characterization for each sample.

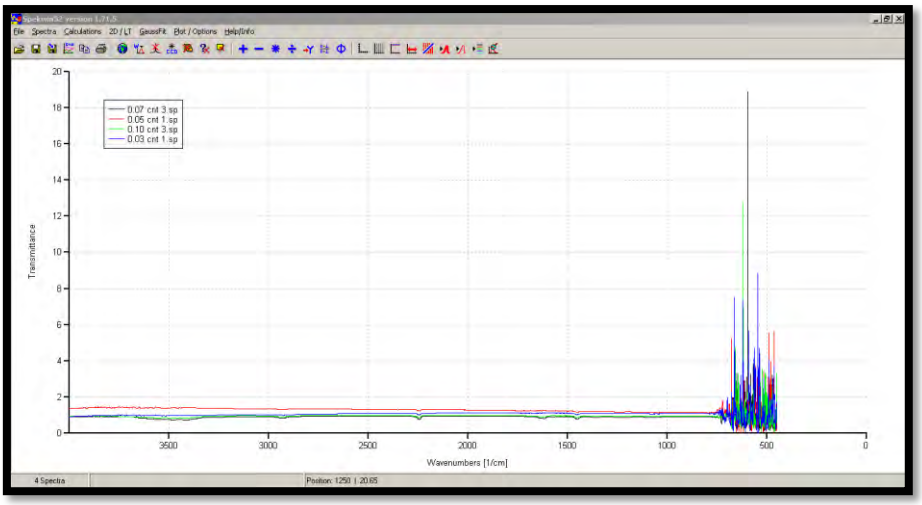


Figure 3.15: Spectrum pattern in Spekwin32-Spectroscopy software

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Physical Properties

This chapter presents the results and discussion obtained from the experiment. The electrospun nanofibers for 0.00wt%, 0.03wt%, 0.05wt%, 0.07wt%, and 0.10wt% concentration of MWCNT in PAN/CNT solution were fabricated by using electrospinning machine. Figure 4.1 shows the image of electrospun nanofiber of PAN/CNT produced from the electrospinning machine on aluminium foil.

Figure 4.1: Electrospun nanofiber of PAN/CNT on aluminium foil

Based on the Figure 4.1, the electrospun nanofiber of PAN/CNT on the aluminium foil appeared in white colour. It can be seen that the nanofibers were distributed in a formation of circular shape on the aluminium foil. This phenomenon reflects the theory of whipping instability during the process in fabricating the electrospun nanofibers. There were no beads appear on the electrospun nanofibers. Heikkilä & Harlin, 2009 stated that the presence of

MWCNT as a conductive filler influence the conductivity of the solution which increase the net charge density of PAN/CNT solution. This phenomenon reinforces the whipping instability that leads to the formation of bead-free nanofibers during the fabrication process of electrospun nanofibers.

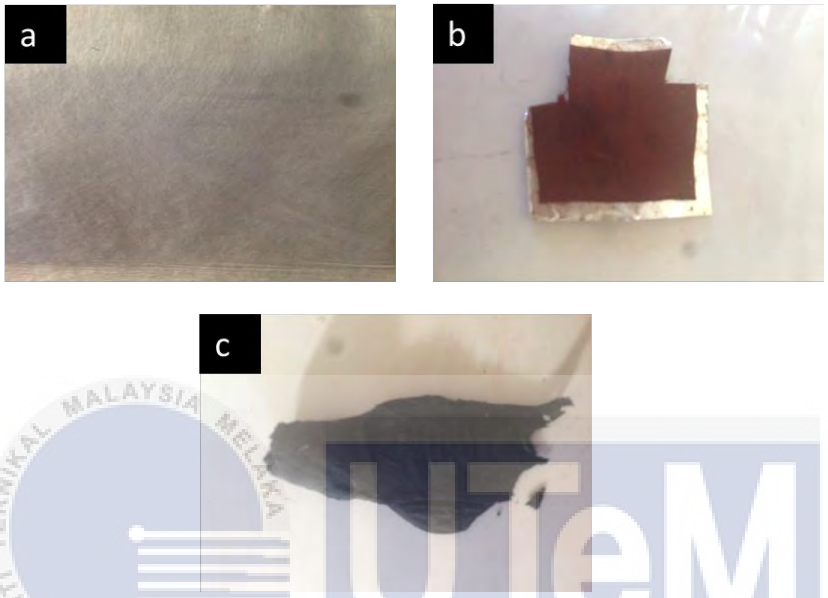


Figure 4.2: The colour change of the nanofibers before and after the heat treatments (a) as-spun PAN/CNT electrospun nanofibers (NF), (b) stabilized nanofibers (SNF), and (c) carbonized nanofibers (CNF)

The fabrication of the electrospun was continued to the heat treatment process of the nanofibers. The heat treatment process consisted of two main process which is stabilization process and carbonization process. The electrospun nanofibers will changes its properties and appearances after undergo these two heat treatment process. Figure 4.2 shows the physical appearances of the electrospun nanofibers starting from normal nanofibers, stabilized nanofibers and lastly the carbonized nanofibers. Based on Figure 4.2, the physical properties of deposited PAN/CNT nanofibers initially appeared in white colour (Figure 4.2 (a)). After the stabilization process at 240°C with heating rate 1°C/min, the white colour of nanofibers changed to dark brown colour (Figure 4.2 (b)). Lastly, after the carbonization process at

1000°C with heating rate of 5°C/min, the dark brown colour of the nanofibers changed to black colour (Figure 4.2 (c)).

The colour of the nanofibers changed from light to dark colour after the heat treatment because the decomposition of other organic compounds and formation of denser structure in polymer have taken place through thermal cyclization and dehydrogenation (Faccini *et al.*, 2015). Other than that, the colour changes of the nanofibers also indicated that the electrospun nanofibers were altered from thermoplastic to thermoset (Cho *et al.*, 2007). After carbonization process, the black colour of the nanofibers indicated that the fibers have the high content of carbon.

4.2 Chemical Characterization

The chemical characterization of electrospun nanofiber PAN/CNT was conducted by using Fourier Transform Infrared Spectroscopy (FTIR) machine. FTIR machine consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. FTIR machine can capture the bonding polymer with coupling agent of the sample. The source develops radiation which passes the sample through the interferometer and reaches the detector as shown in Figure 4.3. Then, the molecule chain structure of the sample will translate into the pattern of spectrum in the Spekwin32-Spectroscopy software. By using Spekwin32-Spectroscopy software, we can see and analyze the pattern of the spectrum for each sample. Figure 4.4, Figure 4.5, and Figure 4.6 below present the FTIR spectra for the samples of normal, stabilization and carbonization nanofibers with different concentration of MWCNT.

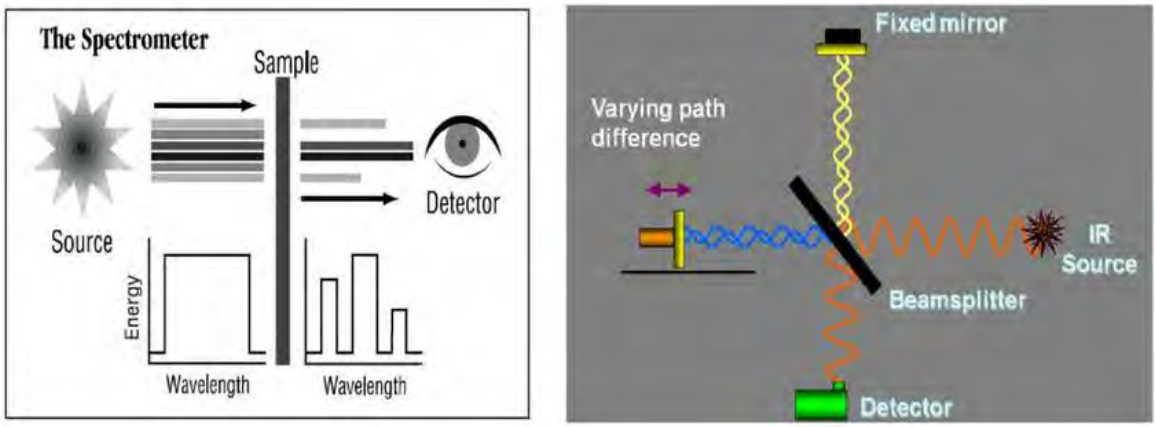


Figure 4.3: Principle operation of the FTIR Spectrometer (Source: Tunde et al., 2015).

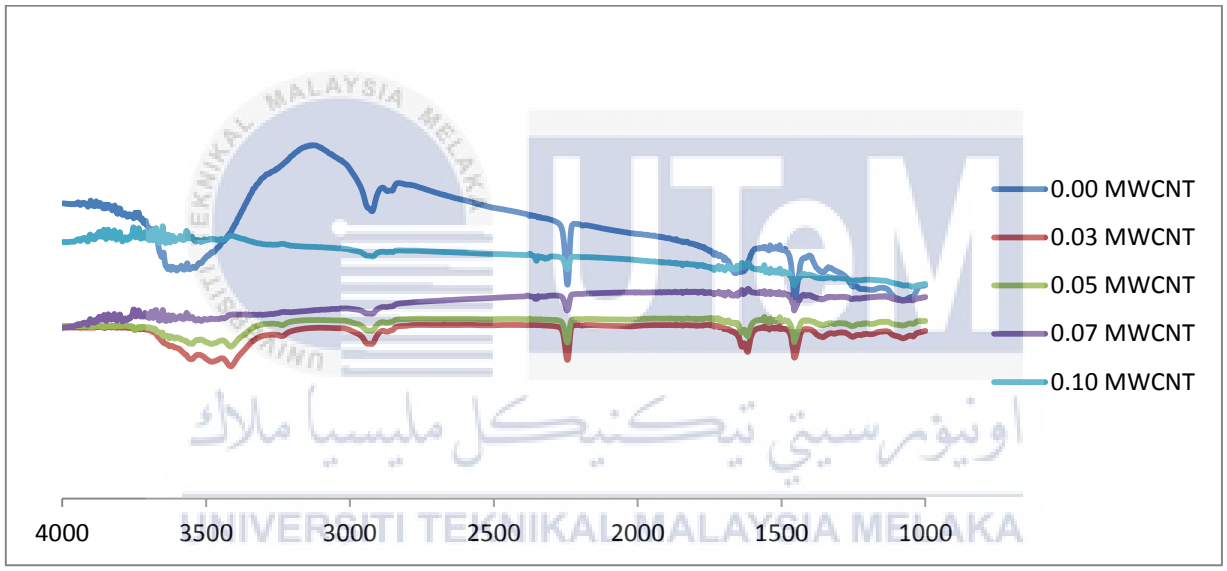


Figure 4.4: FTIR spectra of electrospun nanofiber PAN/CNT (as-spun).

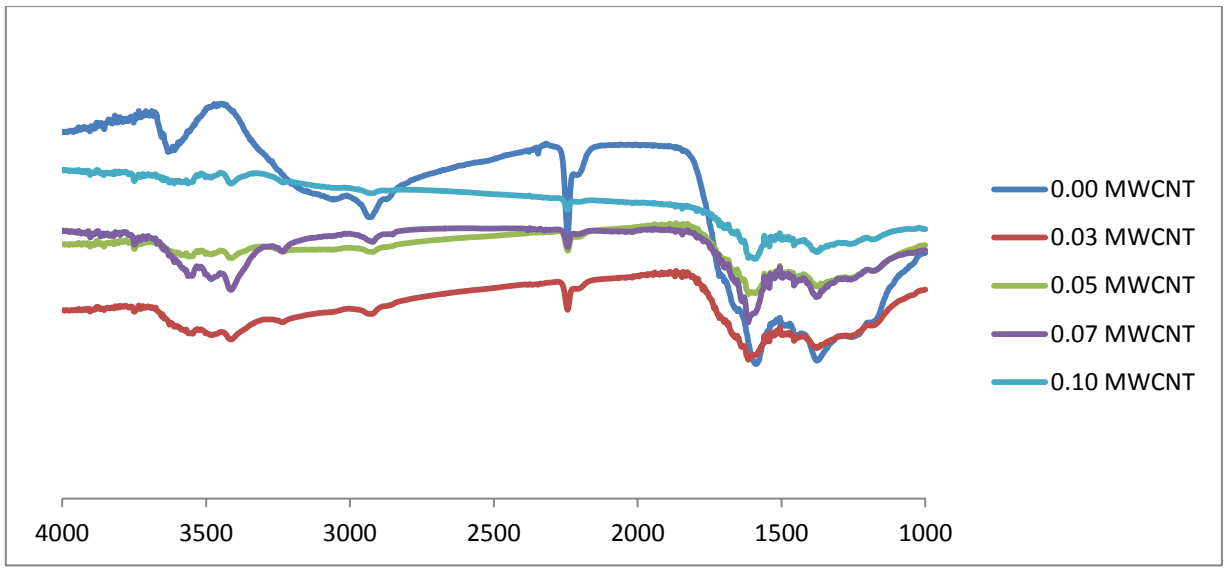


Figure 4.5: FTIR Spectra of electrospun nanofiber PAN/CNT (stabilization)

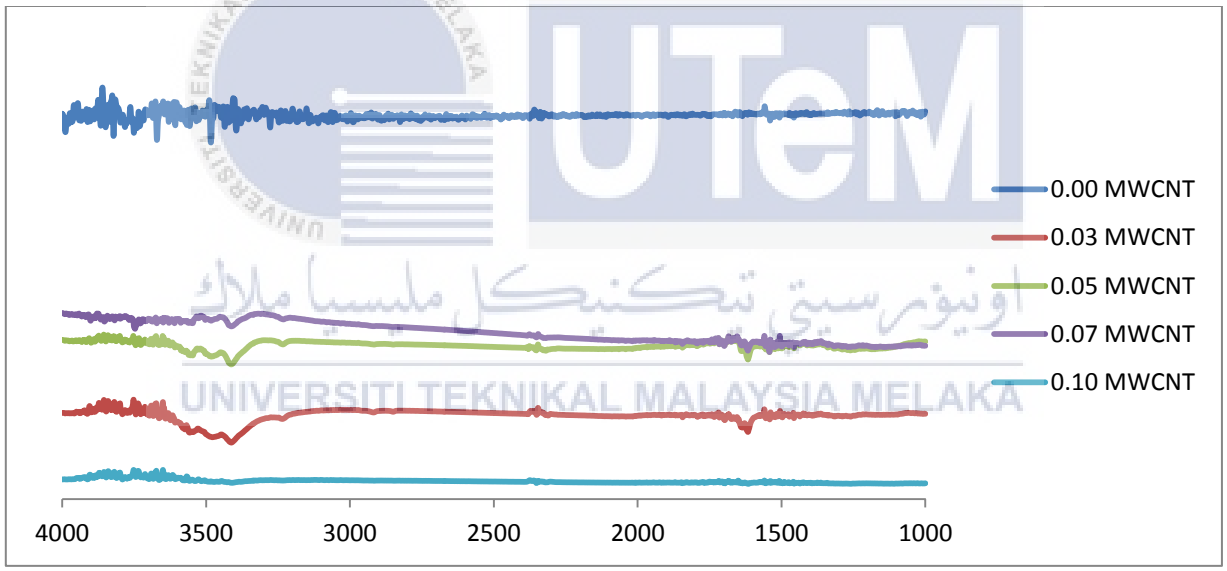


Figure 4.6: FTIR Spectra of electrospun carbon nanofiber PAN/CNT (carbonization)

Figure 4.4, Figure 4.5 and Figure 4.6 show a FTIR spectrum transmittance of PAN/CNT with different concentration of MWCNT which are 0.03wt%, 0.05wt%, 0.07wt% and 0.10wt%. Based on the results, it shows that there were sharp peaks formed by electrospun nanofiber. The formation of PAN explained by the existence of peaks at 1457 cm^{-1} and 2252 cm^{-1} which refer to CH_2 scissoring chains and C≡N group (Akhtar *et al.*, 2011). The presence

of nitrile group (C≡N) located at between 2220 cm^{-1} to 2260 cm^{-1} (Munajat *et al.*, 2016). Akhtar et al., 2011 stated that there is appearance of typical carbonyl (C=O) derived from carboxylate group of MWCNTs for PAN/CNT composite at 1729 cm^{-1} peak. Based on the spectrum pattern, it shows that the higher concentration of MWCNT produces the lower peak. Other than that, the peaks intensity also decreases after the heat treatment process in stabilization and carbonization.

Based on the Figure 4.4 and Figure 4.5, the intensity peaks of spectrum become smaller as the nanofibers undergo heat treatment in stabilization process at 240°C. Stabilization process is a complex reaction which involves cyclization, oxidation, dehydration and cross-linking. The decreasing of intensity peaks at ~ 1400 cm^{-1} (Figure 4.4) and ~ 1600 cm^{-1} (Figure 4.5) is caused by the formation of conjugated C=N from C≡N during stabilization process. Liu, 2010 stated that the peaks in the range of 2180 ~ 2260 cm^{-1} are attributed to three kinds of nitrile groups as shown in Figure 4.7. MWCNT has the properties of high surface area which can reduce the formation of β-amino nitrile in the stabilized nanofiber. The β-amino nitrile is formed by the termination of the cyclization reaction. Chain scission in stabilized fibers depends on the β-amino nitrile. Hence, the lower amount of β-amino nitrile improved the properties of carbon fibers.

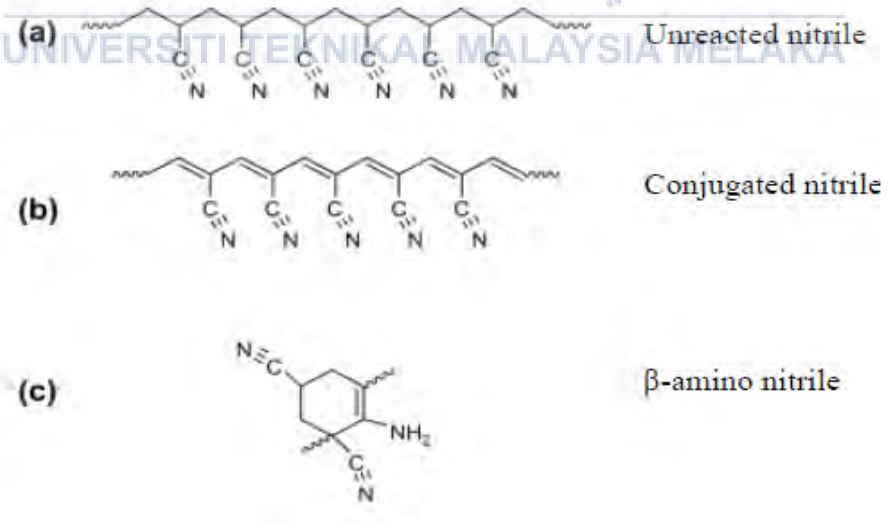


Figure 4.7: Chemical structure of various nitrile groups: (a) unreacted, (b) conjugated, and (c) β-amino nitrile (source: Liu, 2010).

Further heat treatment had been done on carbonization process which contributes to the spectrum in Figure 4.6. It has been found that the intensity peaks at ~1400, ~1600 and ~2250 cm^{-1} in stabilization (Figure 4.5) become smaller and eliminated after undergo carbonization process at 1000°C (Figure 4.6). The peak intensity at ~2250 cm^{-1} was largely decreased after the carbonization process. It was also observed that there is existed some small peaks at ~3400cm^{-1} due to aliphatic CH group is still visible on carbonized nanofibers of PAN/CNT with 0.03wt%, 0.05wt%, and 0.07wt%. However, it seems that carbonized nanofibers of PAN/CNT with high concentration of MWCNT 0.10wt% showed that other compounds of non-carbon element have been fully eliminated rather than PAN/CNT at 0.00wt% concentration of MWCNT.

4.3 Conductivity of Carbon Nanofibers

The resistivity of PAN/CNT carbon nanofibers was determined by using Four Point Probe machine with 100μA. Sample was applied by a force from the Four Point Probe machine and connected to the digital machine as shown in Figure 4.8. 20 readings were taken for one sample and the average value of resistivity were chosen as the result value for sheet resistance.

Figure 4.8: Setup for resistivity test of PAN/CNT carbon nanofibers by using Four Point Probe machine

The result for the conductivity of PAN/CNT carbon nanofibers were calculated by formula in Eq. (3.2). Table 4.1 shows the sheet resistance, Rs (Ω/sq) and conductivity, σ (S/cm) for each sample of PAN/CNT carbon nanofibers (CNF) with different concentrations. The table was interpreted in graph as shown in Figure 4.9 to show the characteristics between the conductivity and the concentrations of MWCNTs in PAN/CNT carbon nanofibers (CNFs).

Table 4.1: Table of conductivity for each sample

Samples	Concentration of MWCNT (wt%)	Sheet resistance, Rs (Ω/sq)	Conductivity, σ (S/cm)
1	0.00	18.651	11.83
2	0.03	12.411	17.78
3	0.05	8.078	27.31
4	0.07	6.309	34.97
5	0.10	3.643	60.56

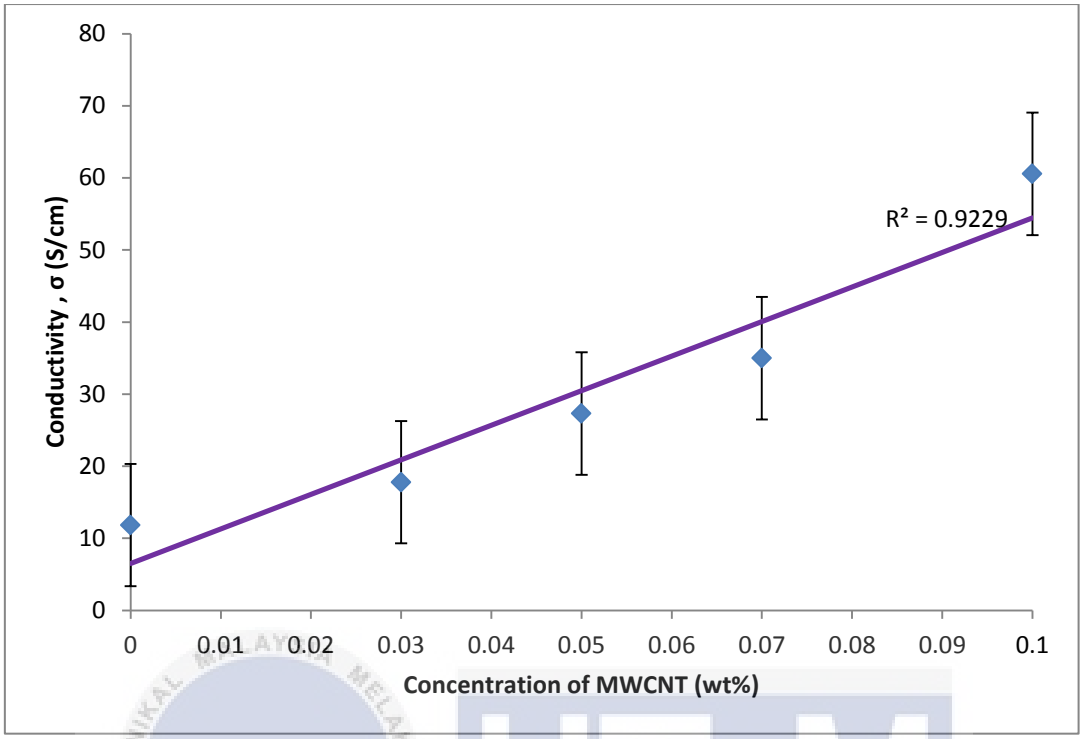


Figure 4.9: Graph of conductivity, σ (S/cm) against concentration of MWCNT (wt%) for carbonized nanofiber (CNFs)

Table 4.1 above shows that the resistivity value of carbon nanofibers (CNFs) was decreased as the concentration value of MWCNT in PAN/CNT carbon nanofibers increased. Then, the conductivity of the carbon nanofibers was calculated from the formulae and shows that the value of conductivity PAN/CNT carbon nanofibers was increased as the concentration of the MWCNT value in PAN/CNT carbon nanofibers is increased. Based on the graph of conductivity, σ against the concentration of MWCNT, wt% for carbonized nanofibers shown in Figure 4.9, the correlation, r value for the best fit line is 0.96. The correlation value is near to 1. It is clearly shown that there is a relationship between the conductivity and the concentration of MWCNT. Hence, it can be concluded that the conductivity of carbon nanofibers is increased as the concentration of MWCNT increased.

The molecule chain structure results in section 4.2 of chemical characterization had shown that the presence of MWCNT in electrospun nanofiber had slightly deformed the formation of the electrospun nanofiber spectrum in FTIR. Then, after the heat treatment has been done in stabilization and carbonization process, the peaks of the spectrum were highly

eliminated after the carbonization process at 1000°C. This phenomenon has allowed the carbon to self-arrange to become a ladder structure polymer which enhances its conductivity of the carbon nanofibers. The elimination of peaks in the FTIR spectrum leads to the enhancement in term of conductivity of the nanofiber. It is due to the formation of the conductor network to transport the electrical charge or electron in the molecule structure.

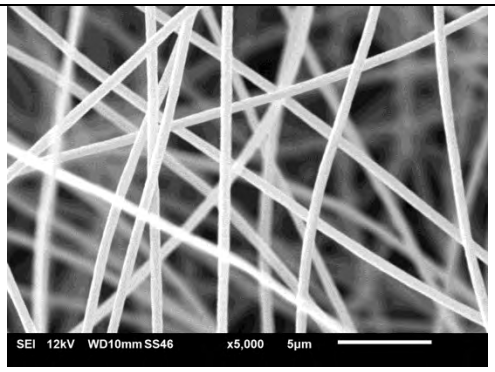
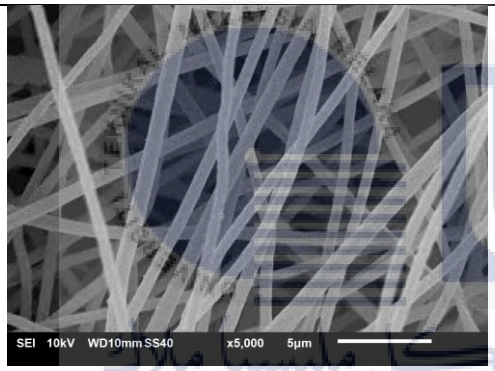
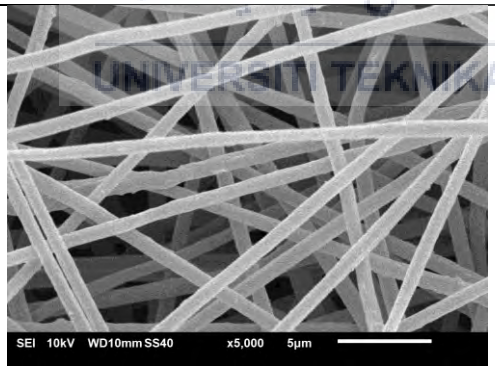
The presence of MWCNTs in the electrospun nanofibers has improved the elimination of the peaks in the spectrum which contribute to increase the formation of conductor network in transporting the electrical charge or electron in the molecule structure. It can be proved from the results obtained above that there was much different value of the conductivity between the PAN/CNT nanofibers with concentration of MWCNT at 0.00wt% and 0.10wt%. The highest concentration of MWCNT at 0.10wt% had higher conductivity value which is 60.56 S/cm better than the conductivity value for concentration of MWCNT at 0.00wt% which is 11.83wt%. Consequently, it can be proved by the finding of I. *et al.* (2014) that the concentration of the MWCNT affect the conductivity of the carbon nanofibers (CNFs). The conductivity of carbon nanofibers increases as the concentration of MWCNT increases.

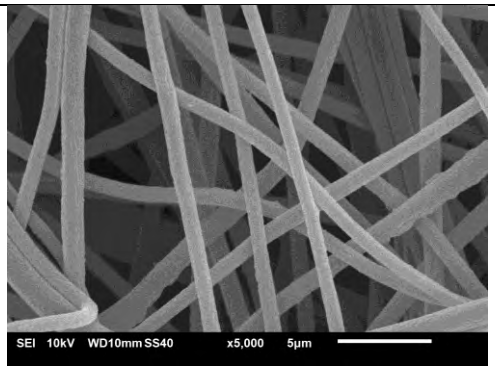
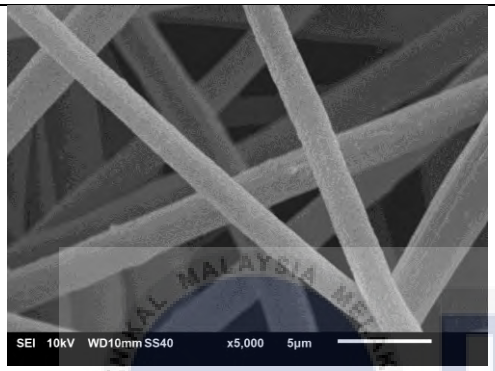
4.4 Morphology of Nanofibers

4.4.1 Fiber Appearance and Diameter

The morphology of electrospun nanofiber PAN/CNT was conducted by using scanning electron microscope (SEM) machine. Then, the diameter of the electrospun nanofibers were analyzed by using Image J software stated in the methodology section. Table 4.2, Table 4.3, and Table 4.4 shows the SEM images (5,000 magnifications) of electrospun nanofiber and fiber diameter with different concentration of MWCNT for as-spun, stabilization and carbonization type. All of the diameter for different concentrations of MWCNT and different stages for as-spun, stabilization and carbonization were interpreted in the Figure 4.10, Figure 4.11, and Figure 4.12.

Table 4.2: Table of SEM images (5,000 maginification) and fiber diameter of electrospun nanofiber with different concentration of MWCNT (as-spun)

SEM images (5,000 magnification) of electrospun nanofiber	Fiber diameter for different concentration of MWCNT (nm)
	0.00 wt% of MWCNT (as-spun) 577 ± 12
	0.03 wt% of MWCNT (as-spun) 573 ± 15
	0.05 wt% of MWCNT (as-spun) 759 ± 74

	0.07 wt% of MWCNT (as-spun) 875 ± 38
	0.10 wt% of MWCNT (as-spun) 1985 ± 93

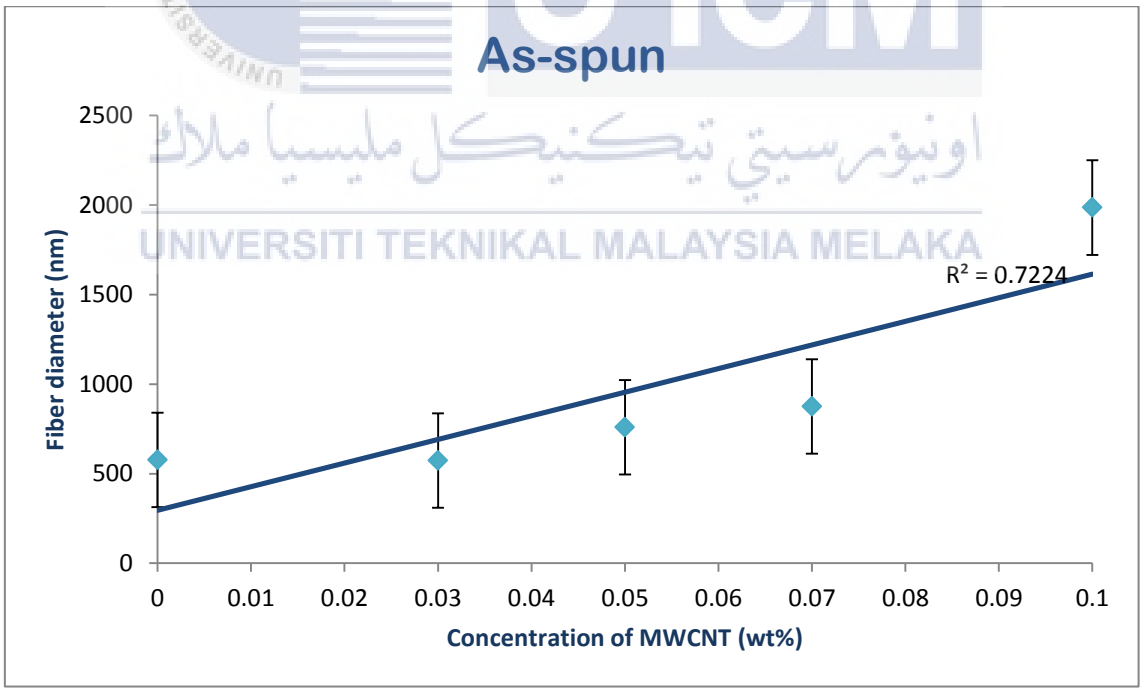
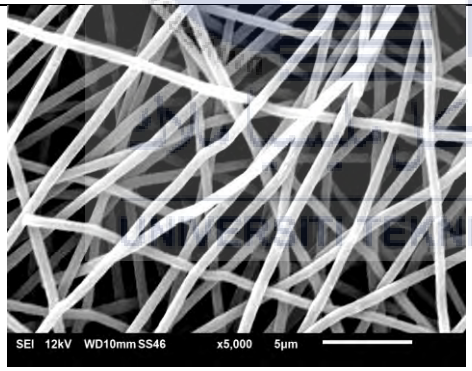
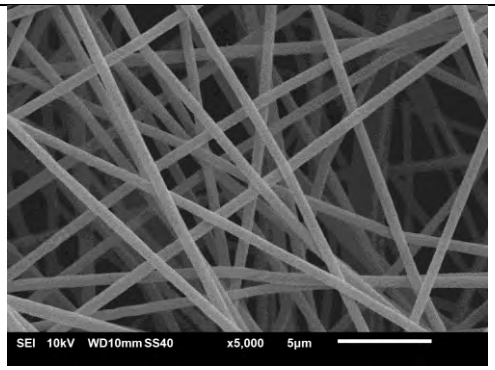
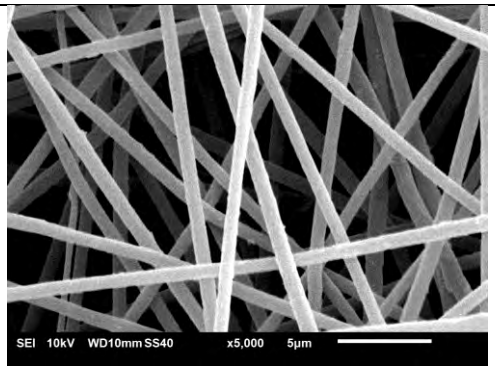
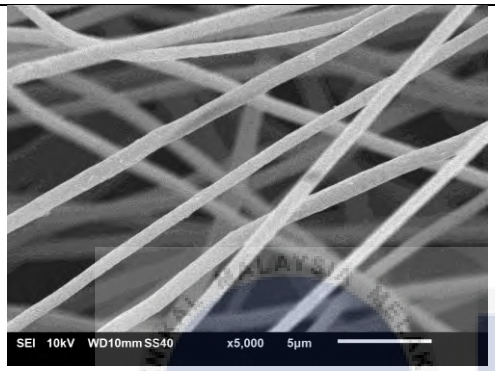


Figure 4.10: Graph of fiber diameter, nm against concentration of MWCNT, wt% (as-spun).

Based on the graph of fiber diameter, nm against concentration of MWCNT, wt% for as-spun nanofibers in Figure 4.10, the correlation, r value for the best fit line is 0.85. The correlation value is near to 1. Hence, it can be concluded that there is relationship between the fiber diameter and the concentration of MWCNT. It is apparent that the fiber diameter is increased as the concentration of MWCNT in PAN/CNT nanofiber increased. Based on the Table 4.2, it can be seen that the appearance of the fiber in SEM image (5,000 magnification) for all concentrations were smooth. The amount of fiber distribution seems to be large and same for all concentrations. However, there are some nanofibers at 0.07wt% concentration of MWCNT that is bound together.

Table 4.3: Table of SEM images (5,000 magnifications) and fiber diameter of electrospun nanofiber with different concentration of MWCNT after stabilization process

SEM images (5,000 magnification) of electrospun nanofiber	Fiber diameter for different concentration of MWCNT (nm)
	0.00 wt% of MWCNT (Stabilization) 508 ± 16
	0.03 wt% of MWCNT (Stabilization) 568 ± 35

	0.05 wt% of MWCNT (Stabilization) 722 ± 62
	0.07 wt% of MWCNT (Stabilization) 824 ± 65
	0.10 wt% of MWCNT (Stabilization) 1973 ± 30

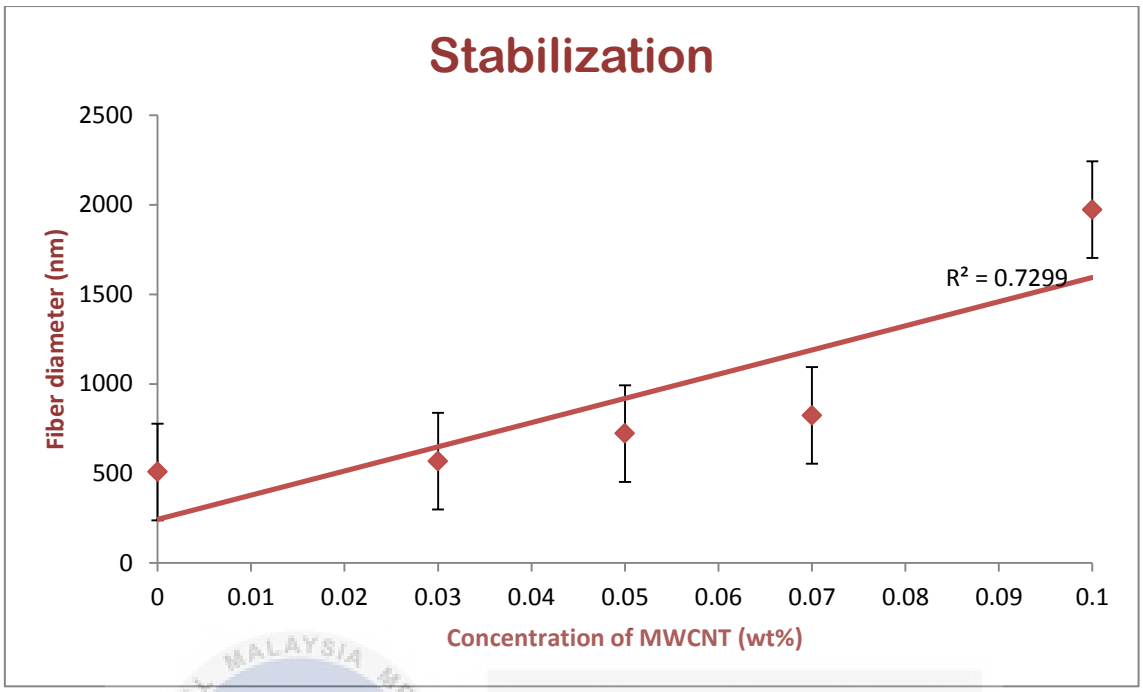
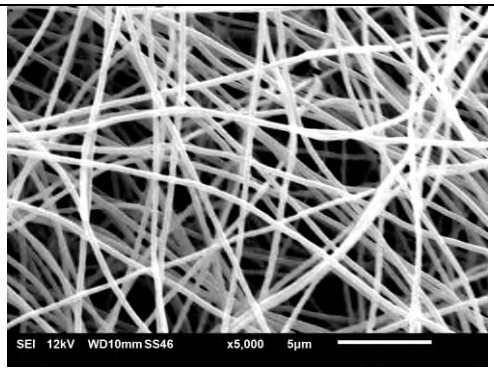
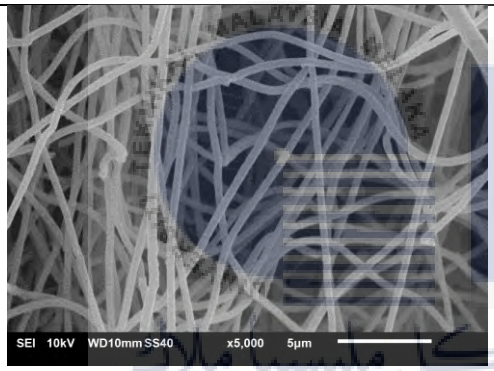
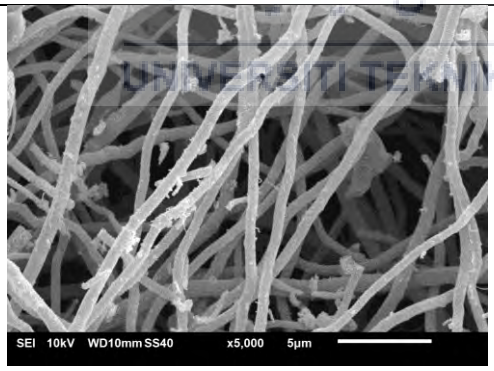
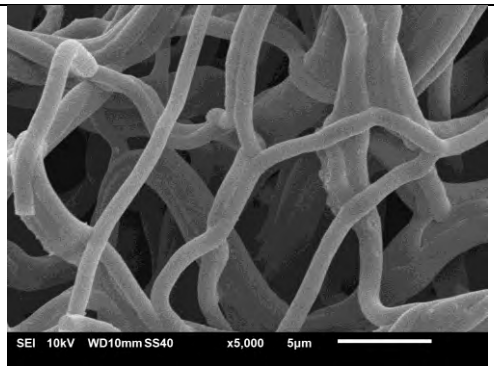
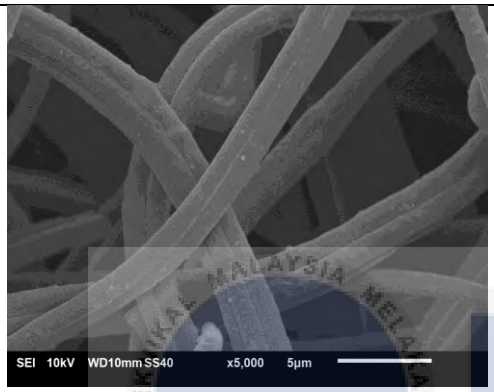


Figure 4.11: Graph of fiber diameter, nm against concentration of MWCNT, wt% (stabilization).

Figure 4.11 reveals the graph of fiber diameter, nm against concentration of MWCNT, wt% after the stabilization process of electrospun nanofibers (SNF). The value of correlation, r for the best fit line in the graph is 0.85. The correlation value is near to 1. Hence, it can be shown that there is a relationship between fiber diameter and the concentration of MWCNT after the stabilization process of the nanofibers. Consequently, it indicates that the fiber diameter is increased as the concentration of MWCNT in PAN/CNT nanofiber increased after the heat treatment in stabilization process. Based on the Table 4.3, it shows that the appearance of the fiber in SEM image (5,000 magnifications) for all concentrations were very smooth. The amount of fiber distribution seems to be large and same for all concentrations.

Table 4.4: Table of SEM images (5,000 maginification) and fiber diameter of electrospun nanofiber with different concentration of MWCNT after carbonization process

SEM images (5,000 magnification) of electrospun nanofiber	Fiber diameter for different concentration of MWCNT (nm)
	0.00 wt% of MWCNT (Carbonization) 333 ± 6
	0.03 wt% of MWCNT (Carbonization) 402 ± 26
	0.05 wt% of MWCNT (Carbonization) 564 ± 28

	0.07 wt% of MWCNT (Carbonization) 791 ± 14
	0.10 wt% of MWCNT (Carbonization) 1056 ± 29

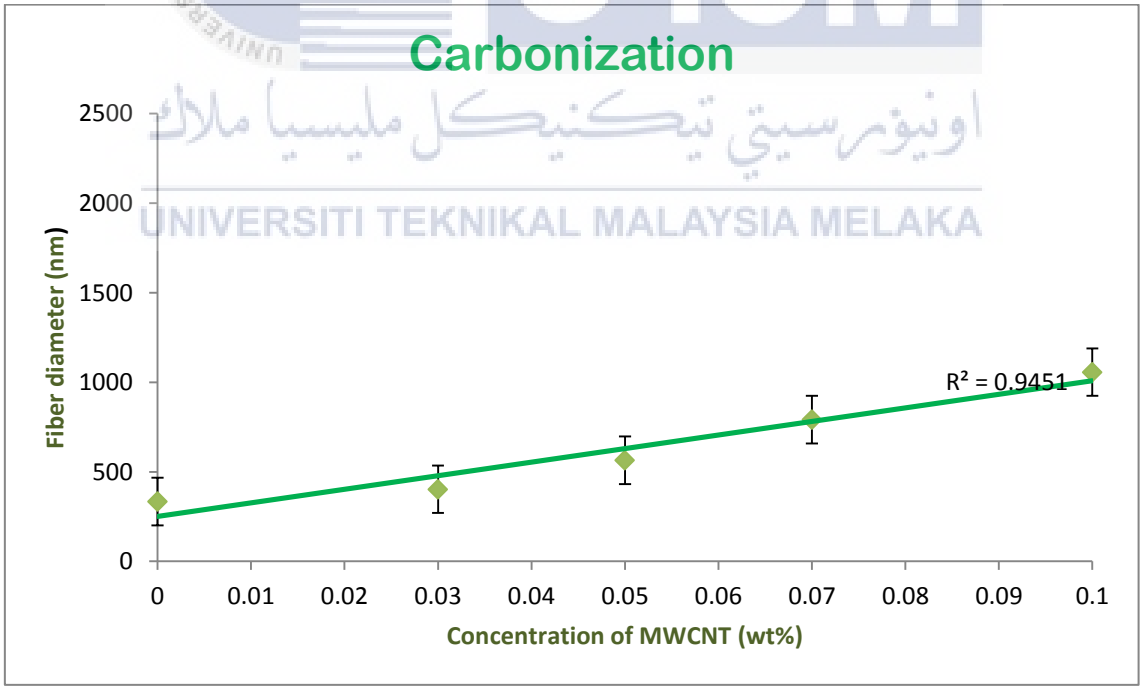


Figure 4.12: Graph of fiber diameter, nm against concentration of MWCNT, wt% (carbonization).

Figure 4.12 presents the graph of fiber diameter, nm against the concentration of MWCNT, wt% after the carbonization process of the nanofibers (CNF). Based on the graph, the correlation, r value for the best fit line in the graph is 0.97. The correlation value is near to 1 which it reveals that there is a relationship between the fiber diameter and the concentration of MWCNT after the carbonization of the nanofibers. In this case, the fiber diameter is increased as the concentration of MWCNT in PAN/CNT nanofiber increased after the heat treatment in carbonization process. Based on the Table 4.4, it can be seen that the appearance of the fiber in SEM image (5,000 magnifications) for only 0.00wt% of MWCNT was smooth. There were some of nanofibers at 0.03wt% of MWCNT that detached to each other and not very smooth. Same case for 0.05wt%, 0.07wt% and 0.10wt% but for 0.05wt%, there were some of the nanofibers that has agglomerates. For 0.07wt% and 0.10wt% of MWCNT, some of the nanofibers were bound and detached to each other.

Based on the observation for the three types of tables and three types figure of graph above, it can be highlight that the diameter of the nanofibers was increased as the concentration of MWCNT in PAN/CNT nanofibers was increased. However, the diameter of the nanofibers for each concentration was decreased after the nanofibers undergo heat treatment in stabilization and carbonization process. This results reflects the finding of Heikkilä & Harlin, 2009 that MWCNT act as a charge carrier which influences the conductivity of solution that may increase the flow rate in the process of fabricate the nanofibers. Hence, it will produce larger diameter of electrospun nanofibers.

Liu, 2010 stated that PAN fibers are more stretchable than the composite fibers. The mixture of conductive filler such as MWCNT in PAN polymer makes it to become composite fibers which reinforced the nanofibers to be higher modulus. The addition of MWCNTs reduces the entropic shrinkage of the PAN fibers and makes this composite nanofiber is harder to be stretched. Hence, the finding provides evidence that the higher concentration of the MWCNT added in the PAN polymer, the lower its entropic shrinkage which contributes to the larger nanofiber production in diameter.

4.4.2 Appearance of CNT in Fiber

The appearance of CNT cannot be seen by using SEM machine on the nanofiber. It is because the size of the MWCNT is too small compared to nanofiber. Figure 4.13 below shows the appearance of MWCNT in nanofiber by using TEM machine magnification at 0.2 µm (Figure 4.13 (a)) and at magnification at 100 nm (Figure 4.13 (b)).

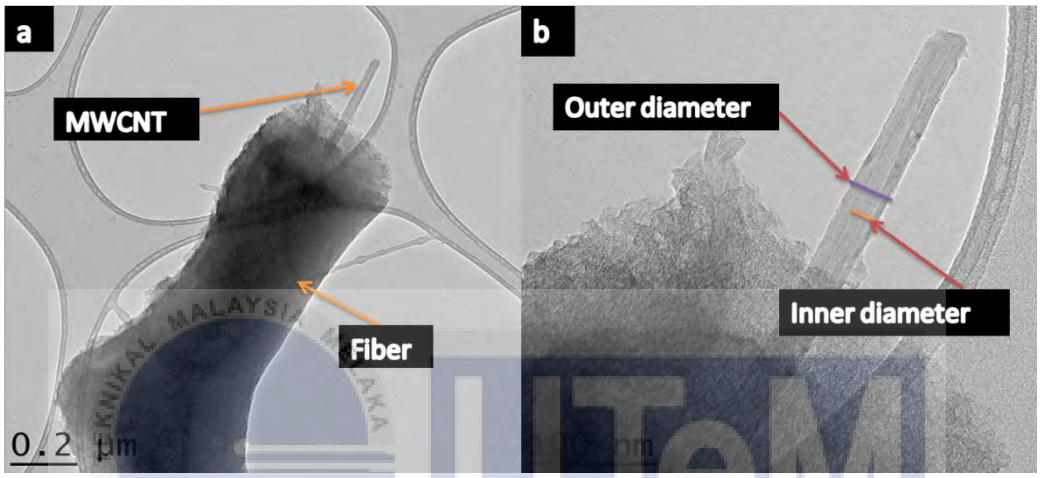
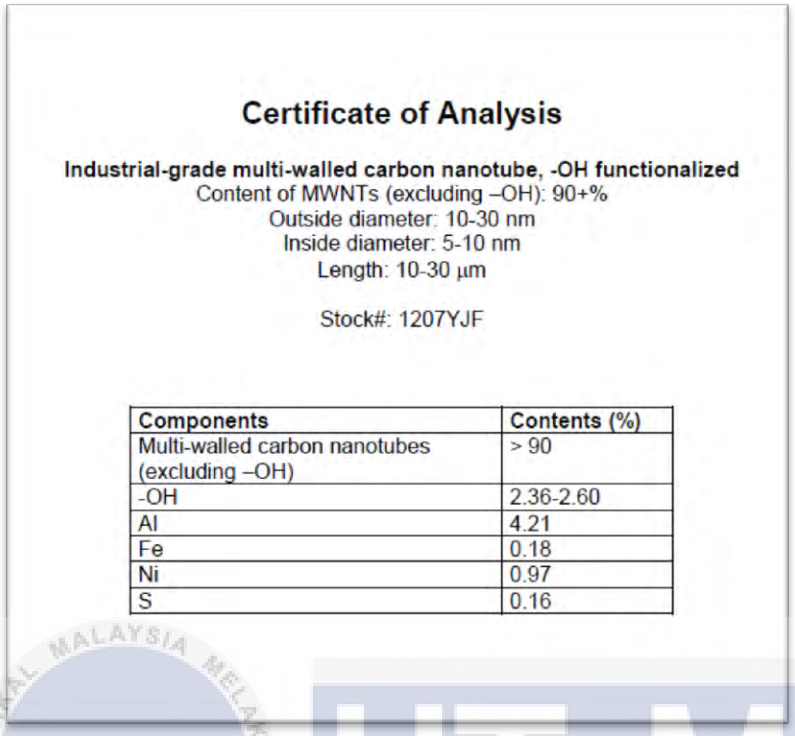


Figure 4.13: The TEM image of the nanofibers (a) magnification at 0.2 µm, (b) magnification at 100 nm (Source: Munajat, N.A, 2018)

Based on the Figure 4.13 (a), it indicates the differences size between MWCNT and nanofiber. The size of MWCNT is smaller than the size of the nanofiber. MWCNT has inner and outer diameter shown in the Figure 4.13 (b). Certificate of analysis for multi-walled carbon nanotubes (MWCNTs) described that the inner diameter of the MWCNT is 5-10 nm while the outer diameter of the MWCNT is 10-30 nm (Figure 4.14). It has been proved by the evaluation of the outer diameter of MWCNT by using image J software as shown in Figure 4.15. The result shows that the outer diameter for MWCNT in Figure 4.13 is 29 nm. Hence, it has been proved based on the identical certificate for the MWCNT that the tiny line in the TEM image is the MWCNT.



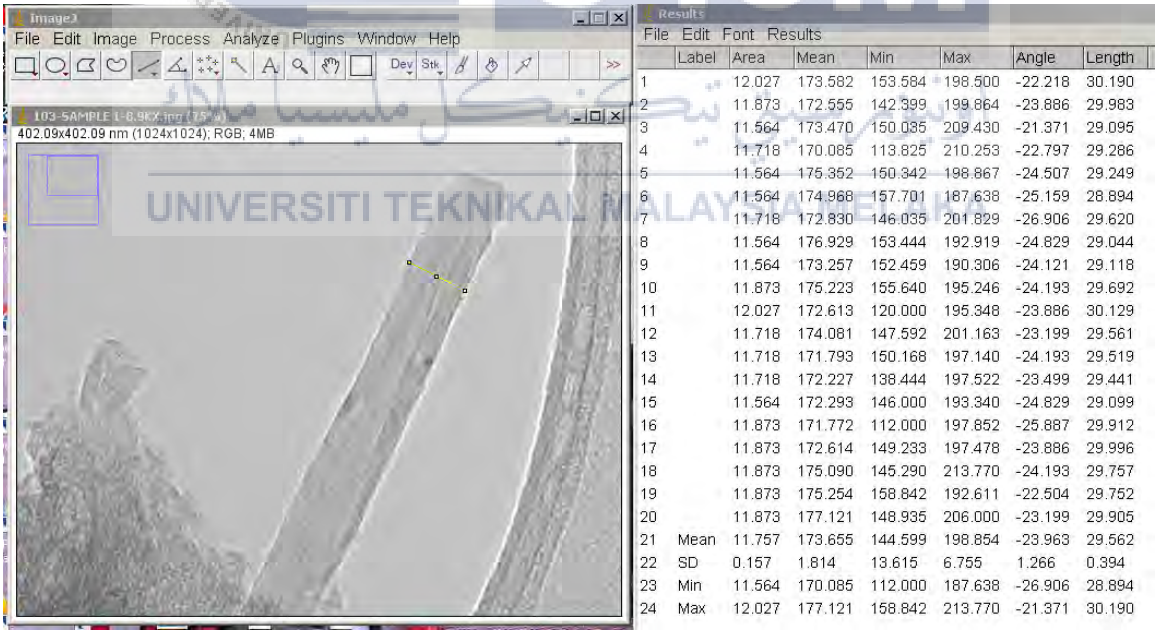
Certificate of Analysis

Industrial-grade multi-walled carbon nanotube, -OH functionalized
Content of MWNTs (excluding –OH): 90+%
Outside diameter: 10-30 nm
Inside diameter: 5-10 nm
Length: 10-30 μm

Stock#: 1207YJF

Components	Contents (%)
Multi-walled carbon nanotubes (excluding –OH)	> 90
-OH	2.36-2.60
Al	4.21
Fe	0.18
Ni	0.97
S	0.16

Figure 4.14: Identical Certificate for MWCNT (Source: Line, n.d.)



	Label	Area	Mean	Min	Max	Angle	Length
1		12.027	173.582	153.584	198.500	-22.218	30.190
2		11.873	172.555	142.399	199.864	-23.886	29.983
3		11.564	173.470	150.085	209.430	-21.371	29.095
4		11.718	170.085	113.825	210.253	-22.797	29.286
5		11.564	175.352	150.342	198.867	-24.507	29.249
6		11.564	174.968	157.701	187.638	-25.159	28.894
7		11.718	172.830	146.035	201.829	-26.906	29.620
8		11.564	176.929	153.444	192.919	-24.829	29.044
9		11.564	173.257	152.459	190.306	-24.121	29.118
10		11.873	175.223	155.640	195.246	-24.193	29.692
11		12.027	172.613	120.000	195.348	-23.886	30.129
12		11.718	174.081	147.592	201.163	-23.199	29.561
13		11.718	171.793	150.168	197.140	-24.193	29.519
14		11.718	172.227	138.444	197.522	-23.499	29.441
15		11.564	172.293	146.000	193.340	-24.829	29.099
16		11.873	171.772	112.000	197.852	-25.887	29.912
17		11.873	172.614	149.233	197.478	-23.886	29.996
18		11.873	175.090	145.290	213.770	-24.193	29.757
19		11.873	175.254	158.842	192.611	-22.504	29.752
20		11.873	177.121	148.935	206.000	-23.199	29.905
21	Mean	11.757	173.655	144.599	198.854	-23.963	29.562
22	SD	0.157	1.814	13.615	6.755	1.266	0.394
23	Min	11.564	170.085	112.000	187.638	-26.906	28.894
24	Max	12.027	177.121	158.842	213.770	-21.371	30.190

Figure 4.15: Result for the outer diameter of MWCNT using image J software

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

As a conclusion, this study was undertaken to fabricate a new electrospun nanofibers by combining polyacrylonitrile (PAN) with conductive particles and to examine the characteristics of the electrospun nanofibers. The conductive particle that has been chosen was multi-walled carbon nanotube (MWCNT) which was supplied from the AMCHALS laboratory. The mixture of PAN with MWCNT was successfully fabricated by using electrospinning machine according to the method used stated in the methodology section in Chapter 3. Five samples of PAN/CNT nanofibers was successfully fabricated with different type concentrations of MWCNT which are 0.00wt%, 0.03wt%, 0.05wt%, 0.07wt%, and 0.10wt%

After the process for the fabrication of electrospun nanofibers was successfully completed, the process was continued with the analysis of characterization for the electrospun nanofibers. The characterizations of the electrospun nanofibers that have been investigated consisted of morphology of the nanofibers, conductivity of the carbon nanofibers, and chemical characterization of the nanofibers. The characteristics of the electrospun nanofibers were successfully examined by using methods stated in the methodology section in Chapter 3.

This study of the characteristics for the PAN/CNT with different concentrations of MWCNT has found that generally the presence of MWCNT in PAN/CNT nanofibers had slightly deformed the formation of the electrospun nanofiber spectrum in FTIR. MWCNT enhanced the heat treatment process in stabilization and carbonization process which made the peaks of the spectrum was highly eliminated after the carbonization process at 1000°C. In this case, it has allowed the high amount of carbon to self-arrange to become a ladder structure

polymer. Furthermore, this phenomenon has enhanced the conductivity of the carbon nanofibers which related to the second characteristics investigated for the PAN/CNT electrospun nanofibers. The results of this investigation show that conductivity of the carbon nanofibers (CNFs) was increased as the concentration of the MWCNT was increased.

The third major finding of the characteristics for the PAN/CNT electrospun nanofibers was the diameter of the nanofiber was increased as the concentration of MWCNT was increased. Other than that, the diameter of the PAN/CNT nanofiber was decreased as undergo the heat treatment in stabilization and carbonization process. Consequently, this study proved that the presence of conductive filler (MWCNT) in PAN precursor polymer enhance the electrospun nanofibers characteristics in term of the molecule chain structure, conductivity and the nanofiber diameter.

5.2 Recommendation

This study has thrown up many questions in need of further investigation. Further investigation and experimentation about the effect of conductive particles and PAN precursor mixture to the nanofibers properties is strongly recommended. A number of possible future studies using the same experimental set up are apparent. It would be interesting to assess the effects of higher concentration for the conductive particle in fabricating the electrospun nanofibers. More information on the effect of conductive particles in composite material would help us to establish a greater degree of accuracy on this matter.

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APPENDICES

APPENDIX A

Polyacrylonitrile (PAN) Specification

SIGMA-ALDRICH

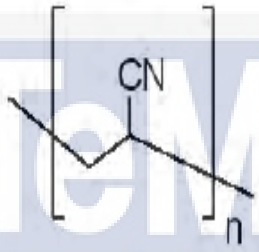
sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
Polyacrylonitrile - average M_w 150,000 (Typical)

Product Number:	181315
CAS Number:	25014-41-9
MDL:	MFCD00084395
Formula:	C3H3N

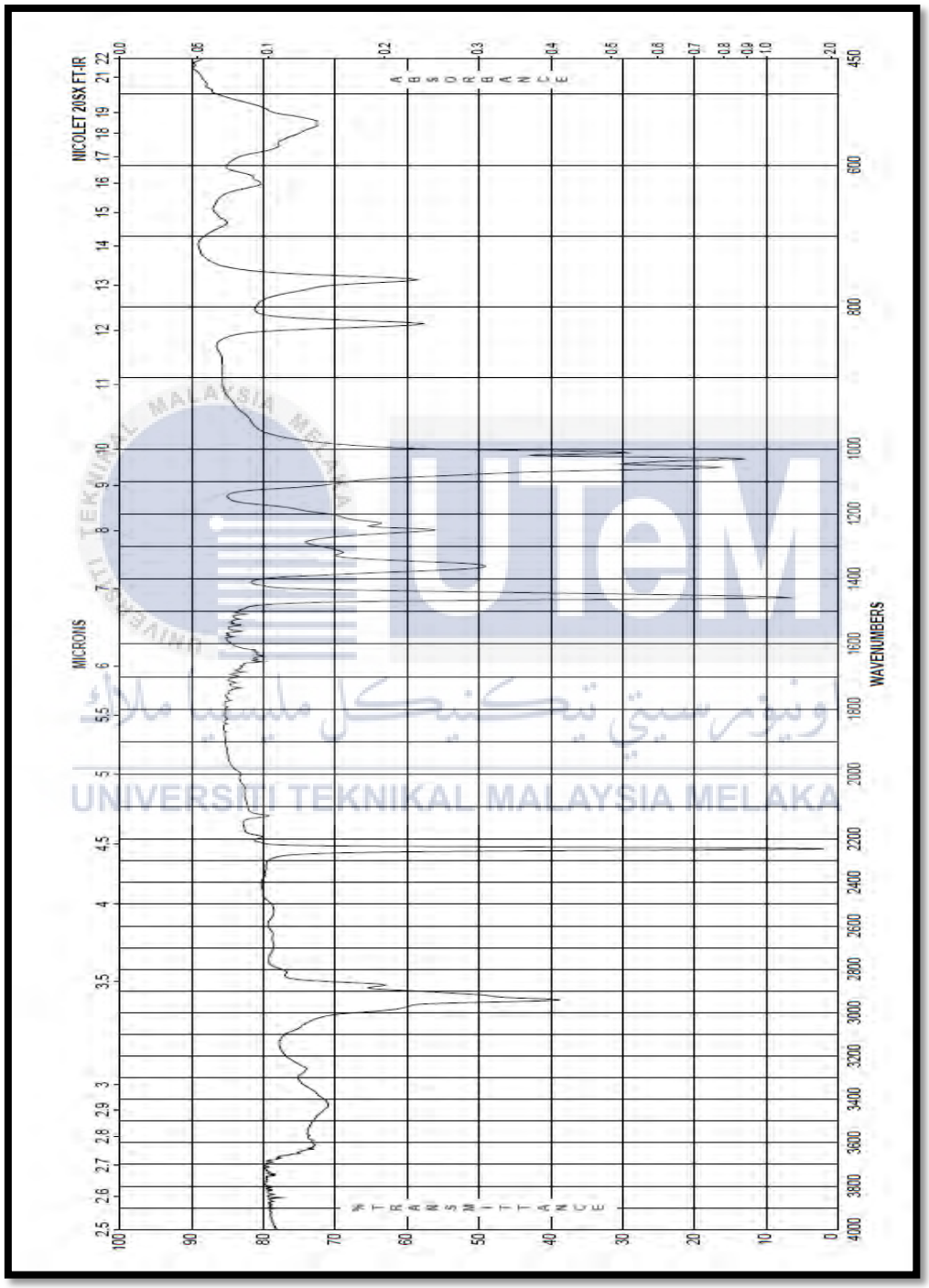


TEST	Specification
Appearance (Color)	White to Yellow
Appearance (Form)	Conforms to Requirements
Powder and Chunks	
Infrared spectrum	Conforms to Structure

Specification Date : 06/21/2010

APPENDIX B

FTIR Spectrum for Polyacrylonitrile (PAN)



APPENDIX C

Identical Certificate of MWCNT

Certificate of Analysis

Industrial-grade multi-walled carbon nanotube, -OH functionalized
Content of MWNTs (excluding –OH): 90+%
Outside diameter: 10-30 nm
Inside diameter: 5-10 nm
Length: 10-30 μm

Stock#: 1207YJF

Components	Contents (%)
Multi-walled carbon nanotubes (excluding –OH)	> 90
-OH	2.36-2.60
Al	4.21
Fe	0.18
Ni	0.97
S	0.16

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